

SYNTHESIS AND EVALUATION OF LAYERED METAL SULFIDES FOR STRONTIUM REMOVAL

Submitted in partial fulfilment of the requirements for the award of
Master of Science in Chemistry

By

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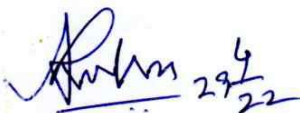
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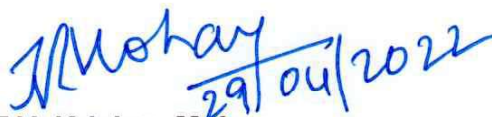
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This is to certify that the dissertation entitled “**Synthesis and Evaluation of Layered Metal Sulfides for Strontium Removal**” submitted by **HARIHARAN R** to the Department of Chemistry, **SATHYBAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, Chennai** in partial fulfilment of the requirement for the degree of Master of Science in Chemistry is the original work of the candidate. This is also to certify that this project work has not formed previously the basis for the award of any degree, diploma, associate-ship, fellowship or similar titles.

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ABSTRACT

Nuclear reactors are indispensable for the energy security of the nation. They produce electricity through controlled nuclear fission reaction. ^{89}Sr and ^{90}Sr are the two major active isotopes of Sr produced in the nuclear reactor during the fission reaction of ^{235}U . ^{90}Sr is considered as the third most important radioactive contaminant after ^{137}Cs and ^{134}Cs ; because of its long half-life (28.78 Y) and high energy β emission (546 KeV and 2.3 MeV from the associated daughter product ^{90}Y). ^{90}Sr has a biological half-life of about 18 years and it is highly radiotoxic due to its chemical similarity to calcium. So, removal strontium activity from nuclear effluents is an important problem attempted by nuclear scientists worldwide. Various types of materials were reported for removing strontium under various conditions. Metal sulfides with layered anionic structures and labile interlayer cations are a new class of sulfide materials that showed excellent and selective ion-exchange properties for Sr. These materials displayed exceptional selectivity and rapid sorption kinetics for soft metal cations like Sr and Cs.

Different types of double metal sulfides were synthesized through hydrothermal route and their strontium removal ability was evaluated. The method adopted is simple and scalable. All the metal sulfides prepared were characterized using ICP-AES for their composition. A mix of double metal sulfides were found to be formed during synthesis. The synthesis parameters were optimized and the materials prepared are studied for their metal ion uptake characteristics. Replacement of Mn powder with MnCO_3 during synthesis led to a more uniform sample with enhanced Sr uptake capabilities. All the metal sulfides were tested for their strontium removal properties. Samples with better uptake properties (KMS1 and KZTS) were studied in detail for their sorption characteristics such as effect of solution pH, maximum Sr uptake, Sr uptake kinetics and selectivity. KZTS showed better Sr uptake compared to KMS1. Both showed faster uptake kinetics with minimal solution pH effect. Iron was found to be strong competitor for Sr in their solutions. Selectivity order of the sulfides prepared under the studied condition was found to be $\text{Fe}^{(2+ \& 3+)} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$. Presence of transition metal cation (Fe^{2+} and Fe^{3+}) was found to cause changes in the metal sulfide lattice during sorption.

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LIST OF ABBREVIATION AND SHORT FORM

BWR	Boiling Water Reactor
HTGR	High Temperature Gas Cooled Reactor
PWR	Pressurized Water Reactor
PHWR	Pressurized Heavy Water Reactor
AGCR	Advanced Gas Cooled Reactor
LWGR	Light Water Graphite Moderated Reactor
FNR	Fast Neutron Reactor
PFBR	Prototype Fast Breed reactor
VVER	Voda Voda Energo Reactor
Cs	Cesium
Sr	Strontium
LLW	Low Level Waste
HLW	High Level Waste
CNTs	Carbon nano tubes
ICPAES	Inductively Couple Plasma-Atomic Emission Spectroscopy
SEM	Scanning Electron Microscopy
PXRD	Powder X-Ray Diffraction
TEM	Transition Electron Microscope
RF	Radio-Frequency
CCD	Charge Coupled Devies
PTFE	Poly-Tetra-Fluoro-Ethylene

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CHAPTER – 1

INTRODUCTION

1.1 NUCLEAR REACTOR

Nuclear reactors operate on the principle of controlled nuclear fission, the process in which a heavy atomic nucleus splits into two lighter nuclei. A large amount of energy is released during this process and the energy is utilised for the electricity generation ([25] Spinrad, Bernard I. and Marcum, n.d.).

According to the fuel, coolant or working principle; several types of nuclear reactors are operating around the world such as

1. Boiling Water Reactor (BWR)
2. High Temperature Gas Cooled Reactor (HTGR)
3. Pressurized Water Reactor (PWR)
4. Pressurized Heavy Water Reactor (PHWR)
5. Advanced Gas Cooled Reactor (AGCR)
6. Light Water Graphite Moderated Reactor (LWGR)
7. Fast Neutron Reactor (FNR)
8. Prototype Fast Breed reactor (PFBR)

Presently, India has 22 operating reactors (18 – PHWRs, 2 – BWRs and 2 – PWRs), with an installed capacity of 6780 MWe. Both BWRs and PWRs use enriched uranium as fuel, light water as coolant and moderator(Breeze, 2019). The Pressurized Heavy Water Reactor (PHWR) use natural uranium as fuel,heavy water (Deuterium Oxide, D_2O) as coolant and moderator(Bajaj and Gore, 2006). PWRs are more popular reactors around the world (around 292 Nos.). Indian PWRs are based on Russians model called VVER and 2units (of 1000 MWe each) of this type are under operation at Kudankulam Nuclear Power Stations.

India has a 3-stage nuclear power program and the three stages of the Indian nuclear power programme are;

Stage1: This stage considered construction of natural uranium fuelled heavy water moderated and cooled pressurized heavy water reactors (PHWR's). Spent fuel from these reactors are reprocessed to obtain plutonium (^{239}Pu).

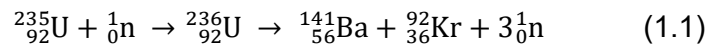
Stage 2: This stage considered construction of fast breeder reactor (FBR) fuelled by plutonium produced in stage 1. These reactors would also breed ^{233}U from thorium.

Stage 3: This stage would comprise power reactors using ^{233}U / Thorium as fuel.

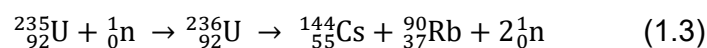
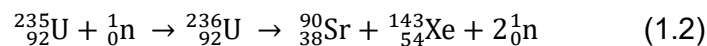
The formulation of the long term, three stage Indian nuclear programme was based on judicious utilization of domestic reserves of uranium and abundant reserves of thorium. The emphasis of the programme was on self-reliance, with thorium utilization as a long-term objective.

1.2 NUCLEAR FISSION

O. Hahn and F. Strassmann have discovered a new type of nuclear reaction; i.e., splitting of uranium and thorium nuclei into two smaller nuclei using neutron bombardment. And they demonstrated the production of nuclei of barium, lanthanum, strontium, yttrium, xenon and caesium nuclei ([6] Hahn and Strassmann, 1939).



L. Meitner and O.R. Frisch suggested that; after the capture of neutron, the uranium nucleus get excited and then split into two fragments of approximately equal masses. These fission products are also radioactive. They undergo decay through emission of beta-ray, neutron or gama radiations and forms stable elements([12]MEITNER and FRISCH, 1939). 50 modes of fission reactions of ^{235}U are known. The fission product fragments normally ranges (of mass number) from 75 to 150. A typical example for the different fissions is given below (Eq. 2 & 3)



The energy and the number of neutrons released during fission reactions vary from one fission reaction to another and the intermediate fission products as well.

The most probable mass fragments that are produced during ^{235}U fission are around mass 95 and 137; which includes isotopes of I, Cs, Sr, Xe, Ba etc. These are shown in (Figure 1.1). For example; Iodine has three major isotopes; ^{129}I , ^{131}I and ^{132}I . Active isotopes of iodine are hazardous to human beings because of its accumulation in the thyroid glands.

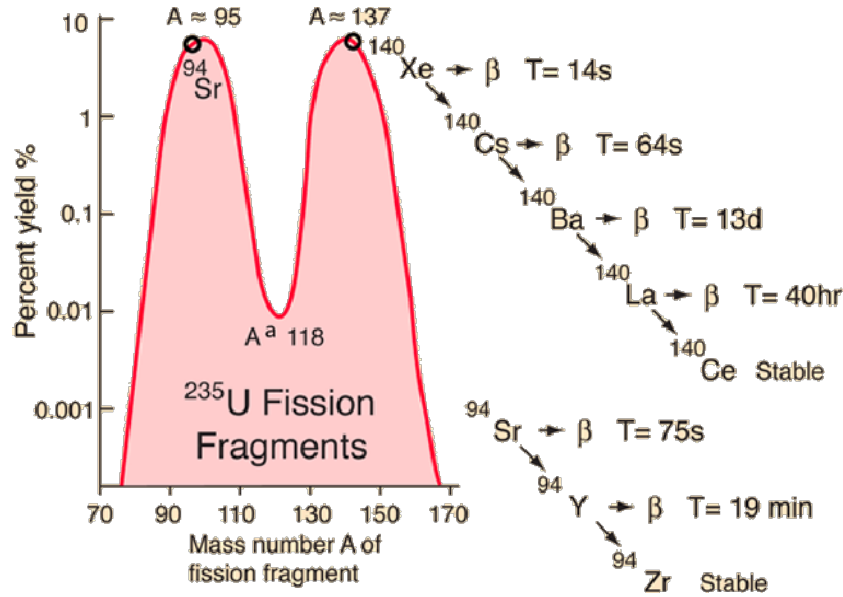


Figure 1.1 Fission yield curve for the thermal fission of ^{235}U

1.3 STRONTIUM

The alkaline earth metal Sr has four stable and natural occurring isotopes with ^{88}Sr being the major isotope. ^{89}Sr and ^{90}Sr are two major active isotopes of Sr produced in the nuclear reactor through nuclear fission. ^{89}Sr has a half-life of 50.57 days and it is used in the treatment of bone cancer. ^{90}Sr has a half-life of 28.8 years. It is a beta emitter and the most responsible for the heat (98%) and radioactivity (97%) in radioactive waste. The decay scheme for the ^{90}Sr has been given in Figure 1.2 ([20]Nam et al., 2017).

