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INFLUENCE OF ADSORPTION PARAMETERS ON CESIUM UPTAKE FROM AQUEOUS SOLUTIONS- A BRIEF REVIEW

Michael Adekunle Olatunji[a], Mayeen Uddin Khandaker[a*], H.N.M. Ekramul Mahmud[b], Yusoff Mohd Amin[a]

[a]Applied Radiation Laboratory, Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia

[b]Polymer Laboratory, Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Abstract: Due to rapid population growth, technological advancement and industrial revolution, the rate of generated waste effluents has become a grave concern. Cesium which possesses high fission yield is generally transferred to liquid wastes especially those emanated from the nuclear power plants, reprocessing of spent fuels, nuclear weapon testing and radionuclides production facilities for medical applications etc. Radiocesium (^{137}Cs) is one of the hazardous radionuclides creates adverse effects on human health and environment. Due to its physical ($T_{1/2}$=30.17 y) and chemical characteristics (alkalinity, solubility etc.), it can be easily assimilated by the living organisms. As a result, the removal of cesium from wastewater is imperative from the health point of view. Several techniques are implemented but in recent time, adsorption has been gaining increasing attention to the scientific community owing to a number of reasons. Hence, this paper presents an overview on sorption of cesium from wastewaters. Consequently, several critical parameters such as sorption capacity, percentage efficiency and the influence of several factors on cesium uptake by various adsorbents have been reviewed in details.

Keywords: Adsorption, liquid radioactive wastes, Cesium, Efficiency, Sorption capacity

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[*] Corresponding author. Tel: 03 7967 4099 ; Fax: 03 7967 4146

E-mail address: mu_khandaker@um.edu.my

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1.0 Introduction

The treatments of low-, intermediate- and high-level contaminated liquid wastes are gaining increasing attentions worldwide owing to a number of imperative reasons: the generation of wastewater is increasing in a rate proportional to the rapid technological advancement and population growth [1,2]. The environmental pollution resulted in the discharge of the wastes in water-bodies and soil which inadvertently results into a prolonged health problem in both human and animals via enhancing radiation burden of the entire ecosystem. Most importantly, the needs to recover limited precious and expensive substances which often get lost through the generated wastes and the demand for wastewater reuse [3] have always been the concern of the scientists and engineers. For safer and effective management, wastewaters containing radioactive materials and heavy metals are of particular concern due to their behaviours within the environment and associated health implications upon exposure to human and animals. The sources of liquid radioactive wastes have always been through nuclear power generation from nuclear plants, reprocessing or recycle of spent fuel, mining and milling of mineral ores, nuclear application involving radioisotopes in medical and agricultural practices, exploration of natural gas and oil, nuclear tests and accidents and so on. From these sources, potential health challenging radionuclides which are always parts of the wastes are being generated and released into the ecosystem. Among the radionuclides of environmental impacts and hazardous effects are uranium, radium, thorium, strontium, cesium, europium, polonium and cobalt. These radionuclides are classified as natural (e.g. uranium, radium, thorium, etc.) and artifical (e.g. cesium, cobalt, strontium, etc.). Apart from the natural radionuclides that take their origins from the formation of the earth, the artificial radionuclides emanated as a part of the wastes from the aforementioned processes and streams. As regards to accidents, the most prominent of such were the Chernobyl in 1986 and the Fukushima accidents in 2011.

This review is focussed on the removal of caesium (Cs) due to its significant health effect to human and environment. As an alkali metal, caesium has similar characteristics as potassium and rubidium, and belongs among the few metals that appear as liquids at near the room temperature. It is a very reactive metal and reacts with water explosively than other alkali metals in the same group even at low temperature [4,5]. Caesium has a higher atomic mass and more electropositive than other non-radioactive alkali metals and it is the most stable chemical element ever known [6–8]. Because of its high reactivity, it is classified as a hazardous material. Cs metal, which behaves similar to potassium, can easily be adsorbed to the body and distributed into the soft tissues of the whole body [9]. Thyroid cancer is one of the terrible consequences of this metal adsorption [10,11]. Its acute poisoning causes medullar dystrophy, asthma, allergy, heart problems, disorders in reproductive function and bone mineralization and damages of thyroid and liver and, mutagenic disorders [12]. Cesium is mined mostly from pollucite, while as a by-product of uranium fission [13], many radioactive isotopes of cesium (^{134}Cs and ^{137}Cs are of significant health concern) are released into the environment. In particular, ^{137}Cs a gamma-emitter, is part of generated wastes from extractive industries, and due to its physical (long half-life, $T_{1/2}$=30.17 y) and chemical (high solubility) characteristics, it could easily transferred to the food chain [14–17].

Moreover, the toxicity, non–biodegradability, ease of migration from underground to surface water as well as soil–to–plants transfer via root uptake leading to external and internal exposures to man have made it as the most important issues to consider. Hence, several separation techniques are being employed to remove cesium from low–, intermediate– and high–level solid and liquid radioactive wastes before disposal. But, the method could vary from conventional to more sophisticated approach as the case may be to treat a particular waste for the total removal of radioactive materials present in a particular waste effluent. Methods such as chemical precipitation, coagulation / co-precipitation, membrane process, reverse osmosis, chemical reduction, solvent extraction and foam flotation have been used to remove radioactive materials, heavy metals and decolouration from liquid processes (fig. 1) [18–31]. Several inorganic, organic, biological, agricultural materials and magnetite or their mixtures have also been used as adsorbents to separate solid radioactive materials from liquid wastes before disposal [14–37]. A host of other novel methods and materials are still being developed and used for treatment of radioactive liquid wastes [38]. Normally, radioactive wastes are classified for effective treatment and management. The classification depends on the characteristics of the radioactive materials present in the wastes, application of radioisotopes, the rate of waste generation and the regulatory frameworks which bound on the disposal of radioactive wastes in a particular place or country [39].

In this review, several factors affecting the removal of cesium from solutions are examined based on the available literature (fig. 1). Sorption capacities and efficiencies of each adsorbent were reported and compared under various conditions.

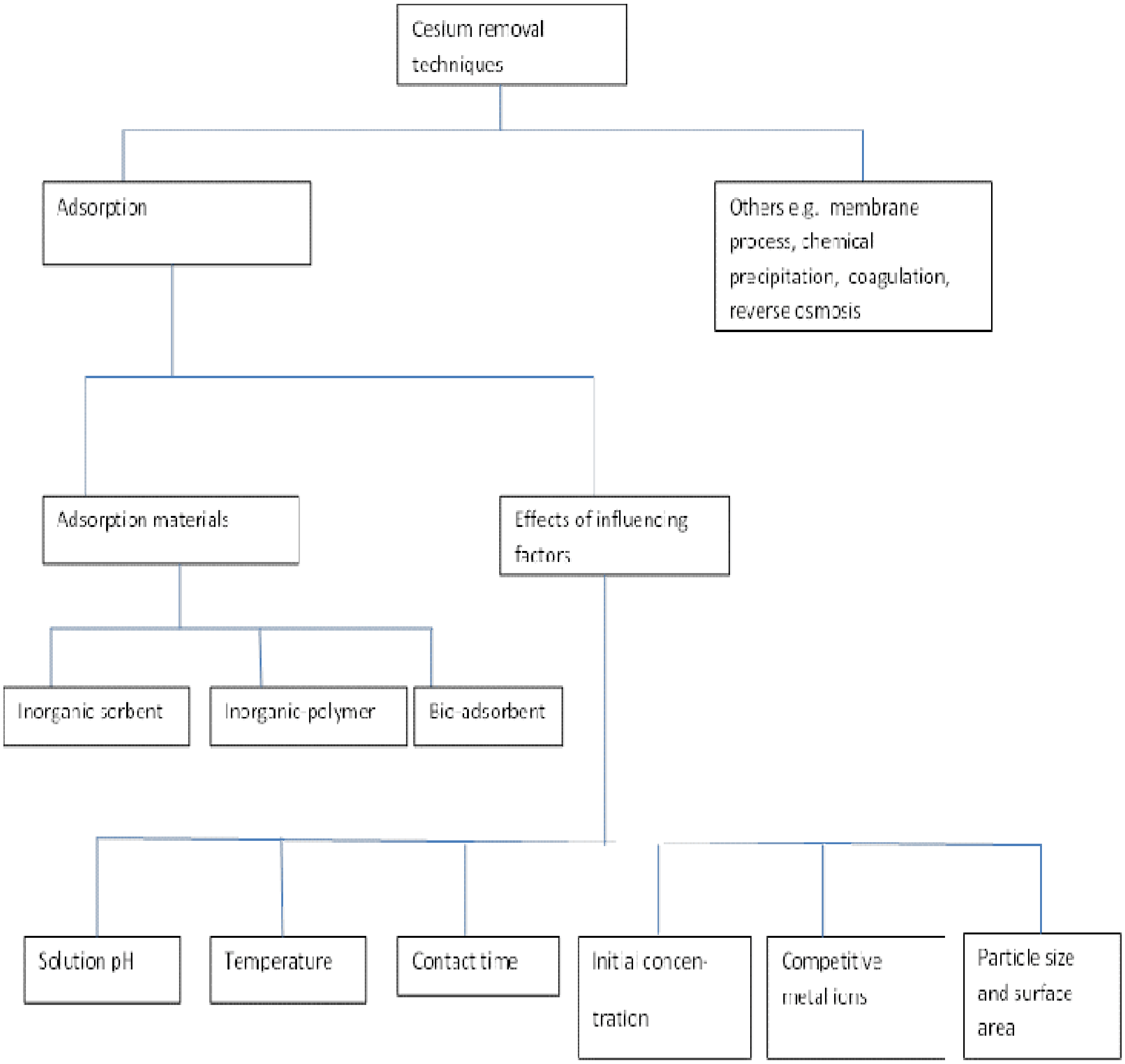

Figure 1: Schematic diagram showing various adsorption materials and adsorption factors.

2.0 Adsorption/ ion exchange of cesium ions onto synthesized and natural adsorbents

This is a method by which a sorbate is removed or accumulated on the immobile solid from its liquid or gaseous surroundings, and usually referred to as liquid-solid interaction. Normally, this process occurs at the phase of the sorbent and so, it is a surface–based phenomenon [40]. Adsorption can take different dimensions, if the process is initiated as a result of weak intermolecular forces (Van der Waals interactions) then it is specifically called physisorption and this force being weak in nature results into reversible adsorption, but if occurs due to the formation of chemical bonds between the molecules of adsorbate and the adsorbent it is known as chemosorption. Ion exchange on the other hand is a reversible chemical process in which an ion from solution exchanges with similarly charged ion attached to the adsorbent, the solid particle [40]. Due to their common features, adsorption and ion exchange are grouped together as sorption processes for effective sequester of toxins from waste/drinking waters [41,42]. Adsorption is recognized as an effective and economic method for the removal of radionuclides compared to the other approaches owing to a number of reasons such as; the ease of design and operation, adsorbate–specificity, better treatment with no/little secondary waste generation, possibility of using at low concentration, high efficient performance, ease of regeneration and reuse, suitability for both batch and column studies, and the availability of the adsorbents [43]. Normally, a good adsorbent must have a large surface area, good macroporous structure and be stable under chemical, radiation and thermal reaction conditions. However, the behaviour and efficiency of adsorbents can also be influenced by the condition of the solution.

2.1 Various adsorbents used in recent time for cesium adsorption

The treatments of waste-water and drinking water for radionuclide decontamination have involved several sorbents in recent time. However, this review focuses on various adsorbents as reported in the literature which are classified as inorganic, inorganic-polymer composites andbio-adsorbents.

2.1.1 Inorganic adsorbents

Several metal oxides, hexacyanoferrates and ferrocyanides of transition metals as well as clay minerals have been reported for adsorption of radioactive materials [44-47,61–67] as mentioned in the Table 1. For radioactive waste treatments, certain characteristics of inorganic adsorbents such as high selectivity, good mechanical, radiation and thermal stability in the solution containing the adsorbate, high porosity, cost effectiveness, environmental friendliness which does not result into generation of secondary contaminants and the possibility of regeneration are usually considered [44,45]. However, the hexacyanoferrate of transition metals is generally too difficult to be separated from the solution due to its fine particulate nature which often create further problems of contamination and hence, needed to be incorporated into supporting materials [48], but it is a highly selective agent with special cubic structure and channel diameter that allows only small hydrated ions such as cesium ions to permeate through and block the larger ones that compete for the sorption sites [49]. On the other hand, metal ferrocyanide sorbents were reported to have good structure, ion exchange ability for cesium from different types of solution such as natural waters and radioactive wastewater, stable in acidic and moderate alkaline medium, stable in radiation and high temperature [50–57]. However, adsorption by ferrocyanides sorbents have been reported to be strongly affected by preparation, difficult to handle for column application due to its fine nature [58,59] and results into large sludge production [60]. In case of clay minerals which are generally less expensive and of larger surface area and layered structure for adsorption have some disadvantages due to competitiveness of other monovalent cations such as K and Na ions with cesium adsorption which may block sorption sites [49]. Some of the inorganic adsorbents that have been commonly used are presented in Table 1 along with their adsorption capacity.

Table 1: Cesium ion adsorption capacities of some inorganic adsorbents

Inorganic adsorbents	Adsorption parameters and adsorbent characterization	Adsorption capacity, cesium (Efficiency ,%)	Comment	Reference

self-assembled mesoporous silica	Adsorbent amount: 0.05g Initial concentration: 10ml of 2ppm Cs solution Cs solution: Acidic and alkaline media. Contact time: 2h Interfering metal ions: Presence of sodium and potassium Characterization: XPS	179 mg/g (~99%)	Sorption kinetic: Fast. Interfering ions: No effect (Na^+ and K^+ ions) Data fitted by: Langmuir model	[8]
Copper ferrocyanide mesoporous silica	Adsorbent amount: 0.1g Initial concentration: 100ml of 0.5-500ppb of both natural and simulated acidic/alkaline solutions. Adsorption parameters studied: pH(0.1-7.3) and competing ions	21.7 mg/g (95%)	Adsorption kinetic: Rapid pH effect: increases Interfering ions effect: Not significant effect Stability: Little leaching of component elements over time. Data fitted by: Langmuir model.	[11]
Prussian blue	Adsorbent amount: 0.1g Initial concentration: 100ml of 0.5-500ppb of both natural and simulated acidic/alkaline Adsorption parameters studied: pH(0.1-7.3) and competing ions	2.6 mg/g (75%)	Adsorption kinetic: Less rapid pH increase effect: Favourable Interfering ions: No effect. Stability: Leaching of component elements. Data fitted by: Langmuir model.	[11]
Activated silico-antimonate	Adsorbent amount: 0.1g. Initial concentration:5ml of 10^{-4} M Contact time: 6h. Adsorption	0.220–0.520 mg/g (30 to >90%)	Adsorption kinetic: Relatively rapid. Results: Temperature increase, Si:Sb ratios (SiSb 1:2) and acidity favoured Cs	[46]

	parameters:Acidity,temperature (303-333K) and silicon/antimony ratios. Characterization: FT–IR, XRD, XRF and DTA–TG		uptake. Adsorption mechanism: Chemisorption which is spontaneous and endothermic in nature. Data fitted by: Pseudo-second kinetic model.	
Hydrous mixed metal oxides	Solution volume: exchanger ratio: 100–400cm^3/g Contact time: 3days. Studied parameters: Temperature and pH Characterization: XRD, TGA and elemental analysis.	2.2–2.9 mmol/g (exchanger capacity)	Effect of temperature increased the crystallinity of the material. Doping with tungsten or niobium increases separation capacity.	[47]
Nickel hexacyanoferrate incorporated into walnut shell	Adsorbent amount: 4g. Initial Concentration:200ml of 5-400mg/L. Studied parameters: Contact time and temperature (298-313K). Characterization: FESEM and TG–DTA.	4.94 mg/g	Adsorption kinetic: Rapid within 2h. Results: Temperature increase and K$^+$ ion favoured Cs uptake. The sorbent was thermally stable. Data fitted by: Feundlich isotherm and pseudo-second order kinetic models Mechanism: Spontaneous and endothermic in nature. Stability: Adsorbent thermally stable.	[49]
Potassium copper ferrocyanide	Initial concentration: 0.015M. Studied parameters: pH	2.25 mmol/g	The sorbent is not stable in acidic pH (<3) and sorption capacity is influenced by	[50]

	and interfering ions		magnesium nitrate of about 0.82M. Desorption is possible with nitric acid.	
Copper (II) ferrocyanide incorporated vermiculite	—	179 mg/g	—	[57]
Manganese–oxide	Studied parameters: pH and interfering ions.	172 mg/g	Cesium uptake favourable over pH 2–10 and the presence of Na^+, Ca^{2+}, Mg^{2+} and K^+.	[61]
Hydrous titanium oxide	Adsorbent amount: 0.1g. Studied parameters: Temperature, contact time and pH. Characterization: IR, XRD and DTA	0.6189–0.4303 mmol/g	pH effect: pH<2 inhibited cesium uptake and pH6 favourable. Equilibration time: 5h. Temperature increase: Favoured Cs uptake and the process was spontaneous and endothermic in nature. Data fitted by: D–R isotherm model.	[62]
Zirconium iodomolybdate	Adsorbent amount: 100mg. Initial concentration: 10ml of 10^{-4}M. Studied parameters: pH (1–8), temperature (25-45°C) and competing ions (Na^+). Characterization: XRD and TGA.	7.94 to 9.62 mmol/g ion exchange capacity (80% sorption)	Adsorption kinetic: Rapid Equilibration time: 2h. Optimum pH: pH3 and %decrease at higher pH. Effects of ionic strength and organic acids: Decreased uptake capacity. Data fitted by: Pseudo-second order and Elovich models. Sorption mechanism: Chemisorption.	[63]