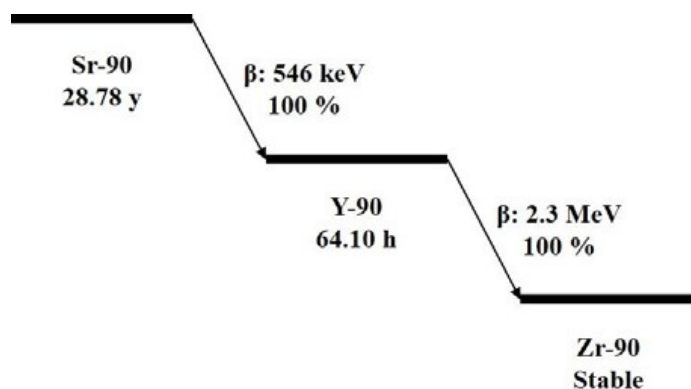


Figure 1.2 Decay profile of ^{90}Sr

^{90}Sr is considered as the third most important radioactive contaminant (after ^{137}Cs and ^{134}Cs) and is of major concern in food and other waste streams after the Fukushima Daiichi, Nuclear Power Plant accident in Japan ([19] NABESHI et al., 2015). Ground water testing by TEPCO (Tokyo Electric Power Company, Japan) at the damaged plant site confirmed the ground water contamination by high levels of ^{90}Sr ("Radioactive isotopes found in groundwater at Fukushima nuclear plant site," n.d.). The biological half-life of ^{90}Sr is about 18 years and it is highly radiotoxic due to its chemical similarity to calcium ([24] Sahoo et al., 2016). Because of it, Sr gets accumulated in bones and leads to bone marrow irradiation from its high energy radiations. So, removal strontium activity from nuclear effluents is an important problem attempted by nuclear scientists worldwide. Some of the fission isotopes of ^{235}U fission along with their decay mode and half-lives was given table No.1.1.

Table 1.1 Fission product along with their decay mode and half-lives

Isotope	Radiation	Half-life
$^{90}\text{Sr} / ^{90}\text{Y}$	B	28 years
^{137}Cs	β, γ	30 years
^{147}Pm	B	2.6 years
^{144}Ce	β, γ	285 days
$^{106}\text{Ru} / ^{106}\text{Rh}$	β, γ	1.0 years
^{95}Zr	β, γ	65 days
^{89}Sr	B	51 days
^{103}Ru	β, γ	39.7 days

⁹⁵ Nb	β, γ	35 days
¹⁴¹ Ce	β, γ	33 days
¹⁴⁰ Ba / ¹⁴⁰ La	β, γ	12.8 days
¹³¹ I	β, γ	8.05 days
Tritium	B	12.3 years

1.4 SORBENTS OR ION EXCHANGE MATERIALS

Sorption is a process by which atoms, molecules or ions are getting attached or associated with a solid phase. Ion exchangers are materials that has the ability to exchange ions between two phases (normally between a stationary phase with another mobile phase). Sorption comprises both adsorption and absorption. Absorption is a bulk phenomenon and adsorption is limited to the surface. But in most of the systems we cannot able to give the correct judgement for adsorption and absorption, so we normally use the terms sorption. Sorption may happen across a gaseous-solid interface (here gas is called sorbate and the solid is called as sorbent) or a liquid-solid interface (here liquid is sorbate and solid is the sorbent). According to the intermolecular forces of attraction acting between the sorbent and sorbate; there may be physisorption (weak physical forces) or chemisorption (strong chemical forces). Physisorption occurs through weak van der Waals' forces of attraction and chemical sorption occurs through ionic or chemical bonds with higher associated heat of sorption. There are different type of ion exchange /sorption materials and a general classification based on different criteria was given in Figure No.1.3.

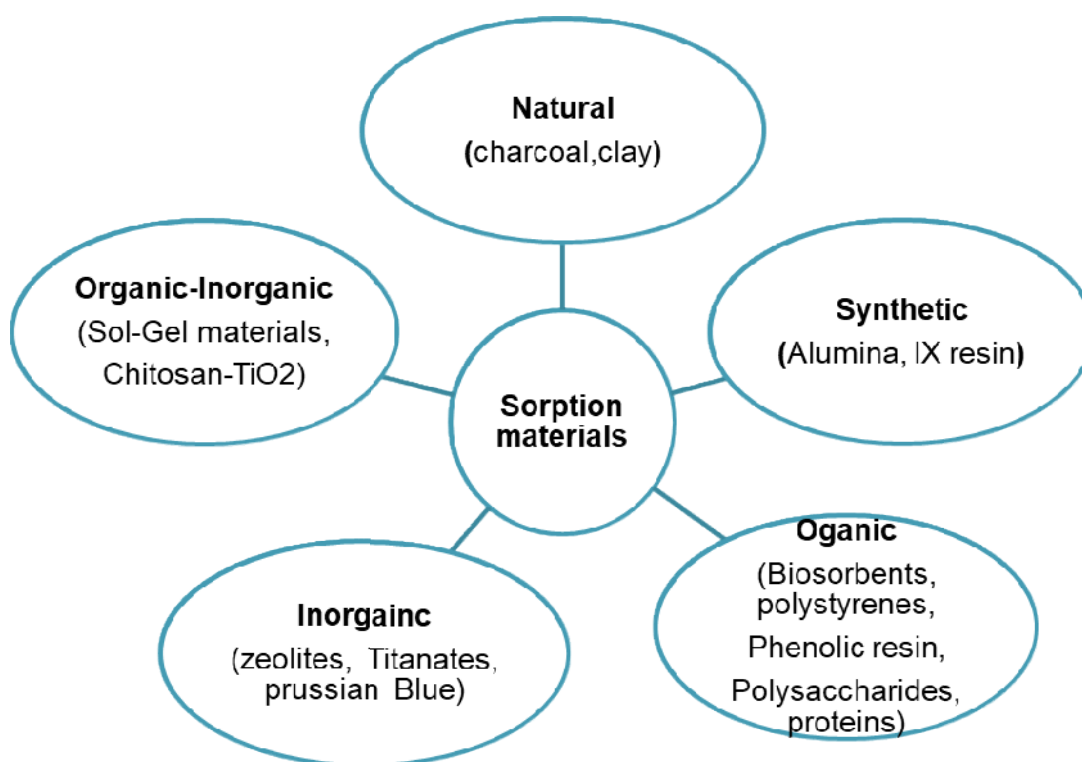


Figure 1.3 Classification of sorbents

Carbon based adsorbents (activated carbons, carbon nanotubes (CNTs) and graphene) are mostly used in heavy metal removal applications owing to their large surface area. Regeneration and reusability is an impediment in the utilisation of the carbon based adsorbents([22] Qasem et al., 2021). Natural, inorganic mineral adsorbents (such as zeolite, silica and clay) are generally utilised in water purification with low operating cost. The natural clay materials have high cation uptake capacity, selectivity, surface hydrophilicity, high swelling or expanding capacity and surface electronegativity. These are cost-effective materials but the removal efficiency may decrease after a few cycles of operations compared to the synthetic inorganic minerals([22] Qasem et al., 2021). Biosorbents are an important class of materials that are used in the current water treatment processes. The functional groups that are responsible for sorption majorly are carboxyl, amino, hydroxyl, phosphate, thiol, etc. The interaction between pollutants and the surfaces of the biosorbents can occur through electrostatic interaction, aggregation, complexation or coordination, microprecipitation, ion exchange, reduction, or oxidation ([22] Qasem et al., 2021). Inorganic ion exchangers have remarkable chemical, thermal, and radiation stability compared to organic ones.

1.5 METAL SULFIDE

Metal sulphides is an important class of materials with wide range application potential. some of them usually exist in nature as minerals such as heazlewoodite (Ni_3S_2), Chalcocite (Cu_2S) and Pyrite (FeS_2). They are mostly semiconductor materials and shows extensive application in catalysis, photoelectricity, photosensors etc. Zinc sulfide(Zns), is an important semiconducting material with wide band gap energyof 3.7eV and a large exciton energy ($\sim 40\text{meV}$). ZnS serve as an important semiconductor photocatalyst to remove toxic or organic water pollutants owing to the highly negative reduction potentials of excited electrons and the rapid generation of electron hole pairs. Copper sulfide(CuS) is another important P-type semiconductor materials with nonlinear optical properties. Transition metal sulphides such as cobalt sulfides (Co_9S_8) and Nickel sulfides (Ni_3S_2) are very important hydrodesulfurization catalyst. It is stable under severe sulfo- reductive conditions in hydro processing of petroleum-based feed stokes.

Metal sulfide ion-exchangers are a new addition to the field of ion exchange materials. Metal sulfides with layered anionic structures and labile interlayer cations are a special class of sulfide materials that shows excellent and selective ion-exchange properties. These materials display exceptional selectivity and rapid sorption kinetics for soft metal ions because of their soft basic frameworks(Manos and Kanatzidis, 2016). Layered metal sulfide have anionic groups as skeletons and cationic groups as equilibrium ions interspersed between these layers. layered metal sulfides possess both labile extra-framework cations, which can be exchanged by other metal ions, and soft S^{2-} ligands, which exhibit strong affinity for soft metal ions (such as Sr^{2+} , Cs^+ , Cd^{2+} , and Pb^{2+}) against hard ions (such as H^+ , Na^+ , Mg^{2+} , Ca^{2+} , and Al^{3+}). In contrast with adsorbents that rely on functional groups to interact with cations, layered metal sulfides have no functional groups and will not be affected by strong acids and bases. As a result, layered metal sulfides can be used with in wide pH range due to their ion-exchange properties. They show good stability, high loading capacity and excellent selectivity in capturing Lewis soft acid cations. Without requiring functionalization, they outperform the most efficient sulfur-functionalized materials in their metal ion removal properties ([8] Manos and Kanatzidis, 2016). Layered metal sulfides are new addition to the field of inorganic ion exchange materials, which shows

exceptional selectivity and rapid sorption kinetics for soft metal cations like Sr^{2+} and Cs^+ ([8] Manos and Kanatzidis, 2016).

CHAPTER – 2

LITERATURE SURVEY

A novel layered metal sulfide ($K_{1.87}Zn_{0.13}Sn_{6.4}S_{12.67}$, KZTS) with high adsorption capacity for Pb^{2+} was synthesized by Jinshui Mao through hydrothermal method (Mao et al., 2021). The maximum adsorption capacity showed was $431.26 \text{ mg} \cdot \text{g}^{-1}$. The KZTS exhibited excellent selectivity against competitive ions such as Ca^{2+} , Cd^{2+} , Co^{2+} , Al^{3+} and Mn^{2+} . Layered metal sulphides with flake-like and polyhedral structures with the formula of $K_{1.67}Zn_{0.67}Sn_{2.17}S_{6.00}$ and $K_{5.84}Zn_{3.47}Sn_{5.04}S_{16.99}$ were prepared by Mingdong Zhang (Zhang et al., 2018). The adsorbent exhibited rapid kinetics, and high affinity and selectivity for Sr^{2+} . Maximum adsorption capacity reported for Sr by KZTS was 19.3 mg/g . A new type of metal sulfide; $K_{2x}Mg_xSn_{3-x}S_6$ ($x = 0.5-1$, KMS-2) and its application for the ion exchange of Cs^+ , Sr^{2+} , and Ni^{2+} in varying conditions was reported by Joshua L. Mertz ([13] Mertz et al., 2013). High distribution coefficients values were reported for KMS-2 (for Cs^+ - $7.1 \times 10^3 \text{ mL/g}$ and Sr^{2+} - $2.1 \times 10^4 \text{ mL/g}$) at neutral pH conditions. Ion-exchange properties of the layered sulfide material $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5-0.95$) (KMS-1) with Cs^+ and Rb^+ cations are reported by Manolis J. Manos ([10] Manos and Kanatzidis, 2009). Exchange capacity reported was 226 mg/g ($pH \approx 7$) and distribution coefficients reported was $2 \times 10^4 \text{ mL/g}$ with 90% removal of $\sim 1 \text{ ppm}$ of Cs^+ within 5 min. Removal of U from sea water conditions using $K_2MnSn_2S_6$ (KMS-1) was also reported by Manos ([9] Manos and Kanatzidis, 2012). Uptake capacity reported for U was 147.6 mg/g and the sorbent U can be eluted using 2 M KCl. A robust acid-stable layered metal sulfide bearing the structure ($KInSn_2S_6$, KMS-5) with strong affinity toward trivalent minor actinides was reported by Chengliang Xiao ([26] Xiao et al., 2017). KMS-5 was showed to simultaneously separate trivalent ^{241}Am and ^{152}Eu from acidic solutions below pH 2 with high efficiency ($>98\%$) and distribution coefficient is as high as $5.91 \times 10^4 \text{ mL/g}$. Layered metal sulfides were tried to incorporate with other matrices for their effective application. A composite membrane with KTS-3 and PAN was synthesized through facile electrospinning by Ho Hyeon Eom ([5] Eom et al., 2021). Maximum capacity reported for the membrane was 131.6 and 32.4 mg g^{-1} for Cs

and Sr respectively with Excellent adsorption performance even at a high flux of $2000 \text{ L m}^{-2} \text{ h}^{-1}$.

Table 2.1 Literature Survey of broad study

S.No:	Adsorbent Material	Capacity	Application	Reference
1.	Bonding of crown ethers to α -zirconium phosphate	$320.16 \text{ mg} \cdot \text{g}^{-1}$	1.The 18 crown 6ether and its derivatives have been stupendous studied as highly exchange ion-exchangers for removal of ^{90}Sr. Further appilication one of the main problem is expensive macrocyclic ligands is loss in solid-liquid media due to their solubility. 2.To overcome this problem we have to developed a new organic– inorganic layer α-ZrP composite by intercalation of 4-amino-benzo-18 crown 6. Which meansattach these macrocyclic ligands to a solid support 3.Typically α-ZrP layer compound it can easily functionalized by intercalculating and modifying, allowing the production of versatile adsorbents with high efficiency. 4.AM-ZrP it has show an excellent selectivity and high	[15]

			adsorption capacity for removal of Sr^{2+} from the complex environment due to the strong complexation.	
2.	Na/K-birnessite type phyllomanganates ($\text{Na}_{0.5}\text{Mn}_2\text{O}_4 \cdot 0.96\text{H}_2\text{O}$ (NMO) and $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$ (KMO)).	9.64 mmol/g and 1.09 mmol/g	1.The birnessite is compared with amorphous MnO_2 it revealed faster sorption kinetics, higher adsorption capacities and higher stability in wider range of pH. 2.The study of these two birnessite type phyllomanganates namely Na-Birnessite (NMO), K-Birnessite (KMO) discussed about the investigation of efficiencies for separation of Sr^{2+} ions, radiometrically using ^{85}Sr (alpha, γ-emitter, $t_{1/2} = 64.8$ d, 512 KeV) tracer solution as well as using solutions of nonradioactive Sr^{2+} and shown high affinity for ^{85}Sr separation.	[2]
3.	nanosubstructured layered sodium vanadosilicate	174.3 mg/g	1.When this has been kept analysis for SEM, EDS and TEM it provides a nanostructure with flake like shape and it provides an extremely large surface area. 2.This is the first study of the ultrafast adsorption of Sr^{2+} while using an	[27]

			nanostructured layered sodium vanadosilicates in a time frame of second at a low with a high adsorption capacity 174.3 mg/g it could be estimated by Langmuir Isotherm. 3. This type of ultrafast adsorption technique has used to removal of radionuclide could allow emergency response at reduce the risk of nuclear accident and reducing environmental damage. 4. The vanadate based material shows some extent have been explored for removing radionuclide from the aqueous solution. Nowadays significant lacks in understanding nanostructured layered sodium vanadosilicate of adsorption capacity, kinetics and working mechanism in removing soluble Sr^{2+}. 5. Nanostructured layered sodium vanadosilicate it is emphasis without doubt, could open an new window for industrial application it is removal of	
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			radiotoxic Sr^{2+} from wastewater.	
4.	BCM@APTES-EDTA	44.86 $\text{mg}\cdot\text{g}^{-1}$	1.The BCM@APTES-EDTA adsorbent used to adsorbed the Sr^{2+} that mechanism has been studied through FTIR and XPS analysis. It emphasis the tertiary amines and carboxylate from inserted EDTA participated in the adsorption Sr^{2+}. 2.In many reaserch have focused on its application of several fields such as papermaking technology, biomedicine such as skin, cartilage and bone regeneration, food like different kinds of nata, agriculture acting as aquifer, sewage purification acting as functional materials, and electrical, magnetic and optical fields with the composite of polyaniline or Fe_3O_4. 3.If compared with other reported modified BC adsorbents as BCM@APTES-EDTA shows high adsorption capacity. 4.The inserted of EDTA into BC avoid the chemical loss of EDTA after	[4]

			adsorption. In reasearchs EDTA modified cellulose has used for removal of the heavy metal. 5.As most of the EDTA modified cellulose reported were powdery, which is difficult to separate and reuse. The purpose of synthesis of BCM@APTES-EDTA is study to evaluate the adsorption performance of radioactive isotopes.	
5.	Core-shell zeolite@Alg-Ca adsorbent	83.31 mg/g	1.Alginate is a polysaccharide it is a abundant resource with low cost and biodegradability. 2.Alginate is broadly used as adsorbent for the removal of various metal ions due to the many carboxylic groups on it, and high affinity of carboxylic groups to metal ions. 3.It is a good immobilizer with the properties of extraordinary resistance to acid, non-toxic and can easily bind divalent cation to form stable and insoluble gel particle in the water solution. 4.zeolite material has most promising materials for the	[29]

			removal of strontium but it is small partical size and weak stability at acid media. So afters the adsorption of the strontium ions it able to recovery the adsorbent it lead an another trouble and restrict its practical application. 5.core-shell zeolite@Alg-Ca particles can easily to be separated from the solution after adsorption, which results in reducing the cost of the adsorption and avoiding secondary pollution.	
6.	metal–organic framework (MOF)	176.56 mg g ⁻¹ and 206.34 mg g ⁻¹	1.Metal organic framework is an ion trapping concept which is design an efficient adsorbent for removal of strontium from the nuclear wastewater. 2.The introduction of sulfate and oxalate into the pore structure of MOF-808, giving MOF-808-SO₄ and MOF-808-C₂O₄ these functionalized material exhibit excellent ability to remove the Sr²⁺ from the acidic solution due to their particular trapping action. 3.Metal organic frameworks (MOFs)	[16]

			is a new class of hybrid porous materials with exceptionally high specific surface areas, high porosity and controllable pore shape, have been extensively used in gas storage, catalysis, and separation. 4. when we used the concept of ion trapping and tried to anchor the functional group that could bond with strontium and improve the adsorption capacity of MOFs.	
7.	Porous three-dimensional reduced graphene oxide merged with WO ₃	149.56 mg g ⁻¹	1. The graphene oxide and WO₃ combination was benefits composites it shows a higher adsorption capacity to remove the Sr²⁺ from aqueous solution over the wide range of pH range. 2. It is an fast adsorption and high adsorption rate of RGO/WO₃ are mostly attributable to the plentiful adsorption sites provided by the dispersed WO₃ nanoparticles on the RGO surface. 3. Hexagonal tungsten bronze structure (h-WO₃) possessed their excellent ion-exchange capacities	[17]

			and high stability and have been developed as promising adsorbents for radioactive ions. But its sedimentation time is long and not easy to separate from aqueous solution after adsorption of metal ions. So we need to overcome this problem by using Graphene oxide (GO), with a two-dimensional monolayer while the GO help it easily disperse in aqueous solution to form a stable colloidal suspension, and also facilitates the preparation of GO-based composites. 4. Nowadays the, graphene-inorganic composite materials, derived by integrating GO sheets with functional inorganic nanomaterials, have been intensively investigated. 5. Some of the important merits the large specific surface area and abundant oxygen-containing groups of GO, h-WO₃ can be efficiently dispersed on its surface and prevent the agglomeration of nanoparticles, GO is a porous materials with excellent adsorption properties,	
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			the loading of h-WO ₃ on RGO sheets can facilitate the separation of GO/WO ₃ from aqueous solution	
8.	Niobate nanofibers	148.92 and 296 m ² g ⁻¹	1. Actually it is the study of nanofibers of sodium niobate with negatively charged layers and readily exchangeable sodium ions between the layers can efficiently remove radioactive Sr²⁺. 2. Niobate adsorbents can be readily dispersed in liquids and easily separated after purification due to their fibril morphology, which significantly enhances their adsorption efficiency and reduces separation costs. 3. In this case of the nanofibers study it can define the Ag₂O anchored sodium niobate nanofibers with fibril morphology, negatively charged thin layers and readily exchangers are potential sorbent for the simultaneous uptake of cations and anions. 4. Niobate nanofibers with chemical formula Nb₂Na₂O₆·H₂O may be obtained from pentaethoxyl niobium solution by simple hydrothermal	[18]

			treatment. They are stable under a wide range of pH conditions and exhibit excellent resistance to radiation. This material possesses a layered structure composed of $[\text{NbO}_6]$ and $[\text{NaO}_6]$ octahedral units which endow these materials with abundant microporous structures, open tunnels and relatively high surface area. These layers carry negative charges, and Na^+ ions remain between the layers. 5. Niobate adsorbents exhibited excellent simultaneously removal abilities for radioactive Sr^{2+} and I from basic aqueous solutions.	
9.	resorcinol formaldehyde polycondensate resin	2.28, 1.25 and 1.15 meq/g	1. It is an batch and column adsorption experiment it is used resorcinol formaldehyde polycondensate resin to conduct the removal of Sr^{2+} in presence of the coexciting cation at pH 7.5–8.5. 2. Sr adsorption capacity in the presence of seawater concentrations of Ca, Mg, K and Na was reduced in both batch and column	[21]