			Sorbent thermal stability: up to 350^{o}C.	
Nickel potassium ferrocyanide immobilized in chitin	Adsorbent amount: 100mg. Initial concentration: 50ml of 10- 400mgCs/L. Contact time: 24h. Studied parameters: pH and interfering ions. Characterization: SEM–EDX and XRD.	80 mg/g	Parameters effects: pH (2.5–6.4) and the presence of monovalent ions (0.01–1M) have no much effect on sorption capacity.	[64]
potassium copper nickel hexacyanoferrate	Adsorbent amount: 100mg. Initial conc.: 10cm^{3} of 3.7mmol/g. Studied parameters: Temperature (≤353K) and initial concentration (3.7-75 mmol/g).	2.215 ─2.257 mmol/g	Temperature increase: Favourable for adsorption. Thermodynamic studies: Endothermic and spontaneous. Data fitted by: Langmuir model and D–R isotherm model.	[65]
potassium nickel hexacyanoferrate loaded–silica gels and–chabazite	Adsorbent amount: 0.07g. Initial concentration: 7cm^{3} of 10ppm Contact time: 7d Studied parameters: neutral pH and the presence of 5M $NaNO_3$. Column experiments were used to estimate dynamic sorption capacity. Characterization. XRD, SEM and IR.	0.123 mg/g(Breakthrough capacity) and 0.179 mg/g (T.capacity) (69% column utilization)	Equilibration time: 2d Influence of sorption parameters: Favourable.	[66]
Bentonite	Studied parameters:	1.334	Optimum pH: pH7.0.	[67]

	Effects of pH, ionic strength and contact time. Characterization: N_2–BET, SEM, XPS and XRD.	mmol/g (89%)	Equilibration time: 7h. Influence of alkali and alkaline earth metal ions: Negative. Data fitted by: Langmuir model.	
Local Taiwan laterite (LTL)	Adsorbent amount: 15g. Initial concentration: 450ml of 1mM- 0.1μM. Contact time: 7d. Studied parameters: Effects of time, sorbent dosage and aqueous temperature Characterization: XRD, SEM/EDS and BET.	0.3 mmol/g	Adsorption kinetic: Rapid. Adsorption mechanism: physicosorption. Equilibration time and temperature: 1h and low temperature (25°C). Desorption is possible at higher temperature (55°C). Thermodynamic studies: Spontaneous and exothermic in nature. Data fitted by: Freundlich and Langmuir isotherm models.	[68]
Zeolite A	Adsorbent amount: 10mg. Initial concentration: 10ml of 100mg/L Treatment conditions: pH 6.0 for 3h. Studied parameters: Effects of pH (2-8), initial concentration (50–150mg/L), time and temperature (298–333K). Characterization: XRD,	207.47–211.41 mg/g	Adsorption kinetic: Rapid within 30mins. Equilibration time: 90-120mins. Effects of parameters: Increase in pH (6-8), temperature, initial concentration and contact time favoured the adsorption. Zeolite structure disruption at acidic pH	[69]

	XRF and thermal analysis.		range. Data fitted by:. Pseudo–second order kinetic and Langmuir isotherm models. Mechanism: Chemical sorption process.	
Clinoptilolites (CLI)	Adsorbent amount: 1g. Initial concentration: 50cm^3 of 10^{-6}– 10^{-1} mol/dm^3 Contact time: 48hrs Studied parameters: Effects of temperature and cesium loading. Characterization: XRD, SEM and BET.	1.31–3.00 mg/g (75-92%)	Equilibration time: 4hrs. NH^{4+}–CLI form was found more favourable for Cs below 60oC temperature. Temperature of < 60^{o}C and low Cs loading: Favourable for Cs adsorption. Data fitted by: D–R isotherm model.	[70]
Sericite	Initial concentration: 100ml of 10–100mgL Cs. Studied parameters: Effects of pH, initial concentration, temperature (15–45^{o}C) and sorbent loading. Characterization: XRD, SEM/EDX and FT-IR.	6.68 mg/g (~80%)	Equilibration time: 120mins. Influence of parameters: Increase in pH 2–5 and 6.0g/L sorbent concentration favourable for Cs uptake but decreased at higher temperature. Thermodynamics: Exothermic and spontaneous. Data fitted by: Freundlich isotherm and pseudo-second order kinetic models.	[71]
Ethylamine-	Adsorbent amount: 0.05g	80.27 mg/g	Influence of the parameters:	[72]

modified montmorillonite	Initial concentration: 25ml of 20–340mg/L. Treatment conditions: 30^{o}C and pH7.5 for 240mins. Studied parameters: The effects of pH (1-10), contact time, initial concentration, temperature and ionic strength. Characterization: FT–IR, BET, SEM and EDS		Increase in pH favoured the adsorption but temperature increase and presence of alkali and alkaline earth metal ions decrease uptake and hence, sorption process was exothermic and spontaneous in nature. Data fitted by: Langmuir isotherm and pseudo-second order kinetic models.	

2.1.2 Inorganic–polymer composites

Enhancement of the adsorption properties of inorganic compounds as sorbents for cesium ion in solution has been realized by the incorporation of polymers. Inorganic compounds of nanosizes with high selectivity, high surface area and high speed of chemical reactions have been incorporated in fibrous and synthetic polymers with ion exchange groups [48]. Technological properties of fibrous polymer matrix (flexibility, chemical stability, high specific surface, low hydraulic permeability, and ease utilization in dynamic sorption regimes) make the synthesized composites of good adsorption materials with high sorption capacity. Some of the polymers such as polyacryonitrile, polyaniline and chitosan have been investigated for cesium ion removal [67,73-78]. Table 2 shows some common inorganic-polymer composites used in the recent time.

Table 2: Adsorption capacities of inorganic-polymer composites for cesium ion removal from solution

Inorganic–polymer composites	Adsorption parameters and adsorbent characterization	Adsorption capacity	Comment	Reference
Chitosan–grafted bentonite	Studied parameters: Effects of pH, ionic	1.164 mmol/g	Equilibration time: 10h Influence of parameters: pH	[67]

	strength and time. Characterization: N_2–BET, SEM, XPS XRD and TGA.		7.0 was favourable but the presence of alkali and alkaline earth metal ions and partial exfoliation of bentonite layer and lower ion-exchange properties of hydroxyl groups decreased the uptake of Cs.	
Chitosan–grafted carbon nanotubes	Studied parameters: Effects of pH, ionic strength and contact. Characterization: N_2–BET, SEM, XPS and XRD.	0.333 mmol/g	Low cation exchange capacity of CNT with high hydroxyl groups lower sorption capacity of the sorbent for Cs. pH and competing monovalent group 1 and divalent group 2 ions greatly influenced sorption capacity.	[67]
Ammonium molybdophosphate incorporated into polyacryonitrile (AMP–PAN)	Adsorbent amount: 0.2g Initial concentration: 15ml of 10mM radioactive laundry wastewater. Treatment conditions: pH5.0, 20°C and 200rpm for 24h. Studied parameters: Effects of pH (≤14), three kinds of surfactants and co–existing metal ions. Characterization: BET, EDS and FT-IR.	0.61 mmol/g	Effect of pH: Constant uptake. Single–and bi–solute competitive adsorption: Cs uptake favourable over Co and Sr. Influence of other parameters: The presence of Na^+ and Ca^{2+} ions suppressed Cs^+ uptake. The presence of cationic surfactants (OTMA and HDTMA) and anionic surfactants (SDBS and SOBS) decreased adsorption of Cs but non–ionic surfactants (Tween 80 and Triton X–100) has no effect. Data fitted by: Langmuir,	[75]

			Freundlich and D–R isotherm models Mechanisms: Ion-exchange and physisorption.	
Ammonium molybdophosphate incorporated into polyacryonitrile	Initial Cs solution concentration: 10ml of acidic tank waste containing 250Bq/ml ^{137}Cs. Treatment conditions: 24h at 23±5^{o}C. Column test at flow rates of 5,10 and 20 bed volume per hour. Influencing parameters: Effects of nitric acid, K^+ and Na^+ up to 2M. Characterization: TGA.	22.5–19.6 mg/g	Effects of parameters: K^+ ion effect is significant on Cs uptake, the effects of both acid and Na^+ is less significant. Data fitted by: Langmuir isotherm model. Dynamic sorption capacity decreased as flow rates increased. Stability: The sorbent thermally stable up to 400^{o}C with 10% weight loss due to water of hydration.	[76]
Tungstate/ polyacryonitrile composite bead	Adsorbent amount: 230mg Initial concentration: 20ml of 0.075mM traceable in 1M HNO_3 Treatment conditions: 25^{o}C temperature and contact time of 480mins. Characterization: SEM.	~8.89-8.91 mg/g	Maximum sorption capacity achieved between 30 and 60 mins. Data fitted by: Langmuir isotherm and pseudo–second order kinetic models. The bead size affects the rate of uptake and optimization of Cs uptake possible with wet beads after coagulation.	[73]

Polyaniline titanotungstate (PATiW)	Adsorbent amount: 50mg. Initial concentration: 5ml of 0.1M Cs. Treatment conditions: 25^{o}C temperature and contact time of 24h. Studied parameters on Cs uptake: Elemental composition, chemical solubility, ion–exchange capacity and pH–titration curve. Characterization: IR, XRD and TGA–DTA.	217 mg/g	Equilibration time: 24h. Sorption distribution coefficient increased with pH (2–9) and temperature (25–60^{o}C). The pH titration curve showed surface precipitation rather than conventional ion exchange or surface adsorption. Effects of metal ions: No effect Data fitted by: Freundlich isotherm model.	[74]
Crystalline manganese dioxide polyacryonitrile	Adsorbent amount: 0.1g. Initial concentration: 10ml of 10^{-4}mol/L. Treatment conditions: 25^{o}C temperature and pH 4.0. Studied parameters: Effects of contact time, temperature (298-338K), interfering ions and pH. Characterization:	0.007 mmol/g	Adsorption kinetic: Rapid. Equilibration time: 35mins. Parameters effects: Adsorption favourable within pH4–9. temperature increase but the presence of mono-and-divalents ions is negative on Cs sorption. Data fitted by: Freundlich isotherm model. Thermodynamic studies: Endothermic and spontaneous in nature. Stability tests: Sorbent stable	[77]

	XRD, FT-IR, SEM, CHN, TGA–DSC and BET.		up to 200kGy radiation dose, 310^{o}C heat, water, dilute acid, ethanol and alkaline solutions but decomposed in concentrated acids. Desorption: Difficult due to chemisorption and irreversible process.	
Potassium nickel hexacyanoferrate loaded polypropylene fabric	0.1g sorbent mixed with 20ml Cs solution. Studied parameters: Effects of contact time, pH and sodium ion concentration. Characterization: XRD, FT–IR–ATR and SEM.	78 mg/g (>95%)	Equilibration time and kinetics: 30mins and rapid. Effects of parameters: Constant uptake within pH6–12, neutral and basic solutions but decreased with increase in sodium concentration. Sorbent structure: Face–centered cubic crystalline.	[48]
Sodium titanosilicate polyacryonitrile composite	Adsorbent amount: 0.1g. Initial concentration: 10ml of 10^{-4}mol/L Treatment condition: pH 6.0 and 25^{o}C temperature. Studied parameters: Effects of pH (1–9), temperature (25–65^{o}C), contact time (5–120mins) and interfering competing ions.	9.80 to 22.06 mg/g (44.42%)	Equilibration time: 130mins Parameters effects: pH 6.0 and increase in temperature favoured the uptake but mono–and–divalent metal ions hindered favourable Cs uptake and hence, the sorption process is endothermic. Data fitted by: Langmuir isotherm model. Stability: Thermal and gamma irradiation stability were 275^{o}C and 200KGy.	[79]

	Column test was performed to estimate the dynamic sorption capacity at 5 and 100% breakthroughs. Characterization: XRD, FT–IR, SEM, BET, CHN and TGA–DSC.			
Copper hexacyanoferrate–polyacryonitrile composite	Adsorbent amount: 0.1g. Initial concentration: 10ml of 10^{-4}mol/L Cs. Treatment conditions: temperature 25^{o}C, pH9.0 and 120mins contact time. Studied parameters: Influence of pH, contact time, temperature and interfering cations. Column studies were performed to fit the dynamic sorption capacity at 5 and 100% breakthroughs. Characterization: XRD, FT–IR, TG–DSC, BET, SEM and XRF.	7.31–11.46 mg/g (63.78%)	Equilibration time: 280 mins. Parameters effects: pH increase (optimum pH9.0), favoured adsorption process. Effect of interfering cations (Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}) negative on Cs adsorption. Thermodynamic studies: Cs uptake is endothermic and spontaneous ion exchange reaction. Data fitted by: Freundlich isotherm model. Stability: The sorbent is thermally stable up to 200^{o}C.	[9]

Whisker–supported ion–imprinted polymer	Adsorbent amount: 0.4g. Initial concentration: 50ml of 10mg/L Cs. Treatment conditions: temperature 25^{o}C and contact time of 2h. Studied parameters: Effects of pH, sorption rate and sorbent loading. Characterization: FT–IR and XRD.	32.9 mg/g	Equilibration time and kinetics: 2h and rapid sorption. Parameters effects: Acidic pH and increase in temperature (from 25 to 55^{o}C) adversely affected Cs sorption until optimum pH6.0 and 0.4g sorbent loading sufficient for maximum sorption. Competitive ions have no significant effect on Cs selectivity onto the sorbent. Data fitted by: Pseudo–second order kinetic and Langmuir isotherm models. Desorption: Possible by 99% using acid at 50^{o}C and 6 cycles reusability of the sorbent.	[80]
Potassium copper nickel hexacyanoferrate–polyacryonitrile	Adsorbent amount: 0.01g. Initial concentration: 10ml acidic solution of 7.5×10^{-5}M Cs. Treatment conditions: Contact time 3h at 25^{o}C temperature. Studied parameters: Effect of shaking time, pH, acid concentration and drying temperature on the ion–exchange	2.85 mmol/g ion-exchange capacity for Cs	Equilibration time: 2h. Parameters: pH (2–12) did not have much influence on the sorption. Increase in drying temperature of the samples increases the exchange capacity. EDTA has a decreasing effect on the distribution coefficient of Cs. Stability: Adsorbent stable to 100KGy gamma-ray dose, thermal (up to110^{o}C) and in dilute acid, water and alkaline solutions but decomposed in	[81]

	capacity of the sample for Cs. Characterization: FT–IR, XRD and BET.		concentrated acid.	