			experiments with highest effect from Ca and Mg. So Ca and Mg are removed more importantly resorcinol formaldehyde resin adsorption process by precipitation, the negative effect of these ions on Sr removal can be significantly reduced. 3. Commercial phenol formaldehyde resins – similar to resorcinol formaldehyde resin – were utilised to treat low and high level alkaline radioactive wastes. 4. Resorcinol formaldehyde resin could be used to simultaneously adsorb Sr along with Cs from radioactive waste solutions. But found that the Resorcinol formaldehyde resin used in their study was highly selective for the removal of Cs compared to Sr from simulated radioactive waste solution. 5. The most objectives study as follows: (i) synthesise and evaluate the performance of RF resin for Sr adsorption in batch and column adsorption methods; (ii) evaluate the pH	
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			effect on Sr adsorption and study the adsorption mechanism using zeta potential measurements; (iii) investigate the effect of co-ions in seawater on Sr adsorption using synthetic seawater in batch and column adsorption methods; and (iv) evaluate the Sr desorption characteristics of the RF resin to obtain useful information on Sr recovery.	
10	Hydroxyapatite-cobalt(II) ferrocyanide, HAFC	12.84 to 13.44 mg/g	1.It is the study of modified and unmodified hydroxyapatite for sorption of both ions were carried out to evaluate the modification process. 2.The modification process enhance the capacity of both Cs and Sr it means that the modification process enhanced the selectivity of cesium ions, and it may be stated that HAFC preferentially takes up Cs^{+} rather than Sr^{2+}. 3.Hydroxyapatite (HA) is one of calcium phosphates; it has unique properties including ion exchange properties, adsorptive ability, and low solubility. So these	[14]

		characteristics make hydroxyapatite extremely important as a water purification material for heavy metal ions and radionuclides. It can accept a series of cationic exchange inside its structure and used for removal of many cations such as Pb^{2+} Sr^{2+} Cd^{2+} Ni^{2+} Cu^{2+} and Cr^{6+}. 4.Modification of hydroxyapatite was carried out to produce composite materials using either inorganic or organic compounds. It is found that the surface modification of adsorbents provides novel binding properties for potentially hazardous metals, therefore, this work focused on modification of hydroxyapatite to improve its sorption properties.	
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CHAPTER – 3

AIM AND SCOPE

^{89}Sr and ^{90}Sr are two major active isotopes of Sr produced in the nuclear reactor during power generation through fission reaction of ^{235}U . ^{90}Sr is considered as the third most important radioactive contaminant after ^{137}Cs and ^{134}Cs ; because of its long half-life (28.78 Y) and high energy β emission (546 KeV and 2.3 MeV from the associated daughter product ^{90}Y). ^{90}Sr has a biological half-life of about 18 years and it is highly radiotoxic due to its chemical similarity to calcium ([24] Sahoo et al., 2016). So, removal strontium activity from nuclear effluents is an important problem attempted by nuclear scientists worldwide.

Various types of materials were reported for Sr removal. Metal sulfides materials were reported recently for the ion exchange removal of different heavy metal contaminants. Metal sulfides with layered anionic structures and labile interlayer cations are a new class of sulfide materials that showed excellent and selective ion-exchange properties. These materials displayed exceptional selectivity and rapid sorption kinetics for soft metal cations like Sr and Cs ([8] Manos and Kanatzidis, 2016).

The objective of this study is to synthesised different types of double metal sulfides through hydrothermal route using literature reported procedures and to evaluate the strontium removal ability of the synthesised materials. The synthesis parameters will be optimised and all the materials prepared will be studied for their metal ion uptake characteristics. Samples with better uptake properties will be studied in detail for their sorption characteristics such as effect of solution pH, maximum Sr uptake, Sr uptake kinetics and selectivity characteristics.

CHAPTER – 4

MATERIALS AND METHOD

4.1 MATERIALS

Mn powder – 99% - extrapure, Tin metal powder 99.9 % AR were procurement from Loba Chemie. K_2CO_3 anhydrous (99.5%) extra pure AR-ACS was procured from SRL, India, Sulpgur Powder 99.0% and Zinc metal (granular) extra pure were procured from Finar, Chemicals. Copper metal turnings LR was obtained from s.d.fine chem. Ltd. $Sr(NO_3)_2$ pure was obtained form Merck, India.

4.2 HYDROTHERMAL SYNTHESIS

The term hydrothermal comes from “hydros”- “Themos”. “Hydros” means water and “Themos” means heat, Where the reactants are heated at elevated temperatures and pressures in presence of water to produce the desired materials. It's very simple and scalable process with minimum synthesis parameters to optimise.

4.3 SYNTHESIS OF VARIOUS LAYERED METAL SULPHIDES

All the metal sulphides were synthesised through literature reported procedures using hydrothermal method. Amounts of various chemical constituents used for the synthesis of the different metal sulphides is given Table 4.1.

Table 4.1 Amount of various chemicals used for the metal sulphide synthesis

Metal sulfide prepared	Chemicals used						
	Sn powder (g)	Mn powder (g)	S powder (g)	K_2CO_3 (g)	Cu turnings (g)	$MnCO_3$ (g)	Zn granulated (g)
KMS1-1	1.788	0.416	1.449	1.042	*	*	*
KMS1-2	1.792	0.416	1.450	1.053	*	*	*
KMS1-3	3.576	0.828	2.894	2.091	*	*	*
KMS1-4	1.789	*	1.445	1.069	*	0.869	*
KZTS	1.788	*	1.448	1.045	*	*	0.504

KCuSnS	1.794	*	1.443	1.037	0.477	*	*
KZTS - 2	3.574	*	2.894	2.094	*	*	0.942

4.3.1 Synthesis of KMS1-1:

KMnSnS was prepared according to the literature reported procedure (Manos et al., 2008). In brief; all ingredients were weighed and transferred to the Teflon lined autoclave, added 10 mL ultra-pure water (de-aerated), mixed well, closed and then kept in cylindrical furnace kept at 200 °C for 96 h. Reaction mixture was then transferred to a beaker after the reaction and washed with demineralised water. Washings were collected and centrifuged, dried at 60 °C to obtain sample **KMS1-1-S1**. Washed precipitate was then sonicated with demineralised water (exfoliation) and all the washing were collected and centrifuged, precipitate collected was dried at 60 °C to obtain the sample **KMS1-1-S2**. The remaining precipitate after sonication was dried at 60 °C and named as **KMS1-1-S3**. All the samples were washed with acetone and then diethyl ether before final drying.

4.3.2 Synthesis of KMS1-2:

All ingredients were mixed well using a mortar and pestle, transferred to the Teflon lined autoclave, added 7 mL ultra-pure water (de-aerated), mixed well, closed and then kept in cylindrical furnace kept at 200 °C for 96 h. The reaction mixture was then filtered (using a Millipore filtration unit, 0.22 µ) and dried at 60 °C to get the **KMS1-2** (Yield - 3.413 g). About 0.5 g of the KMS1-2 was sonicated with demineralised water (exfoliation) and the washings were collected, centrifuged and dried at 60 °C to obtain the **KMS1-2-Sn** (Yield - 0.432 g). The leftover precipitate was dried at 60 °C and named as **KMS1-2-Mn** (Yield - 41 mg). All the samples were washed with acetone and then diethyl ether before final drying.

4.3.3 Synthesis of KMS1-3:

All ingredients were mixed well using a mortar and pestle, transferred to the Teflon lined autoclave, added 10 mL ultra-pure water (de-aerated), mixed well, closed and then kept in cylindrical furnace kept at 200 °C for 96 h. The reaction mixture was then transferred to a beaker, sonicated (exfoliation) multiple times, and the

washings were collected and dried at 70 °C to obtain the **KMS1-3** (Yield - 5.607 g). Remaining precipitate was then dried at 70 °C to obtain the **KMS1-3-Mn** (Yield - 0.756 g).

4.3.4 Synthesis of KMS1-4:

Here we used MnCO_3 instead of Mn powder. All ingredients were mixed well using a mortar and pestle, transferred to the Teflon lined autoclave, added 5 mL ultra-pure water (de-aerated), mixed well, closed and then kept in cylindrical furnace kept at 200 °C for 96 h. The reaction mixture was then filtered (over a Millipore filtration unit, 0.22 μ), washed with acetone and diethyl ether, and then dried at 60 °C to get the **KMS1-4** (Yield - 4.03 g)

4.3.5 Synthesis of KZTS:

KZnSnS was prepared according to the literature reported procedure([11] Mao et al., 2021). Here the manganese has been replaced by zinc. In brief: all the ingredients were mixed well using a mortar and pestle, transferred to the Teflon lined autoclave, added 3 mL ultra-pure water (de-aerated), mixed well, closed and then kept in cylindrical furnace kept at 200 °C for 96 h. The reaction mixture was then transferred to a beaker (after cooling), sonicated (exfoliation) multiple times, and the washings were collected, centrifuged and the precipitate washed with acetone and diethyl ether, dried at 70 °C to obtain the **KZTS** (Yield - 2.613 g)

4.3.6 Synthesis of KCuSnS:

Here the manganese has been replaced by copper. All ingredients were mixed well using a mortar and pestle, transferred to the Teflon lined autoclave, added 5 mL ultra-pure water (de-aerated), mixed well, closed and then kept in cylindrical furnace heated at 200 °C for 96 h. The reaction mixture was then filtered (over a Millipore filtration unit, 0.22 μ) after cooling, washed with acetone and diethyl ether, and then dried at 60 °C. There were two types of phases present in the filtered product. Black coloured lumps were separated by handpicking and named as **KCuSnS-BI** (yield – 1.11 g) and the remaining yellowish-brown precipitate was named as **KCuSnS-YB** (Yield – 2.347 g).

4.3.7 Synthesis of KZTS-2:

Prepared in similar fashion to KZTS reported earlier, except the workup procedure. The reaction mixture was filtered (over a Millipore filtration unit, 0.22 μ) after cooling, washed with acetone and diethyl ether, and then dried at 70 °C to obtain the KZTZ-2 (Yield – 6.523 g, 75.9 %).

4.4 CHARACTERISATION OF THE METAL SULPHIDES

4.4.1 Estimation of composition using ICP-AES

All the above mentioned metal sulphides samples prepared were dissolved in aquaregia and then analysed for their metal ion concentrations using ICP-AES (Ultima 2, Horiba Jobin Yvon, France). About 10 mg of the sample was dissolved in 2 mL of aqua regia and then made up to 50 mL in standard measuring flask for the analysis.

4.5 METHODS

4.5.1 INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROSCOPY (ICPAES)

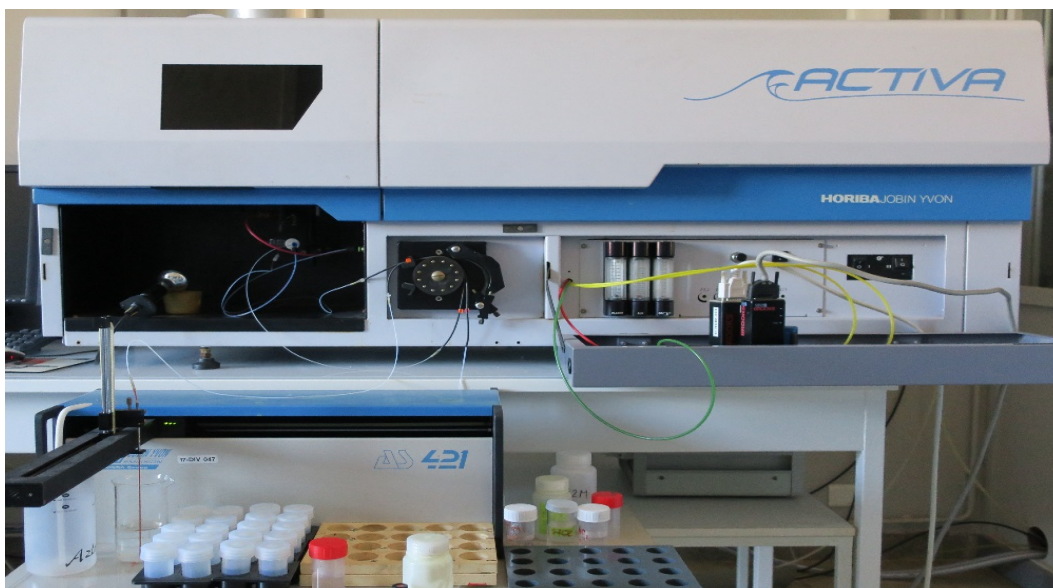


Figure 4.1 ICP-AES INSTRUMENT

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (also referred to as inductively coupled plasma optical emission spectrometry (ICP-

OES)) is an analytical technique used to determine the amount of element present in a sample. The atoms or ions can absorb energy to excite electrons from lower level to their excited levels. Here the source of energy is in the form of heat from an argon plasma that operates at 6000 to 10,000 K. An excited atom will emit radiation characteristic to that particular element while it de-excite to their ground state. Intensity of the emitted radiation can be measured using suitable detectors for the quantitative analysis of that particular element as the emitted light intensity is directly proportional the number of atoms and ions present in the sample.

ICP-AES consist of six parts namely; sample introduction system, plasma torch, radio-frequency generator, optical spectrometer, detector, computerized instrument control.

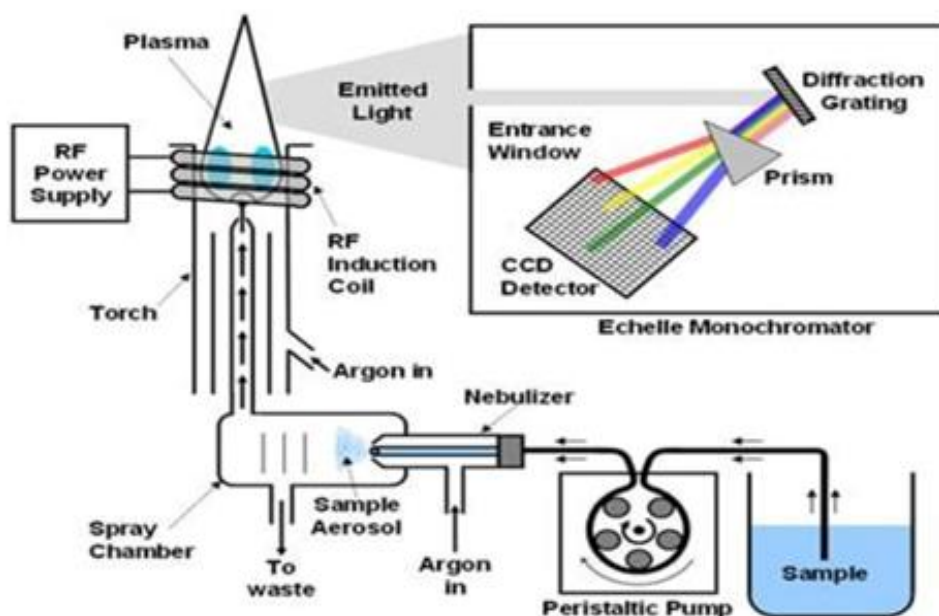


Figure 4.2 Schematic picture of ICP-AES instrument

Sample introduction system consists of peristaltic pump, Teflon tubing, a nebulizer, and a spray chamber. Sample was pumped into the nebulizer unit where it forms an aerosol inside the spray chamber, where the larger droplets were removed and sent to the drain, and the fine aerosol mist has been carried to the plasma torch.

An inductively coupled plasma is formed by seeding ions in a stream of argon which is flowing through the magnetic field (created by a radiofrequency coil) in the region of the induction coil. The ions are formed by subjecting the argon gas to a high voltage spark and this causes small amounts of ionization of the argon. These electrons and ions are then accelerated by the magnetic field and collide with other argon atoms, causing further argon ionization and the subsequent formation of a plasma. The plasma is sustained by continual ionization of the argon via collisions induced by the magnetic field. This transfer of energy is known as inductive coupling. The energy that is transferred to the electrons and ions originates from the RF generator. The plasma is contained within a quartz or ceramic tube known as a torch and can reach temperatures of up to 10,000 K. To prevent melting or damage to the torch the argon is forced to flow tangentially at a high velocity, this cools the inner surface of the torch, forming a compact and stable plasma.

Aerosols generated from liquid or solid samples are fed into the plasma from various types of sample introduction systems or external accessories through a centrally located tube inside the torch. The plasma is at its most energetic and hottest where the sample is injected and the liquid evaporates and completely dissociates into its constituent atoms and ions within milliseconds. An efficient and powerful RF generator will develop and continually sustain a plasma that is capable of completely dissociating almost any sample matrix, thereby reducing oxide formation and other chemical interferences to a minimum

The excited electrons return to a lower energy level (ground state) by emitting light rays that depend upon the characteristic elements and this emitted light is viewed horizontally by an optical channel. The emitted light from the plasma made to focus on the lens and passes through an entrance slit into the monochromator. Basically, the collimator mirror was used for transmitting the entered light into the diffraction grating. The diffraction grating will split the emitted light into the characteristic wavelengths and intensity of the light was measured at very precise wavelengths.

Photomultiplier tube was used as the detector for measuring the intensity of the light. Photomultiplier tube convert the emitted light into an electrical signal.

Photomultiplier tube contain a photosensitive material called photocathode and it emit electrons when subjected to light. The photocathode accelerated the photoelectrons and multiplied over electrode which serves as an electron multiplier through secondary emission which is referred as dyanodes. The current measured at the anode will be proportional to the intensity of the emitted light and voltage applied across the dyanodes. Then it is used computing the signals to find out the concentration of the target analyte in the sample by the system software through calibration.

4.5.2 Powder X-ray Diffraction study of KMS1 and KZTS

Powder XRD spectra of the samples KZTS and KMS1 were recorder using an ARL, Equinox 5000 X-ray Diffractometer by Thermo Scientific, Germany. XRD spectrum is useful in identifying the crystal structure, phase and composition of the compound.

4.6STUDYING THE STRONTIUM REMOVAL ABILITY OF THE SULFIDES PREPARED

Sr removal ability of the all the metal sulfides prepared were tested in batch mode of operations. That a fixed amount of the material is equilibrated with a fixed volume of the Sr test solution. Various parameters such as removal kinetics, maximum Sr uptake capacity, effect of solution pH, selectivity characteristics were studied in detail for KMS1-2-Sn and KZTS.

Batch sorption experiments were carried out by equilibrating known amount of the metal sulfide with known volume of the test solutions for a particular period of time in a rotator kept at 30 rpm. The amount of metal ion removed over the metal sulfide, over a period of time 't' was calculated using the equations 4&5.

$$\text{Uptake (\%)} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (4.1)$$

$$\text{Uptake capacity (mg.g}^{-1}\text{)} = \frac{(C_i - C_t) V}{W} \quad (4.2)$$

Where ' C_i ' and ' C_t ' are the solution concentrations (mg. L⁻¹) of the metal ion at the beginning and at a time 't' respectively, 'V' is the test solution volume (L) and 'W', the amount (g) of metal sulfide used.

CHAPTER – 5

RESULTS AND DISCUSSION

5.1 SYNTHESIS OF LAYERED METAL SULPHIDES

Layered metal sulphides were prepared according to literature procedures except KCuSnS , which is not reported elsewhere. We have tried to optimise the synthesis parameters for increasing the yield (by minimising the losses during washings), getting a more uniform product and also to obtain a material with highest Sr removal ability. Use of Mn powder during KMS1 synthesis leads to formation of Sn rich or Mn rich sulphide phases formation in the reaction mixture which can be separated using repeated exfoliation. Use of MnCO_3 instead of Mn powder was found to reduce the Mn-rich sulphide content in the final product. Use of Carbonate salts instead of metal powders give more scope for the hydrothermal synthesis of other metal sulphides where the metals cannot be utilised as such.

5.2 CHARACTERISATION OF THE METAL SULPHIDES

All the metal sulphides samples prepared were dissolved in aqua regia and analysed for their metal ion concentrations using ICP-AES. The composition arrived based on the elemental analysis was given in Table No. 5.1. Results shows the formation of metal sulfides with varying composition in each synthesis. Which implies that a mix of double metal sulfides are getting formed during the synthesis.

5.3 Sr REMOVAL ABILITY OF THE METAL SULFIDES PREPARED

In order to examine the Sr removal ability of all the metal sulfides prepared; 10 mg of metal sulfides were treated with 2 mL of the 3.963 mM Sr(II) solution for 24 h. The equilibrated solutions were centrifuged and the supernatant solution was estimated for the remaining Sr(II) concentrations using ICP-AES. Sr uptake obtained using the various metal sulfides prepared were calculated and tabulated in Table No.5.2

Sn-rich KMnSnS samples showed better Sr uptake compared to the Mn-rich KMnSnS samples. Replacement of Mn with Zn in the double metal sulfides was resulted an increase the Sr uptake capacity. On comparing the Sr uptake by the

different KMnSnS samples; uptake capacity was found to increase with increase in K content in the sample. This was in agreement with the proposed mechanism of intercalated K^+ ion replacement by the Sr^{2+} ions ([7] Manos et al., 2008). There was quantitative release of K^+ ions during the sorption of Sr^{2+} in the case of KCuSnS-YB sample.