2.1.3 Bio–adsorbents

The characteristics of dead and living biomass have equally been explored in biosorption and bioaccumulation of heavy metals and radionuclides from soils, sediments, surface and groundwater from a long time [82–87]. The fact that these biological / agricultural materials are abundant and affordable in the terrestrial environment and in particular, they have good stability, minimise disposable sludge volume, large porosity, high surface area, natural capacity to accumulate heavy- and radioactive metals and degrade organic compounds, and hence, increase their usage for environmental pollution remediation. In a nutshell, biosorbents have limitedly been used for treatment in real industrial waste effluents and in few cases where they are used [12,14,85–93], a number of factors have been reported to hamper effective binding abilities of biosorbents among which are extreme characteristics such as pH, conductivity and hardness [12,14,85–93].

Table 3: Various bio-adsorbents and their adsorption capacities as reported in literature

Bio-adsorbents	Adsorption parameters and adsorbent characterization	Adsorption capacity	Comment	Reference
Raw pine cone	Adsorbent amount: 1g Initial concentration: 100ml of 50–250mg/L Cs solution. Treatment conditions: Contact time of 30mins at pH8 and room temperature. Studied parameters:	2.28 mg/g	Parameters effects: Increase in pH increases Cs uptake but decrease as initial Cs concentration increases. The presence of Na^+ did not affect Cs uptake much as Ca^{2+}. Data fitted by:	[12]

	The effect of pH (1–10), interfering metal ions. Characterization: FT–IR, BET and XRD.		Pseudo–second order kinetic model.	
Chemically treated pine cone	Adsorbent amount: 1g. Initial concentration: 100ml of 50–250mg/L Cs solution. Treatment conditions: Contact time of 30mins at pH8 and room temperature. Studied parameters: The effect of pH (1–10) and interfering metal ions. Characterization: FT–IR, BET and XRD.	3.58 mg/g	Parameters effects: Increase in pH increases Cs uptake but decrease as initial Cs concentration increases. The presence of alkali metals reduced sorption of Cs as well as changed the rate-limiting kinetics. Data fitted by: Diffusion-chemisorption model.	[12]
Arca shell	Adsorbent amount: 0.5g. Initial concentration: 100ml of known stable solution spiked with 260Bq ^{137}Cs. Treatment condition: Temperature of 25^{o}C. Studied parameters: Effects of pH (1–7), contact time, dosage (0.1–15g/L), initial concentration (10 to	3.93 mg/g / 0.03mol/kg (98.2%)	Adsorption kinetics: Rapid within 60mins. Equilibration conditions: pH5.5, 3h time and adsorbent dosage of 5g/L. Parameters effects: Cesium uptake was increased with initial concentration (beyond 100µg/mL) but the presence of alkali/alkaline earth	[14]

	500ppm) and alkali/alkaline earth metals.		metals to concentration of about 500µg/mL adversely affected sorption percentage. Acidic pH ≤3 hindered Cs uptake. Data fitted by: Langmuir model Thermodynamic studies: Spontaneous and exothermic in nature.	
Polyphenols crosslinked persimmon tannin	Adsorbent amount: 0.01g Initial concentration: 10cm^3 of 0.1mM Cs solution. Treatment conditions: Temperature of 303K and 24h time. Studied parameters: Effects of pH, Na$^+$ ions in solution, initial concentration and temperature. Characterization: FT–IR and BET.	1.34 mol/kg	Adsorption kinetics: Fast in 5mins. Equilibration time: 8h. Parameters effects: Increase in pH positively affects the %uptake of Cs up to about neutral pH. Adsorption not affected by the presence of Na$^+$. Both initial concentration and temperature (up to 323K) increased sorption capacity of Cs onto the sorbent. Data fitted by: Pseudo-second order kinetic and Langmuir isotherm models.	[78]

			Regeneration: Sorbent could be reused for about 4cycles retaining its ion–exchange capacity.	
Polyphenols crosslinked crosslinked tea leaves	Adsorbent amount: 0.01g. Initial concentration: 10cm^3 of 0.1mM Treatment condition: Temperature of 303K for 24h contact time. Studied parameters: Effects of pH, Na$^+$ ions, initial concentration and temperature. Characterization: FT–IR and BET.	1.22mol/kg	Adsorption kinetic: Fast in 10mins. Equilibration time: 8h Parameters effects: Increase in pH positively affects the %uptake of Cs. Uptake amount not affected by the presence of Na$^+$. Increase in initial Cs concentration and temperature (up to 323K) increased Cs sorption capacity. Data fitted by: Pseudo–second order kinetic and Langmuir isotherm models. Regeneration and reusability: Elution possible with acid and reused for about 4cycles showing undiminished capacity.	[78]
Microalgal waste	Adsorbent amount: 10mg. Initial concentration:	1.36 kmol/kg (>85%)	Equilibration time: 60min. Adsorption kinetic:	[85]

	10ml of 0.1mM each of Cs and Na$^+$ solution. Treatment conditions: Temperature of 303K and desired pH for 24h contact time. Studied parameters: The effects of pH and contact time.		Rapid adsorption of Cs over Na$^+$ Optimum pH: pH6.5. Parameters effects: Increase in pH favoured adsorption of Cs. Data fitted by: Langmuir isotherm model. Regeneration and elution studies: Possible elution with acid but simple incineration is proposed as an alternative due to the adsorbent combustible nature .	
Funaria hygrometrica	Adsorbent amount: 50mg. Initial concentration: 4ml of unreported Cs concentration at room temperature. Studied parameters: Effects of pH (1–13), sorbent dosage (5–150mg), time (5–180min) and other cations. Characterization: FT–IR.	~6 mg/g (94%)	Equilibration time: 30mins. Parameters effects: pH increased favoured adsorption and attained maximum between pH6–10. Increase in sorbent to volume ratio increased % sorption. The presence of competitive metal ions affected adsorption of Cs at higher concentrations.	[86]
NaOH treated Funaria	Adsorbent amount: 50mg.	~17mg/g	Equilibration time: 30mins.	[86]

hygrometrica	Initial concentration: 4ml of unreported Cs concentration at room temperature. Studied parameters: Effects of pH (1–13), sorbent dosage (5–150mg), time (5–180min) and other cations. Characterization: FT–IR.		Parameters effects: pH increased favoured adsorption and attained maximum between pH6–10. Increase in sorbent to volume ratio increased % sorption. The presence of competitive metal ions affected adsorption of Cs at higher concentrations. Leaching of exchangeable metal ions and the surface modification by NaOH favoured higher Cs uptake.	
Ocimum basilicum	Adsorbent amount: 0.5g. Initial concentration: 20ml of 100µl of Cs tracer. Treatment conditions: Temperature of 28^{o}C and contact time of 60mins. Studied parameters: The effects of pH, contact time and interfering ions. Characterization: SEM	160 mg/g (48.14%)	Equilibration time: 30mins. Parameters effects: Maximum sorption achieved at optimum pH7. Increase in concentration of treatment acid decreases the uptake of the ions. The presence of divalent ions has no effect Cs sorption but monovalent ions did. Large number of carboxylic groups in	[88]

			mucilage polysaccharide facilitated Cs sorption onto the sorbent.	
Brewery's waste	Adsorbent amount: 0.1g. Initial concentration: 50ml of 1mmol/L. Treatment conditions: Temperature of 30°C and pH4.0. Studied parameters: Effects of contact time and increase in initial concentration.	0.076 mmol/g (90%)	Adsorption kinetics: Rapid within 30mins. Equilibration time: 3h. Parameters effects: Increase in initial concentration reduced Cs efficiency. Data fitted by: Pseudo–second order kinetic and Langmuir isotherm models.	[89]
P. australis	Adsorbent amount: 100mg. Initial concentration: 50ml unreported Cs concentration Treatment condition: Temperature of 30°C, pH5.5 and contact time of 3h. Studied parameters: Effects of contact time, pH (1–10), particle size, interfering ions and desorption/ reusability.	0.122 mmol/g	Adsorption kinetics: Rapid Equilibration time: 30mins. Parameters effects: Highest uptake amount of Cs was at pH4 and no decrease in the presence of alkali metal ions. Particle size of the sorbent affects the uptake with the big sizes showing highest uptake. Chemical treatment of the biomass decrease sorption capacity.	[90]

			Desorption: High concentration of NaOH and KOH suggested for desorption of Cs from the sorbent but has some damages to the capacity.	
Azolla filiculoides	Adsorbent amount: 60mg. Initial concentration: 30ml of 25–600mg/L Cs solution. Treatment conditions: Temperature of 30^{o}C and contact time of 3h. Studied parameters: Effects of pH (2–10), equilibration time, particle size and desorption. Characterization: FT-IR.	195 mg/g	Adsorption kinetics: Rapid within 30mins. Equilibration time: 60mins. Parameters effects: Increase in pH favoured Cs uptake and the pH with highest sorption was in the range pH8–9. Bigger particle size favoured the adsorption Data fitted by: Freundlich isotherm model.	[91]
Coconut shell	Adsorbent amount: 20-100mg. Initial concentration: 10 and 30mg/L Cs solution. Treatment condition: 24h contact time. Studied parameters: Effect of pH. Characterization: SEM.	0.76 mg/g	Adsorption kinetics: Poor and low affinity. Parameters effects: Adsorption not affected by the pH change. pH_{pzc} (point of zero charge) measurement revealed the alkaline nature of the sorbent with pH_{pzc}=10.22.	[92]

Almond shells	Adsorbent amount: 0.1g. Initial concentration: 4cm^3 of 10^{-7}M Cs solution. Treatment conditions: pH6 and temperature of 298K. Studied parameters: Effect of contact time, pH and sorbent dosage.	12.63 mg/g	Adsorption kinetics: Rapid within 20mins. Equilibration time: 60mins. Parameters effects: Change in pH influences uptake amount and efficiency of Cs. Increase in adsorbent dosage increases sorption percentage.	[93]
Almond shell with EDTA	Adsorbent amount: 0.1g. Initial concentration: 4cm^3 of 10^{-7}M Cs solution. Treatment conditions: pH6 and temperature of 298K. Studied parameters: Effect of contact time, pH and sorbent dosage.	19 mg/g	Adsorption kinetics: Rapid within 20mins. Equilibration time: 60mins. Parameters effects: Change in pH influences uptake amount and efficiency of Cs. Increase in adsorbent dosage increases sorption percentage. The presence of EDTA increases the density of negative charges on the sorbent surface and its capacity leading to higher sorption capacity of Cs.	[93]

2.1.4 Advantages and Disadvantages of various adsorbents

Owing to a large volume of waste in the environment, different adsorbents are applicable for removal of the contaminants for large volume reduction and safer disposal. In such a case, discrimination of the adsorbents is extremely difficult, however; the comparison can be made considering the benefits of using each material for particular waste decontamination. Apart from this, they can be classified in terms of basic advantages such as cost implication of adsorbents materials, operational requirements, mechanical strength, chemical, thermal and radiation stability and so on. For instance, decontamination of aqueous solution can be done using any adsorbents having surface functional groups for binding the adsorbates but when it involves recovering valuable adsorbates such as cesium, only polymeric adsorbents are most appropriate due to the difficulty in desorption using other sorbents [94].

In case of inorganic composite adsorbents, a number of available natural materials that do not need much reprocess before use due to their cation exchange capacity (such as naturally occurring clay minerals like zeolite, montmorillonite, bentonite, and coal) have been reported which make them economically feasible in real application at commercial scale [68,69]. The major issue with these materials is the presence of a number of cations that can block active sorption sites and hence, requires pre-treatment with chemicals before use. It was reported that the number, types and locations of cations in the zeolite greatly influenced the selectivity and rate of ion-exchange of zeolite sorbents [69]. Apart from these, titanosilicate materials [95], fly ash, metal transition ferrocyanides [8,11,58] and hexacyanoferrates [64] have also been credited with excellent surface area for adsorption, high cation exchange capacity, compatibility with final waste forms, high swelling, high mechanical strength and radiation stability (up to about 200 KGy). However, apart from the naturally occurring inorganic materials, most of the inorganic material sorbents are quiet expensive to use especially in developing and underdeveloped countries, they are difficult to separate from solution due to their fine microcrystalline nature resulting into secondary waste disposal problems. As regard to liquid radioactive waste, most inorganic sorbents do not withstand high level radiation; they have low chemical stability making difficulty in handling and hence, suffer irreversible structural changes under extreme environmental conditions [95]. They pose limitation due to slow mass-transfer rate in column operation as a result of the fine particle size [79].

On the other hand, due to its excellent binding ability, high porous structure, good mechanical strength for longer use, strong adhesive forces and stability to thermal, chemical and radiation, polymers have been found as good supporting materials to solve most of the aforementioned challenges of inorganic material sorbents [79]. The composites of inorganic-polymer sorbents have better sorption capacity, high selectivity and improved rapid kinetics of adsorption compared to inorganic materials [64]. Contrary to the inorganic materials that generate huge sludge, their composites produce less sludge and are good in preventing the release of the sorbed radionuclides after disposal. The challenge with polymer composites is the limitation to the long-term use due to the polymer biodegradability nature. However, synthetic polymers are more resistible to decomposition or biodegradability over a long-term use compared to the natural polymers [94]. More information on the properties of polymer-inorganic composites that make them useful in environmental remediation, regeneration and reusability has been reviewed by Zhao et al. [96] and Hua et al. [97].

As regard to bio-adsorbents, they are the best alternative for inorganic/organic sorbents and are the most low cost effective materials known. This is due to the fact that they are naturally abound and free in the environment as biomass wastes from dead algae, moss, bacteria or fungi and demonstrate good adsorption for cesium from the radioactive waste effluents. Apart from the low procurement and operational cost, they offer excellent means of minimizing the volume of chemical to be disposed of. The major setbacks with bio-adsorbents are low sorption capacity, high chemical and biological oxygen demand due to dissolution of organic compounds contained in the plant materials and the weakening of active surface functional groups under extreme environmental conditions [98-100]. Comprehensive information on the sorption capacity, mechanism of adsorption and issues regarding regeneration and reusability of bio-adorbents are found in the review work of Kratochvil and Volesky [101]. To use biological/agricultural waste materials, it demands chemical pre-treatment or modification. Review on the advantages and disadvantages of untreated and chemically treated biomass as bio-sorbents is reported by Ingole and Patil, 2013 [100]. Biomass materials are also incorporated into the polymer matrix to enhance its sorption capacity and mechanical strength, but reports are still limited in this area for cesium uptake from its radioactive waste solution [49]. Regeneration and reusability studies are still very limited in bio-sorbents to optimize their usage.

3.0 Factors affecting adsorption of cesium ion from solutions

Decontamination of waste streams by adsorption technique is commonly influenced by a number of factors which require optimization for better adsorption process. Some of these factors are physico–chemical properties of the adsorption materials, solution pH, temperature, influence of co–existing ions, initial cesium concentration, contact time, surface character of the sorbent, sorbent dosage, etc. These factors are discussed briefly as follows:

3.1 Effect of solution pH

A major factor influencing sorption capacity of different sorbents is solution pH. Different sorbents have different behaviours in solution media and therefore, their efficiency in removing sorbate from such solutions [102]. A change in the pH of a solution affects not only the degree of protonation but also the metal chemistry such as speciation and precipitation [103,104] and the surface properties (charge and functional groups) of the sorbents [104].