Table 5.1 Composition of the metal sulfides prepared

Sample Name	Composition as per ICP-AES analysis
KMS1-1-S1	$K_{0.233}Mn_{0.135}Sn_{1.386}S_6$
KMS1-1-S2	$K_{0.269}Mn_{0.837}Sn_{1.196}S_6$
KMS1-1-S3	$K_{0.190}Mn_{4.282}Sn_{0.666}S_6$
KMS1-2	$K_{0.555}Mn_{0.786}Sn_{1.235}S_6$
KMS1-3	$K_{0.576}Mn_{0.402}Sn_{1.375}S_6$
KMS1-3-Mn	$K_{0.153}Mn_{6.014}Sn_{0.542}S_6$
KMS1-4	$K_{0.656}Mn_{0.692}Sn_{1.340}S_6$
KMS1-4-Sn	$K_{0.472}Mn_{0.555}Sn_{1.179}S_6$
KMS1-4-Mn	$K_{0.110}Mn_{1.813}Sn_{0.333}S_6$
KZTS	$K_{0.517}Zn_{0.572}Sn_{1.372}S_6$
KCuSnS-YB	$K_{0.697}Cu_{0.284}Sn_{1.512}S_6$
KCuSnS-BI	$K_{0.181}Cu_{2.773}Sn_{1.639}S_6$

Further; metal sulfide samples, KMS1-2-Sn and KZTS were studied in detail for their uptake properties

5.3.1 Effect of pH

Solution pH conditions are very crucial in deciding the speciation and their removal through sorption by different materials. Effect of solution pH on the Sr removal properties of the metal sulfides were studied in this context

Table 5.2 Sr uptake by the metal sulfides prepared

Sample Name	Sr uptake		K release	K+/Sr ²⁺ ratio
	($\mu\text{mol/g}$)	(%)	($\mu\text{mol/g}$)	
KMS1-1-S1	185 $\pm$ 5	24.9 $\pm$ 0.4	*	*
KMS1-1-S2	280 $\pm$ 6	35.8 $\pm$ 0.6	*	*
KMS1-1-S3	37 $\pm$ 12	4.8 $\pm$ 1.5	*	*
KMS1-2	352 $\pm$ 9	47.2 $\pm$ 1.1	*	*
KMS1-2-Sn	391 $\pm$ 6	56.3 $\pm$ 1.5	*	*
KMS1-2-Mn	22 $\pm$ 10	2.9 $\pm$ 1.4	*	*
KMS1-3	468 $\pm$ 8	59.1 $\pm$ 0.8	*	*
KMS1-3 (Mn)	47 $\pm$ 25	5.9 $\pm$ 3.2	*	*
KMS1-4	553 $\pm$ 10	69.8 $\pm$ 1.3	*	*
KMS1-4 (Sn)	458 $\pm$ 12	57.8 $\pm$ 1.7	*	*
KMS1-4-Mn	67 $\pm$ 6	8.4 $\pm$ 0.9	*	*
KZTS	535 $\pm$ 8	76.4 $\pm$ 1.5	*	*
KZTS-2	547 $\pm$ 5	74.0 $\pm$ 0.7	*	*
KCuSnS-YB	515 $\pm$ 44	71.3 $\pm$ 5.0	1101 $\pm$ 128	2.14
KCuSnS-BI	38 $\pm$ 13	5.0 $\pm$ 1.6	192 $\pm$ 1	5.04

5.3.1.1 KMS1-2-Sn

About 25 mg of the KMS1-2-Sn was treated with 5 mL of the 2.78 $\pm$ 0.13 mM of the Sr(II) solutions, whose pHs were adjusted using dilute HCl or NaOH to the desired value before the experiments. Equilibration was carried out for about 24 h and then samples were taken, estimated for their Sr concentration to compute the Sr removal. pH of the equilibrated solutions was also measured and given in Table No. 5.3. Equilibrium solution pHs were found to move towards neutral region during sorption. Sr uptake from all the solutions was estimated and plotted in Figure 5.1. There was no appreciable effect was not seen on the Sr uptake

capacity of the KMS1 samples and KMS1-2-Sn was able to pick up Sr under a wide range of pH conditions (both acidic as well as basic).

Table 5.3 Sr solution pH before and after equilibration with KMS1-2-Sn

Initial pH	Equilibrium pH
2.0	2.8
3.9	5.1
5.8	6.2
8.2	6.3
9.7	6.5

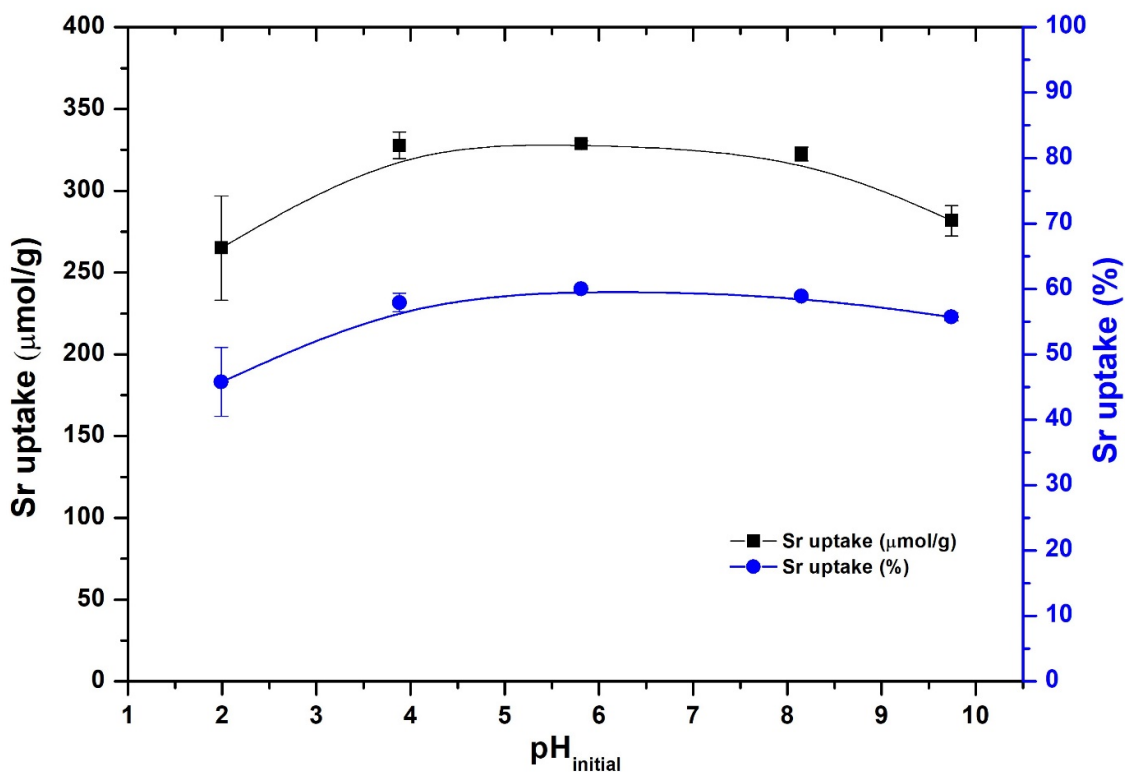


Figure 5.1 Sr uptake by KMS1-2-Sn: Effect of solutio pH

5.3.1.2 KZTS

About 30 mg of the KZTS was treated with 6 mL of the 3.68 ± 0.16 mM of the Sr(II) solutions, whose pHs were adjusted using dilute HCl or NaOH to the desired value before the experiments. Equilibration was carried out for about 24 h and then samples were taken, estimated for their Sr concentration to compute the Sr

removal. pH of the equilibrated solutions was also measured and given in Table No. 5.4. Similar to KMS1-2-Sn; equilibrium solution pHs were found to move towards neutral region during Sr sorption. Sr uptake by the KZTS was estimated and plotted in Figure 5.2. There was no appreciable pH effect was seen on the Sr uptake capacity of the KZTS and it was able to remove Sr under a wide range of solution pH conditions (both acidic as well as basic).

Table 5.4 Sr solution pH before and after equilibration with KZTS

Initial pH	Equilibrium pH
1.9	4.0
3.0	4.2
4.6	4.9
5.3	5.5
5.7	5.5
10.8	7.7

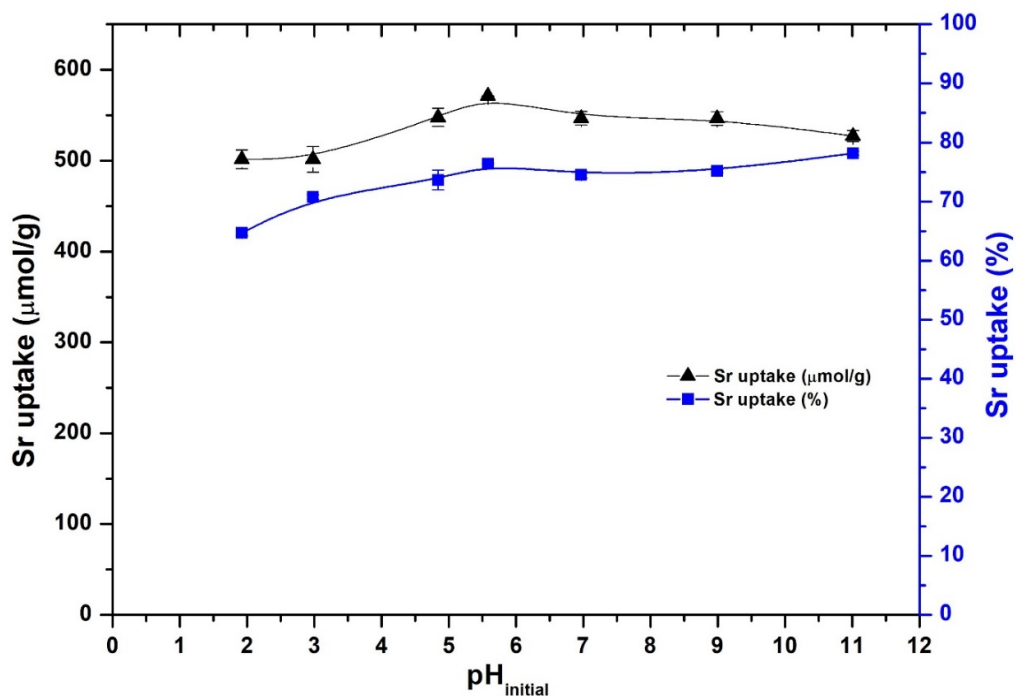


Figure 4.2 Sr uptake by KZTS: Effect of solution pH

The ability of both the KMS and KZTS to remove Sr from solutions have a wide pH range indicated their utility in various industrial effluents ranging from acidic to alkaline conditions.

5.3.2 Effect of initial solution concentration

In order to find the maximum uptake capacity of the metal sulfides; 10 mg of the metal sulfides were treated with 2 mL of the Sr^{2+} solutions of varying concentrations (0.5 to 5 mM) for 24 h. Equilibrated solutions were then estimated for their Sr solution concentration to compute the Sr uptake by the sorbents. Sr uptake capacity obtained with increase in solution Sr concentration was plotted in Figure 5.3 (for KZTS) and Figure 5.4 (for KMS1-2-Sn). Both KMS1-2-Sn and KZTS showed complete uptake of Sr from its low concentrated solutions and the saturated capacities obtained are 549 $\mu\text{mol/g}$ (for KZTS) and 391 $\mu\text{mol/g}$ (for KMS1-2-Sn). KZTS showed better uptake properties compare to the KMS1-2-Sn.