The equilibrium uptake of different radionuclides including cesium in different acidic media using activated and non-activated silico–antimonate (SiSb) has been reported [46]. According to that report, there is a strong uptake and high affinity of the radionuclides to antimonite matrix at low acid concentration (0.1 M) but decreased as the concentration increased to 5 M. The uptake followed selectivity order of Cs^{+}> Eu^{3+} >> Co^{2+}. Adsorption of cesium on CHCF–PAN was carried out at pH values ranging from 1–9 to determine the optimum condition [9]. The result showed that the uptake of cesium was continuously improved from the acidic to alkaline pH (9.0) following other similar reports using copper ferrocyanide functionalized mesoporous silica [11] and aluminum–pillared montmo–rillonite on the removal of cesium and copper from aqueous solutions [105]. Suppression of cesium sorption at acidic conditions was attributed to competition of H_3O^+. In contrast, suppression of adsorption was reported to be due to the electrostatic repulsion of negatively charged calcium hydroxide as pH values varied from 2–11 using nickel (II) hexacyanoferrate (III) functionalized walnut shell ($Ni^{II}HCF^{III}$–WS) [49,106]. Figure 1 shows the sorption percentage of cesium based on solution pH. Chitrakar et al. reported 172 mg/g cesium adsorption capacity for layered manganese–oxide at pH 2–4 and 132 mg/g when pH increased to 10 [61]. Crystalline manganese dioxide polyacryonitrile composite was evaluated for sorptive removal of cesium from mineral acid and weak alkaline solutions within the pH range of 4–9 [77]. The adsorption capacity of 0.007 mmol/g was estimated by Freundlich isotherm model. The sorbent was thermally stable up to 300 ^{o}C and 200 kGy gamma radiation. Desorption of sorbed cesium was very difficult with the eluent. Synthesized KNiHCF was noticed to adsorb cesium in a wide range of pH values (6–12) [48] but only at neutral solution KNiFC–loaded silica gel was reported to remove trace amount of cesium [66]. Maximum uptake of 0.4 to 1.05 mol/mol Cs/Fe was reported using copper–potassium hexacyanoferrate (II) at pH 5–8 [50,107,108], and 27.40 and 50.23 mg/g were reported for a pH range of 1.0–9.0 (but high sorption values obtained at pH 5.5 and 7) using mesoporous silica (IA) and ligand immobilized mesoporous silica (CA), respectively [109]. Zirconium iodomolybdate was also used to remove cesium ions from aqueous solution at pH 1–7, but at pH< 2 the adsorption process was characterised by competition of H^+ and Cs^+ ions on the negatively charged anionic functional groups or dissociated edge of hydroxyl groups on ZIM surface [63,110]. Table 4 shows different adsorbents, solution pH and adsorption percentage as reported in the literature.

Table 4: Comparison of various sorbents, sorption capacities and efficiencies for cesium ions

Types of adsorbent	Material	Sorption medium/ pH range	Sorption capacity (mg/g)	Sorption efficiency (%)	References
Inorganic and its composites	SiSb	Acidic	0.170–0.540	30–>90	[46]
	Activated SiSb (with phosphoric acid)	Acidic	0.220–0.520	30–>90 in 6 h	[46]
	Zeolite A	2.0-8.0	60.5	86.4	[111]
	ZeoliteA	6.0	76.69–78.25	90	[69]
	Ceiling tiles	4.95	0.5	–	[112]
	Stannic phosphate	~2.4	$0.371*10^{-3}$mol /g	37.1–74.1	[113]
	Sericite	2.0–8.0	6.68	75	[71]
	Bentonite	3–10	1.334mmol/g	–	[67]
	Natural clay (Bentonite)	2–12	4.10mmol/kg	90	[114]
	Ferrite	2.4–11	108.58	82	[115]
	Natural magnetite	2.4–11	70.77	61	[115]

Mesoporous silica (IA)	1.0–9.0	27.40	70	[109]
Immobilized mesoporous silica (CA)	1.0–9.0	50.23	85	[109]
Zirconium iodomolybdate	1.0–8.0	–	~90	[63]
Zirconium phosphate	~2.4	$0.915*10^{-3}$mol/g	91.5–98.4	[113]
Raw montmorillonite	3–12	0.4292mmol/g	–	[116]
Phosphate–modified montmorillonite (PPM)	3–12	0.7063 mmol/g	93.87	[116]
Etthylamine–modified montmorillonite	1.0–10.0	80.27	–	[72]
Calcium–saturated montmorillonite	1.0–10.0	60.03	–	[72]
Chinese weathered coal	5.01	–	45–60	[38]
KNiFC–loaded chabazite	3.7–5.83	1.44–1.97(mmol/g)	95	[117]
Copper ferrocyanide functionalized mesoporous silica	7.7	17.1	95	[11]
Copper ferrocyanide	1.1	21.7	–	[11]

	functionalized mesoporous silica				
	Prussian blue	1.1	2.6	–	[11]
	Prussian Blue	7.7	12.5	75	[11]
	Prussian blue	4.0–10.0	110.5	42	[118]
	KNiFC–loaded silica gel	High neutral solution	0.305 mmol/g		[66]
	Natural clinoptilonite	6.5	0.37 mmol/g	–	[120]
	Sulfuric acid crosslinked Pseudochoricystis ellipsoidea	6.5	1.36 mmol/g	–	[85]
	Chabazite and activated carbon mix	5.6–8.5	8.19	–	[16]
	$K_2CuFe(CN)_6$	Acidic	1.3mol/mol	–	[107]
	$K_2CuFe(CN)_6$	8	0.4mol/mol	–	[107]
	Potassium nickel ferrocyanide	Acidic	390	72	[111]
	$Cu_2^{II}Fe^{II}(CN)_6$	5–8	0.99–1.05 mol/mol	~ 100	[108]
	$Cu_3^{II}[Fe^{III}(CN)_6]_2$	Acidic	0.073 mol/mol	~ 100	[108]
Inorganic-Polymer composites	Manganese oxide–polyacrylonitrile	4.0–9.0	0.007 mmol/g	–	[77]
	CHCF-PAN	1.0–9.0	7.31–11.46 (0.084mmol/g)	63.78	[9]

	$Ni^{II}HCF^{III}$–WS	2–11	6±4.3	~ 100	[49,106]
	KNiHCF–loaded PP fabric	2.0–12	78	>95	[48]
	ZrP–AMP	Acidic	0.058mmol/g	96	[120]
	AMP-PAN	2–10	0.610mmol/g, 81mg/g	–	[75,76]
	Whisker–supported ion–imprinted polymer	6.0	32.9	–	[80]
	STS–PAN	1.0–9.0	22.06	44.42	[79]
	KCNF–PAN	2–14	2.85mmol/g	–	[81]
	PB–encapsulated alginate/calcium beads	4.0–10.0	144.72	45	[118]
	Nickel–potassium ferrocyanide immoblized chitin	1.0–9.0	80.7	–	[64]
	Chitosan–grafted–bentonite and CNT	3–10	0.333–1.164mmol/g	–	[67]
	Coal and Chitosan	3.0–6.0	3	–	[121]
Bio-sorbents	O.basilicum seeds	1–7	160	48.14	[88]
	Brewery's waste	4	0.076mol/g	90	[89]
	Moss immobilized silica matrix	1–13	8.5	>94	[87]

	Coconut shell activated carbon	5.7–8.15	0.76	–	[92]
	Almond shells	1.5–4.5	12.63–19* (* with addition of EDTA)	90	[93]
	Azolla filiculoides	2.0–10.0	70.5–195	85.2	[91]
	Ferrocyanide modified algal sorbents	1–10	24.5–198.7	–	[90]
	Native biomass sorbents	1–10	14.5–71.9	–	[90]
	P. australis biomass	5.5	0.122mmol/g	–	[90]
	Arca shell	1–7	3.93	98.2	[14]
	CTL–and–CPT gel	6.5	1.22–1.34 mmol/g	95.2–97.3	[78]
	Raw and modified pine cone	1–10	2.45–2.83	–	[12]

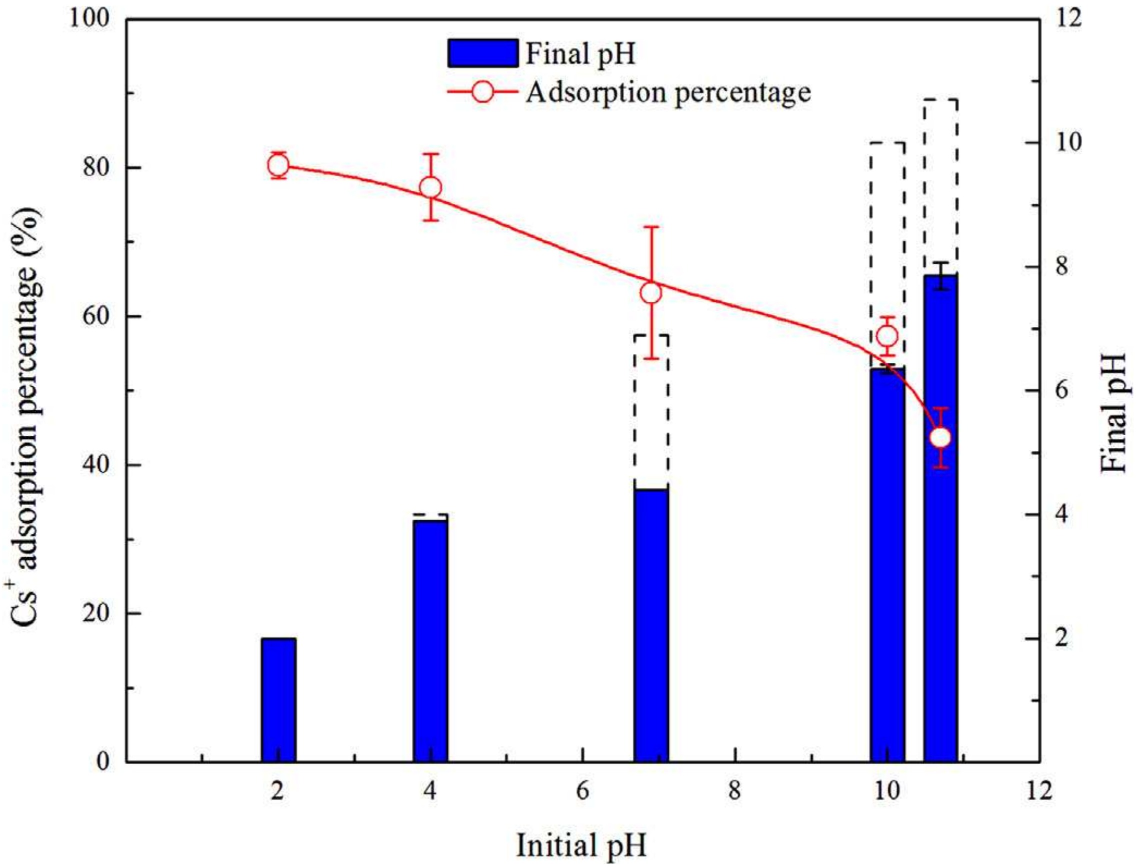

Figure 2: Effect of initial pH on cesium adsorption using Ni^{II}HCF^{III}–WS [49,106]

3.1.2 Effect of temperature on cesium adsorption

Temperature is other important parameter for adsorption studies, and it tells more about the mechanism involved in the sorption process [102]. Basically, there are two major effects of temperature on adsorption process. When temperature is increased, the diffusion rate of the adsorbate molecules is increased across the external boundary layer and in the internal pores of the adsorbent particle, due to the decrease in the velocity of the solution [122]. In the same vein, variation in the temperature of the adsorption system results into variation in the equilibrium capacity of the adsorbent for a particular adsorbate [123].

Therefore, if the rate of adsorption is increased with temperature, the mechanism controlling the process is endothermic but if the rate is decreased with temperature, it is exothermic. The spontaneity of the process depends on whether the change in entropy and the free energy of adsorption system is positive or negative [74]. Positive values of entropy change and negative values of free energy change indicate the solution interface is in random increase and spontaneous sorption process, but negative entropy change and positive free energy change show that the solution interface is slow and hence non-spontaneous sorption process [30]. So, it could be said that temperature is responsible for the behaviour/ nature of sorbate in solution and the availability of active sorption sites on the adsorbent surface as temperature varies [102]. This means that if solution temperature increases, it weakens the electrostatic interactions of the ions in solution and hence, increases their mobility towards sorbent and vice versa. Besides, it is generally known that if sorption is governed by physical phenomenon, an increase in temperature will cause a reduction in sorption capacity [46]. In other words, increase in sorption capacity with temperature is as a result of chemical process involved in the adsorption. For instance, the effect of temperature on sorption of Cs^+, Eu^{3+} and Co^{2+} onto non- activated and activated-SiSb (1:2) from different acidic media was reported to involve chemisorption process and that the equilibrium sorption capacity of the metal ions was increased with temperature (from 303 to 333 K). In 3M H_2SO_4, sorption capacity for Cs at 303, 318 and 333 K are 0.25, 0.24, 0.23 mg/g on non-activated SiSb and 0.36, 0.38 and 0.41 mg/g on phosphoric acid activated-SiSb [46]. Nilchi et al. [9] and El-Naggar et al. [74] also reported similar results with solution temperature ranging from 298 to 338 K [9]. The increase in adsorption coefficient as a result of temperature increase was attributed to the faster migration of ions and stronger electrostatic interactions of adsorbate-adsorbent. In contrast, other phenomena such as surface precipitation of metal oxides or ternary processes were ascribed to influence the adsorption efficiency of Cs and some heavy metals from the solution than temperature (increase of which caused about 50% reduction in efficiency) using manganese oxide-Anfezh mixture as chemisorbent [124]. Table 5 and figure 3 show the effect of temperature on cesium sorption by various sorbents as reported in the literature. The compiled literature generally showed increased distribution coefficient or better sorption capacity of cesium as temperature increased.