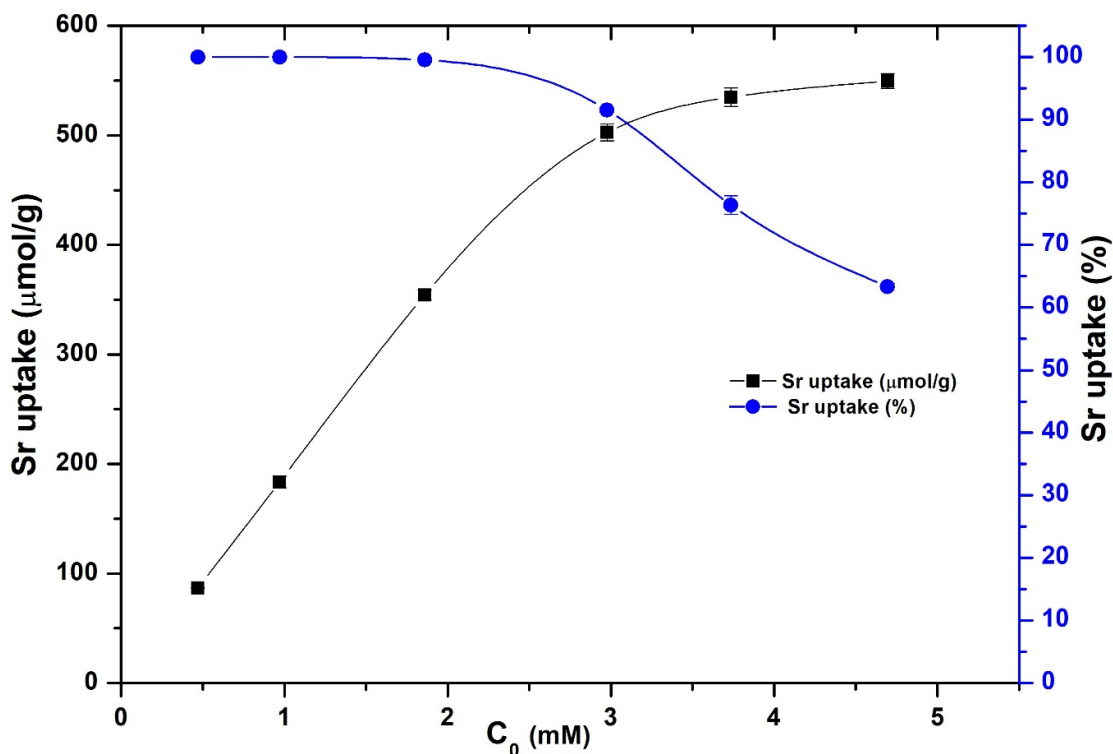


Figure 5.3 Sr uptake by KZTS: Effect of initial solution concentration

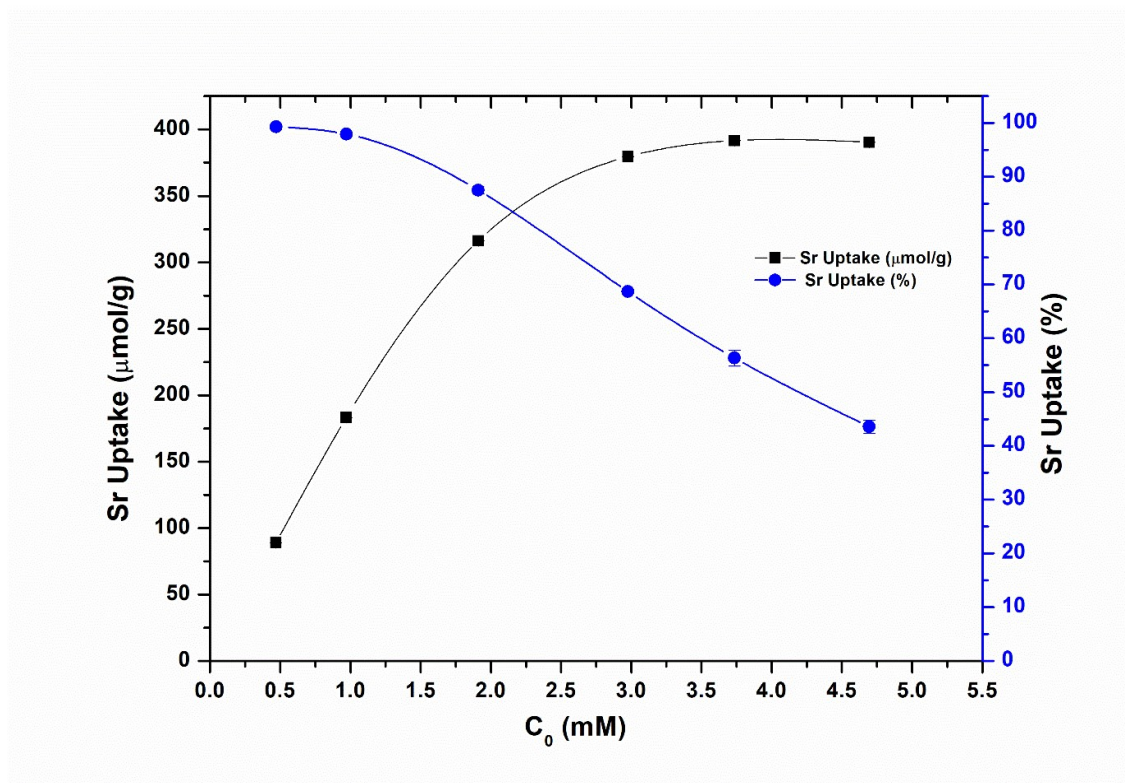


Figure 5.4 Sr uptake by KMS1-2-Sn: effect of initial solution concentrations

5.3.3 Sr uptake kinetics

To study the metal ion uptake kinetics (i.e., the speed at which the metal sulfides remove strontium from the solution) of the metal sulfides prepared; about 70 mg of the samples were equilibrated with 14 mL of the 4 mM Sr test solutions. Samples were collected (about 50 μL) periodically and tested for their Sr concentrations after proper dilution with ultrapure water. Results obtained from the study was plotted in Figure 5.5. Both KMS1 and KZTS showed faster uptake kinetics and attains saturation in less than 10 minutes of equilibration. This indicates utility of the sulfides prepared in real time application where it requires faster removal while using in flow conditions.

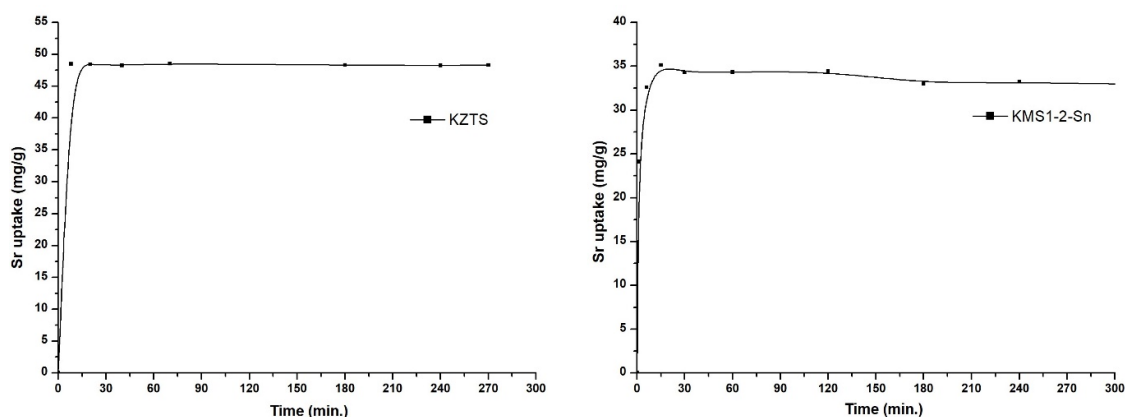


Figure 5.5 Sr uptake kinetics of the metal sulfide prepared

5.3.4 Regeneration and Reuse:

Regeneration and reuse of any sorbent is an important aspect, where easy regeneration and reuse with no or minimum loss of uptake characteristics will make the whole treatment process more economic and environment friendly. Metal sulfides prepared were studied for their regeneration and reuse with this objective. About 10 mg of the sorbents were equilibrated with 2 mL of the 4 mM Sr solution for 48 h. Samples were centrifuged and the centrifugate was analysed for Sr concentrations. Equilibrated samples (after removing the centrifugate completely) were then washed with ultrapure water (2 mL each – twice) and the second washings were collected for Sr analysis. Then the settled samples were treated with 2 mL of the 0.5 M KCL solution (the eluent) and equilibrated for 24 h. The KCl eluted or regenerated metal sulfide sample were again treated with required amount of 4 mM Sr solution for checking the reuse of the sorbents prepared. All samples were collected and analysed using ICP-AES for their Sr concentrations. Results obtained for the studies were given Table5.5.

Table 5.5 Regeneration and reuse of the metal sulfides prepared

Sample Name	Sr Uptake (mg/g)	Desorption (%)		Sr uptake during resorption
		Ultra-pure water	0.5 M KCl	
KMS1-2-Sn	13.3 ± 1.4	7.0	86.3	4.2 ± 1.1
KZTS	47.4 ± 0.7	BDL	87.6	48.6 ± 3.4

KMS1-2-Sn showed Sr elution in ultra-pure washings itself. While KZTS showed no elution of the Sr into the water washings. Sr elution using KCl solution was almost complete (nearly 90 %) which shows the possibility of regeneration and reuse of the same. Resorption studies using 4 mM Sr solutions showed that the KZTS samples retained their Sr pickup ability while KMS1 sample uptake got affected significantly.

5.3.5 Selectivity studies

Selective removal of ions in presence of other competing ions is of very important in any industrial effluent treatments and nuclear industry in particular. Removal of the radioactive ions, whose physical quantity is very minimal but very significant on an activity level, from the non-active competing ions from any active waste streams will make the treatment process more economic and environment friendly. Selective removal of the active ions can reduce the active waste volume, which needs special care or treatment, generated in any nuclear waste treatment processes. Containing the activity to smaller volumes implies better economics and more greener technologies. Selectivity of the prepared metal sulfides for Sr removal was studied in this aspect. Uptake of Sr in presence of other ions such as Ca, Fe, Mg and Na were studied in detail. Two solution conditions; (S1) Sr^{2+} – 1.063 mM, Ca – 3.492 mM, Fe^{2+} – 4.027 mM, Mg – 4.125 mM, Na – 4.409 mM or (S2) Sr^{2+} – 3.957 mM, Ca – 3.593 mM, Fe^{3+} – 3.073 mM, Mg – 3.752 mM, Na – 4.249 mM were applied for the study. Metal ion uptake obtained for the respective metal ions were tabulated in Table 8. Selectivity factor as defined by Eq. 6 was plotted calculated with respect to other competing ions and plotted for both KMS1 and KZTS (Figure 5.6).

$$\text{Separation Factor, } \frac{\text{Sr}}{\text{Mq}} = \frac{\text{Uptake Capacity}_{\text{Sr}}}{\text{Uptake Capacity}_{\text{M}}} \quad (5.1)$$

Selectivity of the metal sulfide was found to depend upon the solution conditions. low Sr separation factor (less than 1) for KZTS from solution S1 may be because of the low concentration of Sr compared to the competing ions. In general metal sulfides showed selectivity towards Sr compared to Ca, Mg and Na. The general trend in the selectivity decreases in the order, $\text{Fe} > \text{Ca} > \text{Mg} > \text{Na}$. Presence of iron was found to affect the Sr uptake significantly.