Table 5: Effect of temperature on cesium sorption by different sorbents

Type of adsorbent	Material	Temperature range (K)	Type of process	Distribution coefficient (mL/g)	Adsorption capacity (mg/g)	Reference
Inorganic adsorbents	Hydrous titanium oxide	298–325	Endothermic	–	0.6189–0.4303mmol/g	[62]
	Clinoptilolites	298–353	Exothermic	92	1.31–3.00	[70]
	Zirconia powder	298–333	Endothermic	–	7.01–9.25mmol/g	[125]
	KCNF	293–353	Endothermic	2.215–2.257	–	[65]
	Sericite	288–318	Exothermic	0.227 L/mg	6.68	[71]
	PPM	283–303	Exothermic	–	0.7063mmol/g	[116]
	Zirconium phosphate–ammonium molybdophosphate	301–323	Endothermic	–	Increase	[126]
	Stannic phosphate	301–333	Endothermic	188.8–386.5	0.653–0.741 ×10^{-6}mol/g	[113]
	Zirconium phosphate	301–333	Endothermic	–	0.984–0.985 ×10^{-6}mol/g	[113]
	Zeolite A	298–333	Endothermic	212.5–225.73	–	[122]
	Zeolite A	298–333	Endothermic	–	76.69–78.25	[69]
	Crushed granite	298 – 328	Exothermic	–	0.83–0.01mmol/g	[127]
	Local Taiwan	298 – 328	Exothermic	25 – 11	0.3–0.2mmol	[68]

	Literite				/g	
	KNiFC–impregnated zeolite	298–333	Endothermic	4200 cm3/g	–	[139]
	Ethylamine–modified montmorillonite	303–333	Exothermic	–	80.27	[72]
	Calcium–saturated montmorillonite	303–333	Exothermic	–	60.03	[72]
	Titanotungstate	298–333	Endothermic	–	19.79–20.82	[128]
	Activated silico-antimonate	303–333	Endothermic	–	0.220–0.520	[46]
Inorganic-Polymer composite	STS–PAN	298–338	Endothermic	8406–10362	19.6–22.9	[79]
	Polyaniline titanotungstate	298–333	Endothermic	–	32.08–33.5	[128]
	Polyaniline titanotungstate	298–333	Endothermic	–	217	[74]
	CHCF–PAN	298–338	Endothermic	1673–2109	–	[9]
	Manganese oxide–PAN	298–338	Endothermic	944–1058.5	–	[77]
	KCNF–PAN	298	–	9.9*10^4cm3/g	2.85mmol/g	[81]
	Nickel hexyanoferrate incorporated walnut shell	298–318	Endothermic	171.4–2264.3	–	[49]

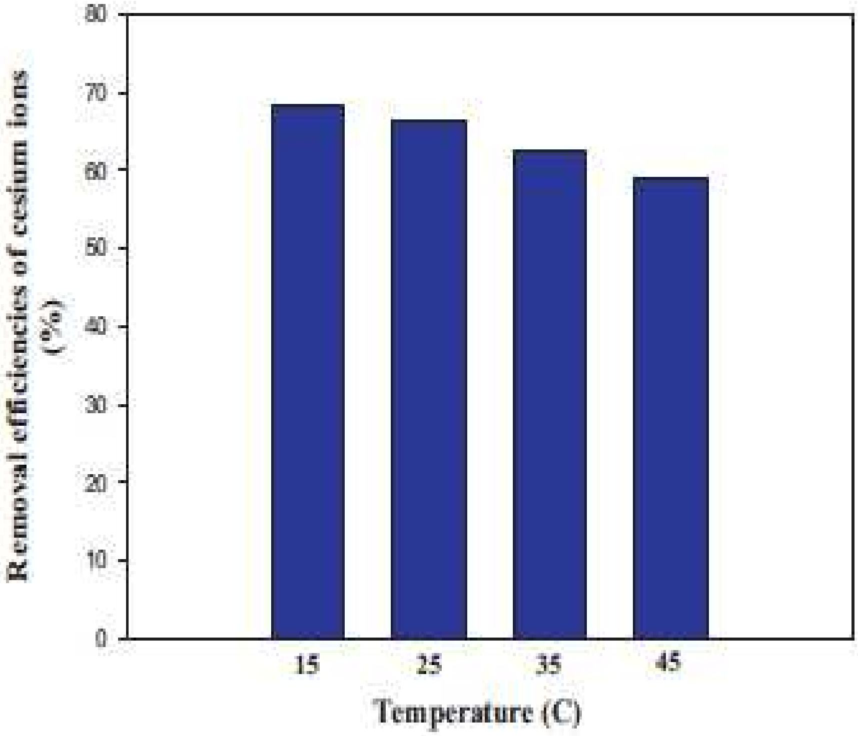

Figure 3: Effect of temperature on removal efficiency of cesium ions using sericite [71]

3.1.3 Effect of contact time on distribution coefficient of cesium

Adsorption time is an important factor that determines if an appropriate technology has been designed. If the treatment technologies implemented for separation of any adsorbates from their solutions are appropriate and considered economically viable then, optimum equilibrium and adsorption time must be short with higher adsorption rate [63]. Variation of contact time results into change in the optimum sorption efficiency of cesium from wastewaters. However, the equilibration time for adsorption of cesium onto different adsorbents also depends on a number of factors such as: the electrostatic attraction of adsorbate-adsorbent, complexation reaction on the outside surfaces of adsorbents, distribution of pores on adsorbents, availability of sorption sites or pores or composition of the adsorbents, interparticle diffusion of cesium on the pores of the adsorbents and other environmental conditions [71,72]. Most of the earlier works reported that initial rapid adsorption of cesium within short contact time before equilibrium was achieved, and it attributes to the availability of large number of sorption sites for cesium from the bulk solution. For instance, Han et al. used copper ferrocyanide to sorb cesium from raw water and found that rapid adsorption occurred in the first 20 mins and then became slowly until equilibrium was attained in 90 mins [129]. Ali synthesized silico–antimonate and modified with phosphoric acid to sorb cesium and other radionuclides from acidic waste–effluent [46]. Rapid equilibrium was attained between 1 and 6 h with >90% uptake of Cs^+ and Eu^{3+} but only 60 % of Co^{2+} could be sorbed onto activated silico–antimonate. Copper (II) ferrocyanide incorporated into vermiculite was also prepared and used to adsorb cesium, showing high affinity for the metal ion with sorption capacity of 0.05 to 0.13 mmol Cs/g (equivalent of 179 mg/g) of the sorbent and the equilibrium was reached within 1–2 h [57]. The compilations of earlier studies based on contact time and adsorption rate are listed in Table 6 while figure 4 shows the effect of contact time on cesium removal by ethylamine–modified montmorillonite.

Table 6: Variation of contact time on the adsorption equilibrium of cesium ions by various adsorbents

Type of adsorbent	Material	Equilibration time (min)	Nature of adsorption rate	Reference
Inorganic adsorbents	Sericite	120	rapid	[71]
	Ethyl–Mt & Ca–Mt	45	rapid	[72]
	FC–Cu–EDA–SAMMS	5	rapid	[11]
	Prussian Blue	60	slow	[11]
	Cu–FC–EDA–SAMMS	≤ 2h	Very rapid	[8]
	Mesoporous and Ligand immobilized silica	1–1.5h	Very rapid	[109]
	Natural clay (Bentonite)	20	Fairly rapid	[114]
	Tin (IV) phosphate	5days	slow	[130]
	Calix[4] arene impregnated zeolite	6h	rapid	[131]
	Activated silico–antimonate	6h	Fairly rapid	[46]
	Non–activated silico–antimonate	6h	slow	[46]
	Copper hexacyanoferrate	72 h–6 months	slow	[108]
	Zeolite A	90–120	Moderately rapid	[69]
	Metals phosphate	60	rapid	[113]
	Chinese weathered coal	400	rapid	[38]
	Zirconium iodomolybdate	80	Rapid	[63]
	PB–coated magnetic nanoparticle	24h	Less rapid	[132]

	PB–caged in diatomite–CNT	10	rapid	[133]
	Zirconyl molybdopyrophosphate	30	rapid	[134]
	Hydrous titanium oxide	5 h	Fairly rapid	[62]
	Ferrite and natural magnetite	60	rapid	[115]
	Crushed granite	8 h	Fairly rapid	[127]
	Clinoptilolites	4 h	rapid	[70]
	Ceiling tiles	240 h	Slow	[112]
Inorganic-Polymer composites	CHCF–PAN	280	Rapid	[9]
	STS–PAN	130	Rapid	[79]
	KNiHCF–loaded PP fabric	30	Rapid	[48]
	Polyaniline titanotungstate	240	Rapid	[128]
	MoHTB–PAN and AMP–PAN–85	100	Fairly rapid	[73]
	MnO_2–PAN	<35	rapid	[77]
	Polyaniline titanotungstate	2 h	rapid	[74]
	CTL–and–CPT gel	8 h	rapid	[78]
	$Ni^{II}HCF^{III}$–WS	2 h	rapid	[106]
	PB–alginate/calcium beads	20	rapid	[118]
	KCNF–PAN	2	rapid	[81]
	STS–PAN	130	rapid	[79]
	Imprinted polymer	2 h	Rapid	[80]
Bio-adsorbents	Arca shell	1 h	Rapid	[14]

	Coconut shell activated carbon	24 h	Very poor	[92]
	O. basilicum seed	30	Varied	[88]
	Brewery's waste	3h	rapid	[89]
	Ferrocyanide algal sorbent	30	Very rapidly	[90]
	A. filiculoides	60	Very rapid	[91]
	Immobilized moss	30	rapid	[87]
	Modified and unmodified algal sorbents	30	rapid	[90]
	Activated carbon from almond shell	60	Fairly rapid	[135]

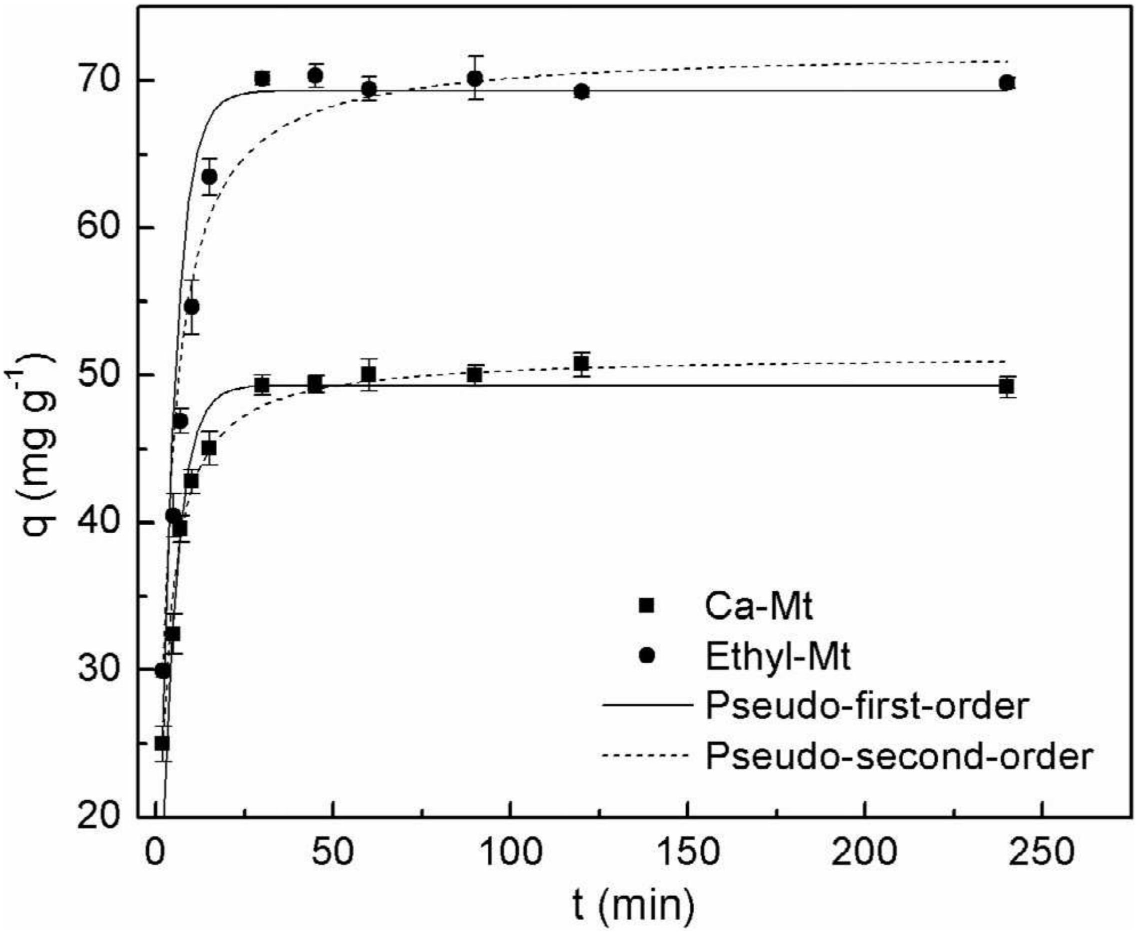

Figure 4: Effect of contact time on Cs adsorption using ethylamine–modified montmorillonite [72]

3.1.4 Effect of initial concentration of cesium on adsorption

This is another important parameter that determines the amount of cesium sorbed onto a particular sorbent. The percentage removal of cesium from the bulk and the sorption capacity of every adsorbent depend strongly on the possible existing relation between the adsorbate and the adsorbent. This, in–turn, depends on the initial concentration of the adsorbate in solution and the available sites or the sorption pores in the adsorbent surface [102]. Most of the adsorbents reported in the literature have their sorption capacity increased as initial cesium concentration increased, probably as a result of increase of driving force for mass transfer at high initial concentration but the percentage removal is decreased which can be attributed to sorbent surface being saturated [11,49,89,102,113,115].

Long et al. used ethylamine–modified montmorillonite and calcium montmorillonite to sorb cesium ions from the initial concentration of 20–230 mg/L and showed that the sorption capacity increased to 80.27 and 60.03 mg/g, respectively [72]. In case of using copper–potassium hexacyanoferrate (II), increasing the cesium concentrations does not influence the sorption capacity of cesium sorbed onto the sorbent [107]. Murthy et al. studied the effects of increasing the initial cesium concentration on sorption by zirconium phosphate-ammonium molybdophosphate and reported that it increases both the amount and percentage removal of cesium which was attributed to the larger sorbent surface sites, but influenced by variation in the acidity of solution [126]. Similar investigation was reported by El–Kamash using zeolite A but the higher uptake capacity was attributed to the higher probability of collision between cesium ion and the zeolite particles [69]. Table 7 shows the range of initial bulk concentration and percentage removal of cesium using various adsorbents.

Table 7: The effect of initial concentration and percentage removal range on cesium adsorption by various adsorbents

Type of adsorbent	Material	Initial concentration (ppm)	Uptake percentage (%)	Reference
Inorganic Adsorbents	Stannic phosphate	1.0×10^{-8}–1.0×10^{-2} M	74.1–34.1	[113]
	Zirconium phosphate	1.0×10^{-5}–1.0×10^{-2} M	98.4-91.5	[113]
	PB	150–280	42	[118]
	FC–Cu–EDA–SAMMS	500–50 ppb	decrease	[11]

	PB	500–50	decrease	[11]
	PUP/CNT/DM/PB	10	95.96	[134]
	Ferrite	0.001–0.1 mol/L	decrease	[115]
	Crushed granite	10^{-3} – 10^{-7}M	0.83–0.01 mmol/g	[127]
	Clinoptilolites	10^{-6} – 10^{-1} mol/dm^3	92	[70]
	$K_2Ni[Fe(CN)_6]$	10–400	Decrease	
	Ethylamine montmorillonite	20-340	Increase	[72]
	LTL	10^{-3}–10^{-7}M	Increase	[68]
	Ceiling tiles	0.114–23.9	Increase	[112]
Inorganic-polymer composites	ZrP–AMP	3.76.0×10^{-5}–7.52×10^{-3} M	4-96	[126]
	PB–coated MNP	50–2780	96mg/g	[132]
	Nickel–potassium ferrocyanide loaded chitin	41,000Bq/L	>97.7	[64]
	NiHCF–WS	1–100	99.1–70	[106]
	Imprinted polymer	2–500	Increase	[80]
	Silico–titanate–loaded membrane sheets	25.30	99.98	[136]
	PATiW	660–6600	Increase	[128]
	PATiW	13–13290	Increase	[74]
	PB–alginate/calcium beads	150–280	45	[118]
Bio-adsorbents	Coconut shell activated carbon	10–30 mg/L	No affinity	[92]
	Brewery's waste	0.157–6.189 mmol/l	6.3–2.5	[89]
	Azolla filiculoides	25–600 mg/L	68	[91]
	Raw and modified pine cone	50–250 mg/dm^3	0.89–2.76mg/g capacity	[12]

	Walnut shell	5–400	decrease	[49]
	Arca shell	10–500	Increase	[14]
	Crosslinked–persimmon tannin (CPT) and crosslinked tea leaves (CTL)	0.2–8.0mM	Increase	[78]

3.1.5 Effect of competing ions on the adsorption of cesium

Adsorption of cesium ions from solution onto sorbents could be greatly influenced by the presence of competing ions for the binding sites on adsorbent surfaces. The selectivity of sorbents for cesium depends largely on the similar behaviours of cesium and other ions in solution and towards the sorbent. Alkali and alkaline earth metal ions are the major competing metal ions reported to influence cesium selectivity onto the sorbents. According to Ding et. al. [106], the influence of competitive ions showed that the distribution coefficient was strongly decreased in the presence of Na^+ and K^+ ions as their concentration increase from 100–1000 mg/L. A compilation of different investigations using various sorbents and condition of competitive ions on distribution coefficient of cesium uptake is presented in Table 8 and figure 5. Meanwhile, the effects of competing ions on adsorption depend on the intrinsic nature of the adsorbent surface, the pH of the solution, the chemical properties of the cesium, etc. [63].

Table 8: Adsorbents and conditions of competitive ions on distribution coefficient of cesium uptake.

Type of adsorbent	Material	Dosage (g/L)	Competing ions/solution condition	Distribution coefficient, Kd(L/g)	Sorption capacity (mg/g)	Percentage reduction (%)	Reference
Inorganic Adsorbents	Raw bentonite	66.7	Synthetic groundwater	1.9	–	–	[137]
	Activated bentonite	66.7	Synthetic groundwater	8.9	–	–	[137]
	Cu–FC–EDA –SAMMS	0.05g	3 M Na^+	10^5	–	–	[8]

Cu–FC–EDA–SAMMS	0.05g	1M K^+	111	–	–	[8]
ZIM		1×10^{-6} –1 M Na^+	–	–	88-34	[63]
IA and CA	–	0.1–3.5mM Na^+, K^+	–	–	Decrease	[109]
KNiFC–loaded chabazite	–	10^{-3}–5M Na^+	10^4cm^3/g	–	–	[117]
KNiFC–loaded silica gel	–	10^{-3}–5M Na^+	10^4cm^3/g	–	–	[66]
NaSM zeolite	10	0.0119M K^+	4.65	–	–	[131]
ISM–25mg Calix[4]arene	10	0.0119M K^+	27.63		99.64	[131]
Aluminum-pillared montmorillonite	–	1.95g/L K^+	0.4	–	–	[105]
FC–Cu–EDA–SAMMS	1	Sequim Bay seawater	240	–	–	[11]
FC–Cu–EDA–SAMMS	1	Hanford groundwater	1400	–	–	[11]
Na–illite	–	0.01–1M Na+	1.75–6.95	–	–	[138]
Natural Clinoptilolite	–	0–3M Na^+	2000 –~300cm^3/g	–	–	[139]
KNiFC–impregnated zeolite	–	0–3M Na^+	2000–~500cm^3/g	–	–	[139]
Antimony silicate	5	0.23g/L Na^+, 3.9 g/L	1	–	–	[140]

			K^+				
	Iron fericite	–	0	~6.5	108.58	~82.5	[115]
	Iron fericite	–	0.05–0.4M Na^+, Mg^{2+}, Al^{3+}	–	–	~30–~15	[115]
	Natural magnetite	–	0	~0.2	70.77	~60	[115]
	Natural magnetite	–	0.05–0.4M Na^+, Mg^{2+}, Al^{3+}	–	–	~30–~15	[115]
	Crushed granite	15g	0.001–1M Na^+, K^+, Ca^{2+} and Mg^{2+}	Decrease	Decrease	Decrease	[127]
	CoHCF–doped sol-gel	–	0.5–100M Na^+	–	0.60–0.61mmol/g	Decrease	[141]
	CoHCF–doped sol-gel	–	10-100M Ca2+	–	0.60-0.46mmol/g	Decrease	[141]
	Vermiculite	50mg	10^{-5}M Na^+	–	–	80	[142]
Inorganic-polymer composites	Bentonite and CNT–based composites	–	0.001–0.4M K^+	decrease	decrease	decrease	[67]
	CHCF–PAN	–	0	1.67	7.31–11.46	63.78	[9]
	CHCF–PAN	–	10^{-4}M K^+	0.17	–	–	[9]
	CHCF–PAN	–	10^{-4}M Na^+	0.23	–	–	[9]
	CHCF–PAN	–	10^{-4}M Ca^{2+}	0.54	–	–	[9]
	CHCF–PAN	–	10^{-4}M Mg^{2+}	0.32	–	–	[9]
	NiHCF–WS	5	0	10.8	–	–	[106]

	NiHCF–WS	5	1 L/g K^+	3.5	–	–	[106]
	NiHCF–WS	5	0.1 L/g Na^+	4.7	–	–	[106]
	KNiHCF–loaded PP fabric	36mg/L	0.1–1M/L Na^+	–	–	decrease	[48]
	Nickel–potassium ferrocyanide immobilized chitin	–	0–1M Na^+	–	68.7	88.2	[64]
			0.01–0.1M K^+	–	51.4	96.2	
			0.01–0.5M NH_4^+	–	52.8	70.6	
			0.01–0.5M Rb^+	–	62.7	80.8	
	AMP–PAN		0.2–20mM Na^+, Ca^{2+}	0.46-0.38	–	85-89	[75]
	AMP–PAN	0.108	1M Na^+	76.2	–	–	[76]
	MnO_2–PAN	–	0	0.944	–	–	[77]
	MnO_2–PAN	–	10^{-4}M Na^+	0.412	–	–	[77]
	MnO_2–PAN	–	10^{-4}M K^+	0.257	–	–	[77]
	STS–PAN	–	0	8.41	–	–	[79]
	STS–PAN	–	10–4M Na^+, K^+	1.84, 1.29	–	–	[79]
	STS–PAN	–	10^{-4}M Ca^{2+}, Mg^{2+}	2.41, 2.72	–	–	[79]
Bio-adsorbents	O. basilicum seed	–	Li^+,Na^+,K^+	–	160	48.14	[88]
	Immobilized moss	0.2–1.2 g	150mg/L Na^+ & K^+	–	–	99 &94	[87]
	Raw pine cone	–	0	–	0.89	–	[12]
	Raw pine cone	–	0.5M Na^+ and Ca^{2+}	–	0.48 and 0.27	46 and 70	[12]
	Modified pine cone	–	0	–	1.31	–	[12]

	Modified pine cone	–	0.5M Na+ and Ca^{2+}	–	0.89 and 0.27	37 and 63	[12]

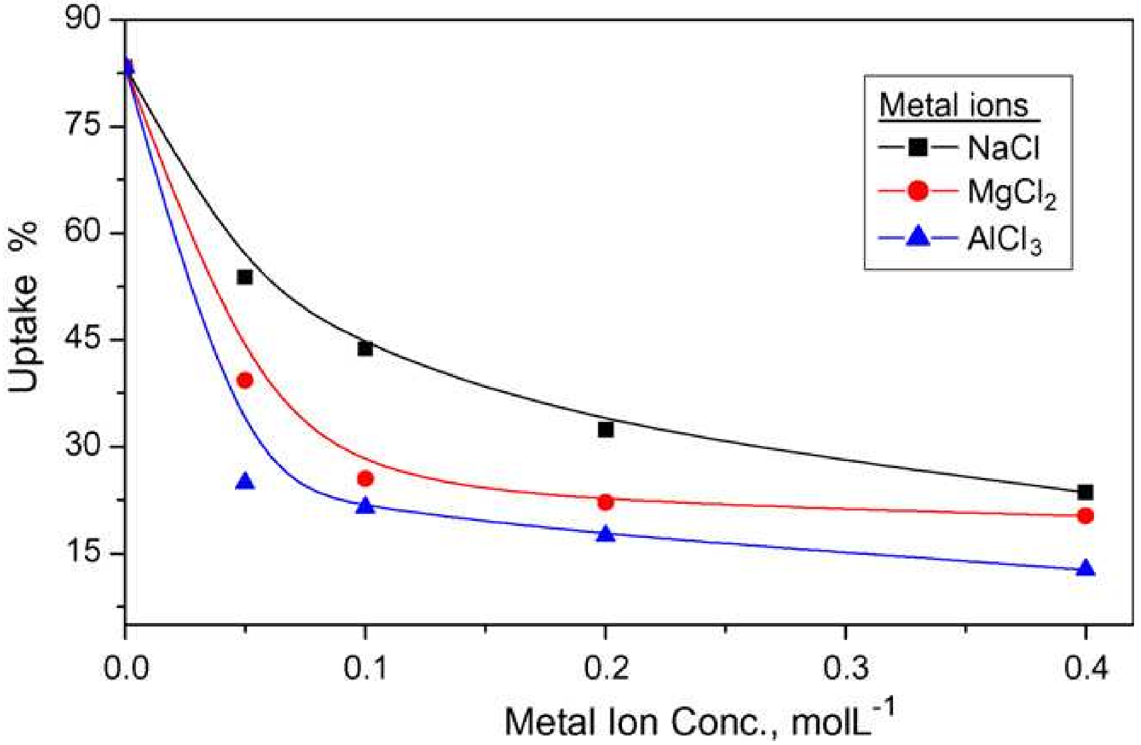

Figure 5: Effect of competing ions on the adsorption of cesium [115].

3.1.6 Effects of adsorbent particle size and surface area

Apart from the properties of the adsorbates and solution, the intrinsic nature of adsorbents plays an important role in adsorption [89]. The size of particles of adsorbents has been found to influence the sorption capacity of the sorbent [91,128]. This is because the bigger the particle size, the smaller the sorbent surface area and vice versa [143]. An excellent sorbent for sorption must have larger surface area i.e., more sorption sites or higher pore volume and reduced effective density for the adsorbate. Mashkani et al. found that azolla filiculoides of 2–4 mm particle size could be used in large–scale application owing to its higher sorption capacity compared to others of different sizes [91]. Ofomaja et al. reported that the bulk density of raw pine cone reduced from 0.499 to 0.427 g/cm^3 which is attributed to the opening of pore spaces after chemical treatment and hence, the increase in sorption capacity as a result of enhanced surface areas and reduced point of zero charge pH_{PZC} [12]. The stability and ease of separation of Prussian blue were enhanced when coated with magnetic nanoparticle (MNP), providing longer contact time with adsorbate in wastewater and better sorption capacity of up to 96 mg/g [132].

Sangvanich et al. [11] and Lin et al. [8] synthesised and characterised copper ferrocyanide functionalized mesoporous silica and found to have an excellent porous structure with 900 m^2/g and ~1000 m^2/g, respectively for surface area, 3.5 nm pore size and ligand loading capacity of 3.6–4.9 silane/nm^2 elemental and 3.7 silane/nm^2 gravimetric. The sorbent was reported to outperform Prussian blue in acidic waste stimulant with maximum capacity of 21.7 mg/g against 2.6 mg/g and 95% as against 75% removal in seawater [11]. Similar investigations were reported for spongiform Prussian blue based adsorbent [133] and Prussian blue caged in alginate/calcium beads [118] used for cesium removal. An hydrous titanium oxide was characterised to have surface area 216 m^2/g and it was discovered that as the surface area increases, the capacity of the sorbent increases [62]. Raw montmorillonite and phosphate-modified montmorillonite were used to sorb cesium from aqueous solution [116]. The surface area was found to increase from 2.6 to 115.9 m^2/g and the pore volume increased from 0.011 to 0.1 cm^3/g after the modification. The sorption amount equally increased as a result of modification from 0.4292 mmol/g for the raw montmorillonite and to 0.7073 mmol/g for the modified montmorillonite. Ethylamine–modified montmorillonite was described by characterisation to be favourable for positively charged Cs^+ sorption through electrostatic interactions and more negative charge due to surface hydroxyl groups of the sorbent [72]. The surface area was increased after modification from 71.15 to 154.17 m^2/g and microporous volume from 0.00844 to 0.04846 cm^3/g, hence, providing larger sorption sites for the adsorption with sorption capacity increasing from 60.03 to 80.27 mg/g.

The SEM/EDS studying of Cs adsorption on crushed granite revealed it has extensive sorption sites for Cs adsorption but the affinity is reduced as temperature increases due to the enhancement of Cs desorption [127]. The synthesized sol–gel encapsulated cobalt hexacyanoferrate was used to extract cesium from water by solid phase extraction (SPE) [141]. The characterisation of the sorbent material shows that increase in pore size does not cause a corresponding increase in sorption capacity. The pore volume and surface area were increased after modification under different conventions for an improved uptake capacity (from 0.43 to 0.61mmol/g) by controlling the amount of HCF in the silica sol–gel solid sorbent [141]. The surface area was increased from 408 to 457 m^2/g while the pore volume was 0.194 to 0.217 cm^3/g. Loos–Neskovic et al. found that the prepared copper-potassium hexacynoferrate sorbent has surface area and pore volume of 46 m^2/g and 0.042 m^3/g, respectively [107]. Hanafi prepared activated carbon from almond shell and characterised it for cesium and other radionuclides sorption from solution [135]. He reported that the surface area of the activated carbon increased as activation time increased, with the highest area obtained being 1288 m^2/g and micropore volume 0.35 cm^3/g having ash content of 0.21%. The uptake efficiency could reach about 90% as reported. Similarly, activated carbon and chabazite zeolite were used for Cs–137 and I–129 removal from aqueous solution [16]. The sorbents micropore areas were reported as 2.72×10^5 m^2/g for chabazite, 7.68×10^5 m^2/g for activated carbon and 6.17×10^5 m^2/g for mixed sorbent. However, for simultaneous removal of the ^{137}Cs and ^{129}I from aqueous solution, the mixed sorbent was prepared at 7:3 ratio given adsorbed amount to be 0.062 and 0.00058 mol/kg, respectively for Cs and I ions [16]. Approximately 8 nm diameter, length of 100–200 nm and interlayer spacing of 0.72 nm were reported for titanate nanofiber and nanotube used to sorb Cs and I ions from water by Yang and colleagues [144]. The sorbents can remove up to 80% Cs^+ within the Cs concentration of 80 ppm but reduced to 36% as concentration increased to 125 ppm. Abusafa and Yücel used different cationic forms of natural zeolite (clinoptilolite) to sorb cesium and the important physical properties of the sorbent for adsorption were reported as apparent density (1.3889 g/cm^3), pore volume (0.2216 cm^3/g), pore diameter (0.050 μm) and BET surface area (17.5 m^2/g) [70]. The distribution coefficient of cesium was reported to reduce as the initial concentrations reduced, which is attributed to site heterogeneity. Ceiling tiles have also been used with the intra- and inter-fiber pore diameters ranging between 1 and 2 μm, pore volume 0.72 cm^3/g and density of 0.21 g/cm^3 [112]. Other researchers have also used this sorbent and characterised with similar results reported such as Levit and Teather reported the pore volume of their ceiling tiles ranged from 0.5–0.7 cm^3/g, fiber pore diameters of 1.5 nm and 20 μm [145] and 0.1–1 μm [146]. Czech smectite–rich clay material mixed with sand was previously used and the BET surface area and exchangeable cation capacity were analysed [137]. The highest surface area was obtained in sedimentary clay (153 m^2/g) and least was in raw-bentonite (97 m^2/g) and distribution ratio of cesium for all the selected clays increased as clay fraction in clay/sand mixture. Kim et al. characterised their sericite as having BET surface area of 0.021 m^2/g and cation exchange capacity of 3.25 meq/100g [71]. The sericite material has a low adsorption capacity of 6.68 mg/g much lower than 32.3 mg/g reported for ion–imprinted polymer [80] but better than 0.5 mg/g achievable using ceiling tiles [112]. The surface areas of 71.29, 78.82, 18.52 and 27.92 m^2/g were reported for carbon nanotube, chitosan-grafted carbon nanotube, bentonite and chitosan-grafted bentonite composite, respectively [67]. The morphology and surface diameter of the nanoplate–like CS nanostructure were also reported.