Table 5.6 Competitive sorption of metal ions by the metal sulfides

Sample Name	Conditions used	Sr uptake		Ca uptake		Fe uptake		Mg uptake		Na uptake	
		$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%
KMS1-2-Sn	25 mg to 5 mL of S1	64.1	30.6	114.9	16.7	708.3	89.4	54.1	6.7	26.7	3.1
KZTS	30 mg to 6 mL of S1	35.2	16.6	199.4	28.6	532.4	66.3	77.8	9.5	44.6	5.0
KMS1-2-Sn	25 mg to 5 mL of S2	104.5	13.4	82.8	11.7	363.7	60.1	39.2	5.3	31.6	3.8
KZTS	30 mg to 6 mL of S2	191.3	24.3	126.6	17.7	187.5	30.7	65.4	8.8	BDL	BDL

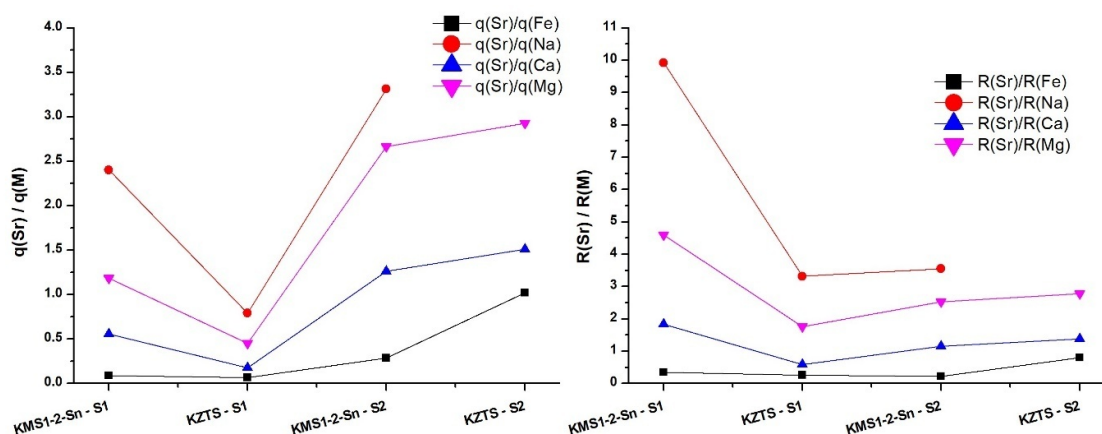


Figure 5.6 Separation or selectivity factor for KMSs and KZTS using (a) solution 1 and (b) solution 2

There was release of both K^+ and Mn^{2+} (from KMS1-2-Sn) and K^+ and Zn^{2+} (from KZTS) ions to the equilibrated solution during the course of study. There was a 1:1 correlation in total charge balancing in the case of solution 1 (which used Fe^{2+} ions). While there was more release K^+ and Mn^{2+} (from KMS1-2-Sn) and K^+ and Zn^{2+} (from KZTS) compared to the sorbed species in the case of solution 2 (which used Fe^{3+} ions). A release ratio of 1:1.35 was observed for KMS1-2-Sn and 1:1.41 ratio was observed for KZTS. There was no release of Sn in both the cases. Which implies structural changes to the metal sulfide backbones during sorption from solution containing transitions metal cations.

5.3.6 Powder X-ray Diffraction study of KMS1 and KZTS

Powder x-ray diffraction measurements showed that the Sr exchanged KZTS material is isostructural with the pristine KZTS which implies a topotactic ion exchange. A shift of the (003) and (006) Bragg peaks to lower 2θ values (or higher d-spacing) was observed in the diffraction patterns of Sr^{2+} exchanged products in the case of KZTS (Figure 5.7). While in the case of KMS1; Sr sorbed sample showed different powder x-ray diffraction spectra compared to the as synthesised one (Figure 5.8). This is in agreement with the results obtained during the regeneration and reuse study. KZTS was found to retain the Sr removal ability after regeneration while the strontium removal ability of the KMS1 sample was reduced significantly.

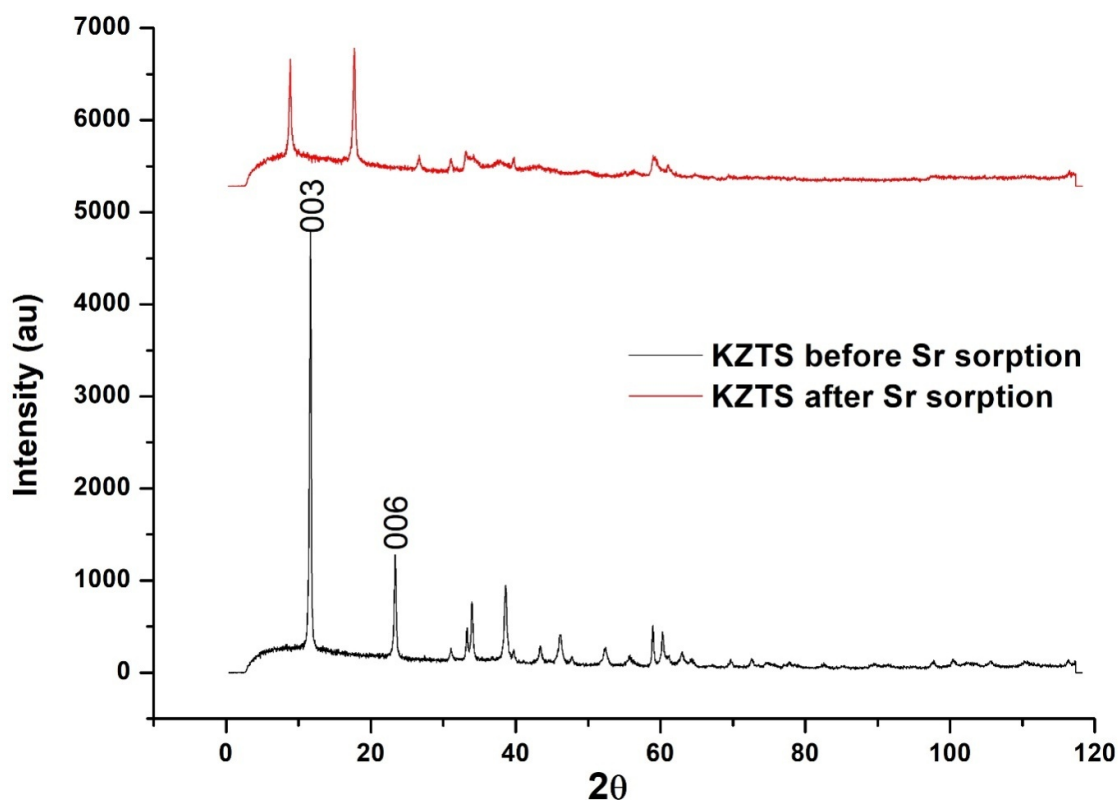


Figure 5.7 Powder XRD spectra of KZTS before and after Strontium sorption

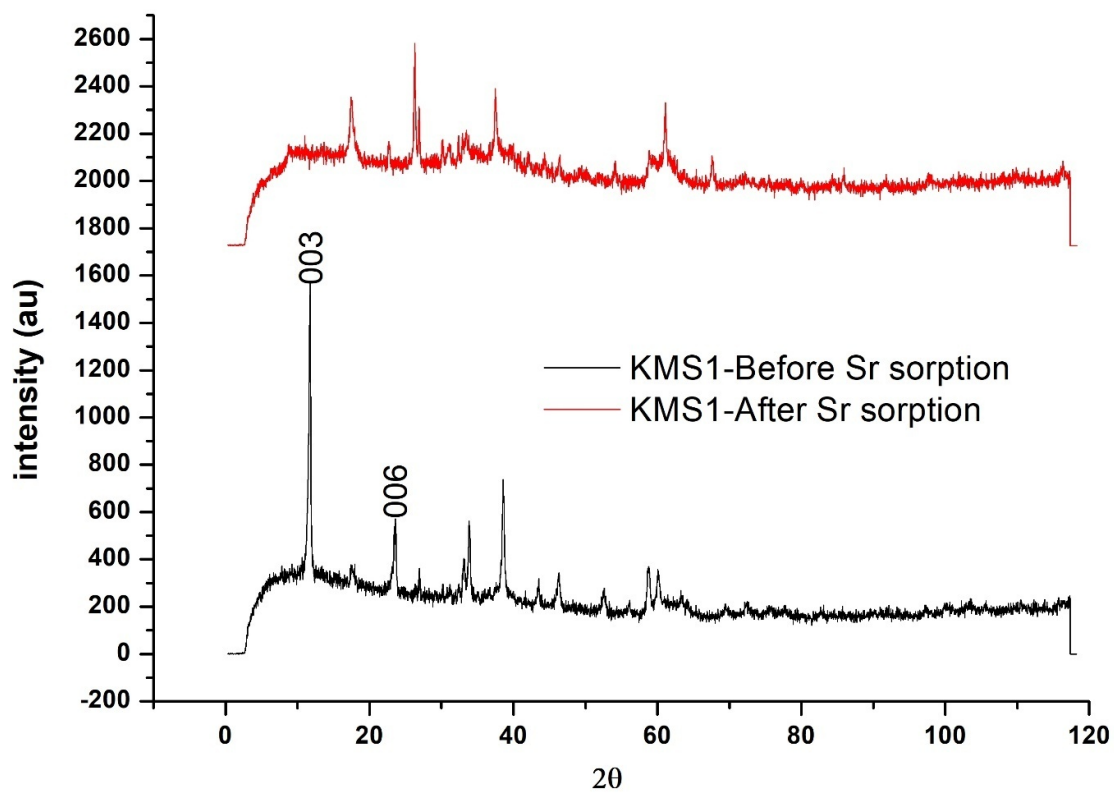


Figure 5.8 Powder XRD spectra of KMS1-2-Sn before and after Strontium sorption

CHAPTER – 6

SUMMARY AND CONCLUSIONS

Different types of bimetallic metal sulfides were synthesised using hydrothermal synthesis method. The method adopted is simple and scalable. All the metal sulfides prepared were characterised using ICP-AES for their composition. A mix of double metal sulfides were found to be formed during synthesis. Replacement of Mn powder with MnCO_3 led to a more uniform sample with enhanced Sr uptake capabilities. This opens a new way for utilising the hydrothermal method for the preparation of sulfides of certain metals whose metallic form cannot be used directly. All the metal sulfides were tested for their strontium removal properties. KZTS showed better Sr uptake compared to KMS1. Both showed faster uptake kinetics with minimal solution pH effect. Presence of iron in solutions was found to decrease the Sr uptake. Selectivity order under the studied condition was found to be $\text{Fe} > \text{Ca} > \text{Mg} > \text{Na}$. Presence of transition metal cation (Fe^{2+} and Fe^{3+}) was found to cause changes in the metal sulfide lattice during sorption. More studies are required to conclude on the structural changes happening during the Sr sorption under different solution conditions.

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