Silico–antimonate materials are also good sorbents for sorption due to better surface area and could be enhanced by activation or by incorporation of organic ion exchanger. It has been reported that the surface of phosphoric acid activated silico–antimonate contains hydroxyl and phosphate groups which may enhance the ion exchange affinity because an increasing amount of water content increases the porosity of sorbent material and localization of protons [46]. Besides, sodium titanosilicate–polyacrylonitrile composite was analysed and found to have a BET surface area of 96.66 m^2/g, larger inner particulate pore size compared to near surface and wider dispersion of STS powder throughout the binding matrix, ensuring fast and high adsorption level [79]. The sorbent is reported to have high gamma radiation stability up to 200 KGy which is an important factor for the removal and immobilization of fission product from radioactive waste solution. Stannic and zirconium phosphates have been reported to display such resistant or stability to radiation of up to 300 mCi Ra–Be neutron and 1.72 Gy/h gamma-dose rate [113].

The synthesised ammonium molybdophosphate–polyacryonitrile bead was reported after adjustment for large–scale application to have surface area of 32.69 m^2/g, pore volume of 0.17 cm^3/g and bead diameter of 1–2mm [75]. Griffith et al. reported the surface area of microporous tungstate/ polyacryonitrile composites used to sorb cesium and strontium from acidic radioactive waste stimulant as ranged between 31 and 36 m^2/g with granular particle of mesh size less than 0.3 mm giving optimal adsorption in column operation [73]. Polyacryonitrile–based manganese dioxide composite was characterised and used for cesium removal with BET surface area reported to be 53.03 m2/g by Nilchi et al. [77]. Colloid stable sorbents prepared from latex particles functionalized with transition metal ferrocyanides was reported to have large surface area of 960 m^2/g [58]. The effect of ferrocyanide composition and content in polymeric matrix was evaluated on selectivity and sorption capacity of the sorbents and it was shown that unmodified latexes has only about 10% Cs retention whereas, the modified latexes could remove as much as 99% Cs (0.053–0.084 meq/g) from the solution over a wide pH range. Nilchi et al. reported BET surface area of 73.58 m^2/g for the prepared copper hexacyanoferrate–polyacrylonitrile composite used to sorb cesium with adsorption dynamic capacity of 7.31 and 11.46 mgCs/g at 5% and 100% breakthrough [9]. The effects of contact time, temperature and initial cesium concentration were investigated on the cesium adsorption.

Chinese weathered coal was used to sorb Am(III), Eu(III) and Cs(I) and was reported to have surface area between 1.319 and 19.533 cm^2/g, total pore volume 0.007 and 0.061 cm^3/g and pore size of 9.080 and 16.420 nm at point of zero charge (5.030–6.650) [38]. The sorbent has functional oxidized groups (such as carboxyl, hydroxyl, phenol, etc) with surface charge controlled by pH change. Ethylenediaminetetracetic acid (EDTA) and its other degradation products were reported to have BET surface area of 54.30 cm^3/g and cation exchange capacity of 26.42 meq/100g [147].

4.0 Future direction and recommendations for Cs adsorption

In adsorption studies, rapid kinetics, high sorption capacity, selectivity, volume reduction and compatibility of the adsorbates with the sorbents for safe disposal are priorities. As such, the choice of adsorption materials, methods of preparation and immobilization are normally considered for a particular adsorbate. A survey through the literature suggests that extensive research is needed on sorbents selection for higher adsorption of Cs from the environment.

Cost involvement of the adsorbents' precursors and /or the adsorbents are crucial issues in adsorption technique to access the feasibility of implementation of the process in real wastewater treatment technologies. Virtually, till now, no report is available in the literature on this and this makes it impossible to be certain if these materials as reported could be used in developing nations in particular. Several factors are responsible for high cost of adsorbents which include availability, the form of the precursors and the adsorbents, processes involved before its usable form, treatment conditions, production period, location, etc [148,149]. These factors are important to be considered before any materials are regarded as low cost. Particular interests should be given to research on bio-sorbents and naturally occurring inorganic sorbents like clay minerals since the materials involved are mostly free in the natural environment and they appear as the main hope for less economically buoyant nations from the materials procurement cost point of view. In addition, studies should focus on the chemical modifications of these waste materials to enhance their sorption capacity, mechanical stability and surface functional groups maintenance under different radioactive waste solution conditions. This is because the feasibility and efficiency of sorption process do not lie only on the physico-chemical properties of the adsorbents but as well as on the composition of the wastewaters and other surrounding influencing factors. Until now, progress in wastewater managements and technologies is mostly depended on pilot investigations carried out with specific waste effluents which are often simulated and as a result, serious attentions should be given to real industrial waste effluents for extensive studies[101]. Information from various investigations available in the literature suggests several factors affecting sequestering of cesium from radioactive wastewaters are still less considered and this makes drawing general conclusion difficult. Every system should be considered independently for better understanding of the mechanism of the adsorption. In addition, special care should be given to the choice of modification agents for bio-sorbent materials. This is because certain chemical agents and conditions inhibit activation of binding sites in them such as acetone, detergent, high temperature, autoclaving, etc. [150]. Characterization of bio-sorbent materials surface characteristics and pore sizes should be given particular attention as this will no doubt promote improvement on the sorbent performance which is less considered. Regeneration studies as mentioned before are still limited for reuse of all the adsorbents to ascertain their lifetime in practical application. This is an issue that needs to be urgently addressed, as there is no point in acquiring high cost materials that have low operational cycles. Importantly, research should focus on possibility of recovering of adsorbed cesium without disrupting the active sorption sites of the sorbents by the eluents. So far, few reports have suggested polymeric composites as the best adsorbents for metal recovery due to high desorption properties of the adsorbents[94]. Finally, efforts should be taken to consider the health implications of these adsorbents before application.

5.0 **Conclusions**

The review presents comprehensive information on the removal of cesium from industrial effluents by adsorption technique.. Effects of important factors associated with the adsorption of cesium from solutions are compiled and discussed accordingly. Several sorbents used in recent time to remove cesium from various solutions are highlighted. Specific advantages and disadvantages of each sorbent were discussed. The effects of the factors on adsorption capacity and efficiency of the adsorbents are discussed. Future direction on adsorption technique is discussed; particular attention is advocated for bio-sorbents and naturally occurring inorganic sorbents, regeneration, reusability and cost involvement of the precursors and the adsorbents. Issues related to the health implications of these adsorbents are advocated for general public safety. Since the success of wastewater technologies mostly hinges on pilot studies and the previous studies are virtually conducted under batch conditions hence, more column experiments should be given serious attention to make steps forward real industrial realization. Finally, as the rate of waste effluents has not been reduced by previous efforts, more studies are advocated into various novel sorbents that could reduce or eliminate the cesium from the waste solution before disposal.

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7.0 **Disclosure**

The authors declare no conflict of financial interest or any other.

8.0 REFERENCES

1. D.W. Seckler, World water demand and supply, 1990–2025: Scenarios and issues, Iwmi, 1998.

2. I.A. Shiklomanov, World water resources, A New Appraisal and Assessment for the 21st Century, 1998.

3. A. Camacho, M. Montaña, I. Vallés, R. Devesa, R. Céspedes-Schánez, I. Serrano, S. Blázquez and V. Barjola. Behavior of natural radionuclides in wastewater treatment plants. J. Environ. Radioct. 109: 76-83, 2012

4. W.C. Butterman, W.E. Brooks, Jr. Reese, G. Robert G. (2004). "Mineral Commodity Profile: Cesium". United States Geological Survey. Retrieved Oct., 2014

5. Kaner, Richard (2003). "C&EN: It's Elemental: The Periodic Table – Cesium". American Chemical Society. Retrieved Oct., 2014

6. A.F. Holleman, E. Wiberg, N. Wiberg. "Vergleichende Übersicht über die Gruppe der Alkalimetalle". Lehrbuch der Anorganischen Chemie (in German) (91–100 ed.). Walter de Gruyter. pp. 953–955. ISBN 3-11-007511-3, 1985

7. A. Coghill, R.L. Garson (eds). The ACS Style Guide: Effective Communication of Scientific Information (3rd ed.). Washington, D.C.: American Chemical Society. 127. ISBN 0-8412-3999-1, 2006

8. Y. Lin, G.E. Fryxell, H. Wu , M. Engelhard. Selective Sorption of Cesium Using Self-Assembled Monolayers on Mesoporous Supports. Environ. Sci. Technol. 35, 3962-3966, 2001

9. A. Nilchi, R. Saberi, M. Moradi, H. Azizpour and R. Zarghami. Adsorption of cesium on copper hexacyanoferrate-PAN composite ion exchanger from aqueous solution. Chemical Engineering Journal, 172: 572-580, 2011

10. S. Rengaraj, K.H. Yeon, S.H. Moon, Studies on adsorptive removal of Co(II), Cr(III), and Ni(II) by IRN77, J. Hazard. Mater. 92: 185, 2002

11. T. Sangvanich, V. Sukwarotwat, R.J. Wiacek, R.M. Grudzien, G.E. Fryxell, R.S. Addleman, C. Timchalk, W. Yantasee, Selective capture of cesium and thallium from natural waters and simulated wastes with copper ferrocyanide functionalized mesoporous silica, J. Hazard. Mat. 182: 225–231, 2010

12. A.E. Ofomoja, A. Pholosi and E.B. Naidoo. Kinetics and competitive modelling of cesium biosorption onto chemically modified pine cone powder. J. Taiwan Inst. Chem. Engr. 44: 943-951, 2013

13. R.R. Sheha, Synthesis and characterization of magnetic hexacyanoferrate (II)polymeric nanocomposite for separation of cesium from radioactive wastesolutions, J. Colloid Interface Sci. 388, 21–30, 2012

14. S. Dahiya, R.M. Tripathi and A.G. Hedge. Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass. J. Hazard. Mat. 150: 376-386, 2008.

15. B.W. Mercer, L.L. Ln Ames Jr., L.B. Sand, F.A. Mumplon (Eds.), Zeolite Ion Exchange in Radioactive Municipal Wastewater Treatment in Natural Zeolites, Occurrence, Properties Use, Pergamon Press, Oxford, pp. 451–459, 1978

16. K.C. Song, H.K. Lee, H. Moon, K.J. Lee, Simultaneous removal of the radiotoxic nuclides ^{137}Cs & ^{129}I from aqueous solution, Sep. Purif. Technol. 12: 215–217, 1997

17. ICRP. Individual Monitoring for Internal Exposure of Worker: Replacement of ICRP Publication 54, Pergamon Press, ICRP Publication, p. 78, 1998

18. A. Mellah, S. Chegrouche and M. Barkat, The precipitation of ammonium uranyl carbonates (AUC): thermodynamic and kinetics of investigation, Hydrometallurgy 85: 163–171, 2007

19. T.S. Singh, K.K. Pant, Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina, Sep. Purif. Technol. 36: 139–147, 2004

20. S. Jennewein, H. Park, J.M. DeJong, R.M. Long, A.P. Bollon, R.B. Croteau. Coexpression in yeast of Taxus cytochrome P450 reductase with cytochrome P450 oxygenases involved in Taxol biosynthesis. Biotechnol. Bioeng. 89:588–598. (PubMed: 15672381), 2005

21. S. Chellam, D.A. Clifford. Physical–chemical treatment of groundwater contaminated by leachate from surface disposal of uranium tailings. J. Environ. Engr. 128:942–952, 2002

22. D.H. Phillips, B. Gu, D.B. Watson, C.S. Parmele. Uranium removal from contaminated groundwater by synthetic resins. Water Res. 42:260–268, 2008

23. A. Morel, K. Zuo, X. Xia, J. Wei, X. Luo, P. Liang, X. Huang. Microbial desalination cells packed with ion-exchange resin to enhance water desalination rate. Bioresource Tech., 118: 43-48, 2012

24. H. Wang, P. Zhang, X. Ma, S. Jiang, Y. Huang, L. Zhai, S. Jiang. Preparation, characterization of electrospun meso-hydroxylapatitenanofibers and their sorptions on Co(II). J. Hazard. Mat. 265: 158-165, 2014

25. M.A. Barakat. New trends in removing heavy metals from industrial wastewater. Arab. J. Chem.4: 361-377, 2011

26. M.A. Barakat, E. Schmidt. Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. Desalination, 256: 90-93, 2010

27. M. Hepel, Z. Xingmin, R. Stephenson and S. Perkins. Use of Electrochemical Quartz Crystal Microbalance Technique to Track Electrochemically Assisted Removal of Heavy Metals from Aqueous Solutions by Cation-Exchange Composite Polypyrrole-Modified Electrodes. Microchemical J. 56: 79-92, 1997

28. D. Rana, T. Matsuura, M.A. Kassim, A.F. Ismail. Radioactive decontamination of water by membrane processes — A review. Desalination, 321: 77-92, 2013

29. M. Gamal Khedr. Radioactive contamination of groundwater, special aspects and advantages of removal by reverse osmosis and nanofiltration. Desalination, 321: 47-54, 2013

30. R. Kamaraj, S. Vasudevan. Evaluation of electrocoagulation process for the removal of strontium and cesium from aqueous solution, Chemical Engineering Research and Design (2014), http://dx.doi.org/10.1016/j.cherd.2014.03.021

31. D.R. Raut, P.K. Mohapatra, M.K. Choudhary, S.K. Nayak. Evaluation of two calix-crown-6 ligands for the recovery of radio cesium from nuclear waste solutions: Solvent extraction and liquid membrane studies. J. Membrane Sci. 429: 197-205, 2013

32. D. Humelnicu, M.V. Dinu, E.S. Dragan. Adsorption characteristics of $UO_2{}^{2+}$ and Th^{4+} ions from simulated radioactive solutions onto chitosan/clinoptilolite sorbents. J. Hazard. Mat. 185: 447-455, 2011

33. Y. Huang, W. Wang, Q. Feng, F. Dong. Preparation of magnetic clinoptilolite/$CoFe_2O_4$ composites for removal of Sr^{2+} from aqueous solutions: Kinetic, equilibrium, and thermodynamic studies. J. Saudi Chem. Soc. 2013

34. N.T. Tavengwa, E. Cukrowska, L. Chimuka. Preparation, characterization and application of $NaHCO_3$ leached bulk U(VI) imprinted polymers endowed with γ-MPS coated magnetite in contaminated water. J. Hazard. Mat. 267: 221– 228, 2014

35. R. Apak, G. Atun, K. Gücülü , E. Tütem. Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. II. Usage of coal fly ash. J. Nucl. Sci. Technol. 33, 396, 1996

36. C. Liu, Y. Huang, N. Naismith, J. Economy and J. Talbott. Novel polymeric chelating fibers for selective removal of mercury and cesium from water. Environ. Sci. Technol. 37, 4261–4268, 2003

37. M.N. Delisee, A. Fromage, A. Surface complexation modeling of Yb(III) and Cs(I) sorption on silica. J. Colloid Interface Sci. 212, 228, 1999

38. J. Wu, Q. Xu, T. Bai. Adsorption behavior of some radionuclides on the Chinese weathered coal. Appl. Rad. Isot. 65: 901-909, 2007

39. R. O. Abdel Rahman, H. A. Ibrahium and Yung-Tse Hung. Liquid Radioactive Wastes Treatment: A Review. Water 2011, 3, 551-565; doi:10.3390/w3020551

40. V.K. Gupta, Suhas. Application of low-cost adsorbents for dye removal – A review. J. Environ. Manag. 90: 2313-2342, 2009

41. M.D. LeVan, G. Carta, C.M. Yon. In: R.H. Perry, D.W. Green, J.O. Maloney (Eds.), Adsorption and Ion Exchange, seventh ed. Perry's chemical engineers' handbook McGraw-Hill, New York, 1997

42. D.A. Clifford. Ion Exchange and Inorganic Adsorption. In: Letterman, R.D. (Ed.), Water Quality and Treatment, fifth ed. McGraw-Hill, New York, 1999

43. E. Zakharchenko, O. Mokhodoeva, D. Malikov, N. Molochnikova, Y. Kulyako, G. Myasoedova. Novel sorption materials for radionuclide recovery from nitric acid solutions: solid-phase extractants and polymer composites based on carbon nanotubes. Procedia Chemistry 7: 268 – 274, 2012

44. IAEA. Application of Ion Exchange Pro- cesses for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers, IAEA Technical Reports Series No. 408, Austria, 2002

45. F. Fu, Q. Wang. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manage. 92: 407-418, 2011

46. I.M. Ali. Sorption studies of ^{134}Cs, ^{60}Co and $^{152+154}$Eu on phosphoric acid activated silico-antimonate crystals in high acidic media. Chem. Engr. J., 155:580-585, 2009

47. T. Möller, A. Clearfield and R. Harjula. Preparation of hydrous mixed metal oxides of Sb, Nb, Si, Ti and W with a pyrochlore structure and exchange of radioactive cesium and strontium ions into the materials. Micro. And Meso. Mat. 54: 187-199, 2002

48. Y. Bondar, S. Kuzenko, D.H. Han and H.K. Cho. Development of novel nanocomposite adsorbent based on potassium nickel hexacyanoferrate- loaded polypropylene fabric. Nanoscale Research Letters 9:180, 2014

49. D. Ding, Y. Zhao, S. Yang, W. Shi, Z. Zhang, Z. Lei and Y. Yang. Adsorption of cesium from aqueous solution using agricultural residue- Walnut shell: Equilibrium, kinetic and thermodynamic modeling studies. Wat. Res.47: 2563-2571, 2013

50. E.F.T, Lee and M. Streat. Sorption of Caesium by Complex Hexacyanoferrates III. A Study of the Sorption Properties of Potassium Copper Ferrocyanide. J. Chem. Technol. Biotechnol. 33A, 80-86, 1983

51. V. Pekarek and U. Vesely. Synthetic inorganic ion exchangers—II: Salts of heteropolyacids, insoluble ferrocyanides, synthetic aluminosilicates and miscellaneous exchangers. Talanta 19, 1245-1283, 1972

52. J.B. Ayers and W.H. Waggoner. J. Inorg. Nucl. Chem. 33, 721, 1971

53. F.M. Mekhail and K. Benyamin. Radiochim. Acta. 55, 95, 1991

54. M. Ishfag, H.M.A. Karim and M.A. Khan. J. Radioanal. Nucl. Chem. 170, 321, 1993

55. W.E. Prout, E.R. Russell and H.J. Groh. J. Inorg. Nucl. Chem. 27, 473, 1965

56. F. Sebesta, J. John and A. Motl. Phase II Report on Evaluation of PAN as a Binding Polymer for Absorbers used to Treat Liquid Radioactive Wastes; SAND 96-1088; Sandia National Laboratory: 1996.

57. V.V. Strelko, V.K. Mardanenko, V.V. Yatsenko and N.M. Patrilyak. Russ. J. App. Chem. 71, 1746-1749, 1998

58. V. Avramenko, S. Bratskaya, V. Zheleznova, I. Shevelev, O. Voitenko and V. Sergienko. Colloid stable sorbents for cesium removal: Preparation and application of latex particles functionalized with transition metals ferrocyanides. J. Hazard. Mat. 186: 1343–1350, 2011

59. L. Johansson, C. Samuelsson and E. Holm. Adsorption of caesium in urine on copper hexacyanoferrate(ii)— A contamination control kit for large scale in situ use. Radiat. Prot. Dos. 81 (2): 147–152, 1999

60. T.P. Valsala, S.C. Roy, J.G.Shah, J. Gabriel, Kanwar Raj, V. Venugopal. Removal of radioactive caesium from low level radioactive waste (LLW) streams using cobalt ferrocyanide impregnated organic anion exchanger. J. Hazard. Mat. 166: 1148–1153, 2009

61. R. Chitrakar, Y. Makita, A. Sonoda. Cesium ion uptake by synthetic K-birnessite
$K_{0.30}(Mn^{4+}{}_{0.90}Mn^{3+}{}_{0.03\□0.07})O_2{}^{\cdot}0.5H_2O$. Chem. Lett. 42, 1032–1034, 2013

62. E. Metwally, T. El-Zakla, and R.R. Ayoub. Thermodynamics Study for the Sorption of ^{134}Cs and ^{60}Co Radionuclides from Aqueous Solutions. J. Nucl. Radiochem. Sci. 9 (1): 1-6, 2008

63. R.R. Sheha and S.H. El-Khouly. Adsorption and diffusion of cesium ions in zirconium (IV) iodomolybdate exchanger. Chem. Engr. Res. Des. 91: 942–954, 2013

64. C. Vincent, A. Hertz, Th. Vincent, Y. Barre, E. Guibal. Immobilization of inorganic ion-exchanger into biopolymer foams – Application to cesium sorption. Chem. Engr. J. 236: 202–211, 2014

65. M.M. Ishfaq, H.M.A. Karim and M.A. Khan. A radiochemical study on the thermodynamics of cesium adsorption on potassium copper nickel hexacyanoferrate (II) from aqueous solutions. J. Radioanal. Nucl. Chem. 222 (1-2): 177-181, 1997

66. H. Mimura, M. Kimura, K. Akiba and Y. Onodera. Selective removal of cesium from highly concentrated sodium nitrate neutral solutions by potassium nickel hexacyanoferrate(ii)-loaded silica gels. Solvent extraction and ion exchange, 17:2, 403-417, 1999

67. S. Yang, C. Han, X. Wang and M. Nagatsu. Characteristics of cesium ion sorption from aqueous solution on bentonite- and carbon nanotube-based composites. J. Hazard. Mat. 274: 46–52, 2014

68. T.H. Wang, M.H. Li,W.C. Yeh, Y.Y. Wei and S.P. Teng. Removal of cesium ions from aqueous solution by adsorption onto local Taiwan laterite. J. Hazard. Mat. 160: 638–642, 2008

69. A.M. El-Kamash. Evaluation of zeolite A for the sorptive removal of Cs^+ and Sr^{2+} ions from aqueous solutions using batch and fixed bed column operations. J. Hazard. Mat. 151: 432–445, 2008

70. A. Abusafa and H. Yücel. Removal of ^{137}Cs from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite. Sep. Purificat. Tech. 28: 103–116, 2002

71. J.O. Kim, S.M. Lee and C. Jeon. Adsorption characteristics of sericite for cesium ions from an aqueous solution. chemical engineering research and design 92: 368–374, 2014

72. H. Long, P. Wu and N. Zhu. Evaluation of Cs^+ removal from aqueous solution by adsorption on ethylamine-modified montmorillonite. Chem. Engr. J. 225: 237-244, 2013

73. C.S. Griffitti, V. Luca, F. Šebesta and P. Yee. Separation of Cesium and Strontium from Acidic Radioactive Waste Simulants Using a Microporous Tungstate/ Polyacrylonitrile (PAN) Composite Adsorbent. Sep. Sci. Tech., 40:9, 1781-1796, 2005. DOI: 10.1081/SS-200064561

74. I.M. El-Naggar, E.S. Zakaria, I.M. Ali, M. Khalil and M.F. El-Shahat. Chemical studies on polyaniline titanotungstate and its uses to reduction cesium from solutions and polluted milk. J. Environ. Radioact. 112: 108-117, 2012

75. Y. Park, Y.C. Lee, W.S. Shin, S.J. Choi. Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate–polyacrylonitrile (AMP–PAN). Chem. Engr. J. 162: 685–695, 2010

76. T.A. Todd, N.R. Mann, T.J. Tranter, F. Šebesta, J. John, A. Motl. Cesium sorption from concentrated acidic tank wastes using ammonium molybdophosphate-polyacrylonitrile composite sorbents. J. Radioanal. Nucl. Chem. 254 (1): 47–52, 2002

77. A. Nilchi, R.Saberi, S.R. Garmarodi and A. Bagheri. Evaluation of PAN-based manganese dioxide composite for the sorptive removal of cesium-137 from aqueous solutions. Appl. Radiat. Isot. 70: 369–374, 2012

78. M. Gurung, B.B. Adhikari, S. Alam, H. Kawakita, K. Ohto, K. Inoue and H. Harada. Adsorptive removal of Cs(I) from aqueous solution using polyphenols enriched biomass-based adsorbents. Chem. Engr. J. 231: 113–120, 2013

79. R. Saberi, A. Nilchi, S.R. Garmarodi and R. Zarghami. Adsorption characteristic of ^{137}Cs from aqueous solution using PAN-based sodium titanosilicate composite. J Radioanal Nucl Chem. 284:461–469, 2010

80. Z. Zhang, X. Xu and Y. Yan. Kinetic and thermodynamic analysis of selective adsorption of Cs(I) by a novel surface whisker-supported ion-imprinted polymer. Desalination 263: 97–106, 2010

81. A. Nilchi, H. Atashi, A.H. Javid and R. Saberi. Preparations of PAN-based adsorbers for separation of cesium and cobalt from radioactive wastes. Appl. Radiat. Isot. 65: 482–487, 2007

82. C.N. Sawyer. Milestones in the Development of the Activated Sludge Process. Water Pollution Control Federation 37 (2): 151–162, 1965. JSTOR 25035231

83. E.J. Alleman and T.B.S. Prakasam. Reflections on Seven Decades of Activated Sludge History. Water Pollution Control Federation 55 (5): 436–443, 1983. JSTOR 25041901

84. A. Schildmeyer, M. Wolcott, D. Bender. "Investigation of the Temperature-Dependent Mechanical Behavior of a Polypropylene-Pine Composite". J. Mater. Civ. Eng. 21 (9): 460–466, 2009. doi:10.1061/(ASCE)0899-1561, 21:9(460), 2009

85. K. Inoue, M. Gurung, B.B. Adhikari, S. Alam, H. Kawakita, K. Ohto, M. Kurata and K. Atsumi. Adsorptive removal of cesium using bio fuel extraction microalgal waste. J. Hazard. Mat. 271: 196–201, 2014

86. B. Krishna, S. Rao, J. Arunachalam, M. Murali, S. Kumar and V. Manchanda. Removal of ^{137}Cs and ^{90}Sr from actual low level radioactive waste solutions using moss as a phyto-sorbent. Sep. Purif. Technol. 38 (2): 149–161, 2004a

87. M.B. Krishna, J. Arunachalam, M. Murali, S. Kumar and V. Manchanda. Performance of immobilized moss in the removal of ^{137}Cs and ^{90}Sr from actual low-level radioactive waste solutions. J. Radioanal. Nucl. Chem. 261 (3): 551– 557, 2004b

88. D. Chakraborty, S. Maji, A. Bandyopadhyay, S. Basu. Biosorption of cesium-137 and strontium-90 by mucilaginous seeds of Ocimum basilicum. Bioresour. Techn. 98: 2949–2952, 2007

89. C. Chen, J. Wang. Removal of Pb^{2+}, Ag^{+}, Cs^{+} and Sr^{2+} from aqueous solution by brewery's waste biomass. J. Hazard. Mat. 151: 65–70, 2008

90. R. Jalali-Rad, H. Ghafourian, Y. Asef, S.T. Dalir, M.H. Sahafipour, B.M. Gharanjik, Biosorption of cesium by native and chemically modified biomass of marine algae: introduce the new biosorbents for biotechnology applications. J. Hazard. Mat. B116: 125–134, 2004

91. S.G. Mashkani, P.T.M. Ghazvini. Biotechnological potential of Azolla filiculoides for biosorption of Cs and Sr: Application of micro-PIXE for measurement of biosorption. Bioresource Technology 100: 1915–1921, 2009

92. M. Caccin, F. Giacobbo, M. Da Ros, L. Besozzi, M. Mariani. Adsorption of uranium, cesium and strontium onto coconut shell activated carbon. J. Radioanal. Nucl. Chem. 297:9–18, 2013

93. A. Alarifi and H.A. Hanafi. Adsorption of cesium, thallium, strontium and cobalt radionuclides using activated carbon. J. At. Mol. Sci. 1(4):292–300, 2010

94. Worch, Eckhard. Adsorption technology in water treatment: Fundamentals, processes, and modeling. Walter de Gruyter, 2012

95. K. Popa and C.C. Pavel. Radioactive wastewaters purification using titanosilicates materials: State of the art and perspectives. Desalination 293: 78-86, 2012

96. X. Zhao, L. Lv, B. Pan, W. Zhang, S. Zhang and Q. Zhang. Polymer-supported nanocomposites for environmental application: A review. Chem. Engr. J. 170:381-384

97. M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv and Q. Zhang. Heavy metal removal from water/wastewaterby nanosized metal oxides: A review. J. Hazard. Mater. 211-212: 317-331, 2012

98. I. Gaballah, D. Goy, E. Allain, G. Kilbertus and J. Thauront. Recovery of copper through decontamination of synthetic solutions using modified barks. Met. Metall. Trans. B 28, 13–23, 1997

99. G. Crini and P.M. Badot. Application of chitosan, a natural amino polysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Prog. Polym. Sci, 33: 399-447, 2008

100. N.W. Ingole and V.N. Patil. Cadium removal from aqueous solution by modified low adsorbent(s): A state of the art. IJCSEIERD. 3(4): 17-26, 2013.

101. D. Kratochvil and B. Volesky. Advances in the biosorption of heavy metals. TIBTECH, Vol. 16, July 1998

102. M.T. Yagub, S.T. Kanti, A. Sharmeen and H.M. Ang. Dye and its Removal from aqueous solution by Adsorption: A review, Advances in Colloid and Interface Science 2014, doi: 10.1016/j.cis.2014.04.002

103. L. Zhang, L. Zhao, Y. Y and, C. Chen. Removal of lead from aqueous solution by non-living rhizopus nigricans. Water Res. 32: 1437–1444, 1998.

104. B. Nandi, A. Goswami and M. Purkait. Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies. Applied Clay Science. 42(3-4): 583-590, 2009

105. D. Karamanis, P.A. Assimakopoulos, Efficiency of aluminum-pillared montmo-rillonite on the removal of cesium and copper from aqueous solutions, Water Res. 41: 1897–1906, 2007

106. D. Ding, Z. Lei, Y. Yang, C. Feng, Z. Zhang. Selective removal of cesium from aqueous solutions with nickel (II)hexacyanoferrate (III) functionalized agricultural residue–walnut shell. J. Hazard. Mat. 270: 187–195, 2014

107. C. Loos-Neskovic, S. Ayrault, V. Badillo, B. Jimenez, E. Garnier, M. Fedoroff, D. J. Jones and B. Merinov. Structure of copper-potassium hexacyanoferrate (II) and sorption mechanisms of cesium. J. Solid State Chemistry 177: 1817–1828, 2004

108. S. Ayrault, B. Jimenez, E. Garnier, M. Fedoroff, D. Jones, C. Loos-Neskovic. Sorption Mechanisms of Cesium on $Cu^{II}{}_2Fe^{II}(CN)_6$ and $Cu^{II}{}_3[Fe^{III}(CN)_6]_2$ Hexacyanoferrates and their Relation to the Crystalline Structure J. Solid State Chem. 141: 475, 1998

109. Md.R. Awual, S. Suzuki, T. Taguchi, H. Shiwaku, Y. Okamoto and T. Yaita. Radioactive cesium removal from nuclear wastewater by novel inorganic and conjugate adsorbents. Chem. Engr. J. 242: 127–135, 2014

110. C. Hurel, N. Marmier, A.C.M. Bourg, F. Fromage. Sorption of Cs and Rb on purified and crude MX-80 bentonite in various electrolytes. J. Radioanal. Nucl. Chem. 279, 113–119, 2009

111. I.M. Ismail, M.R. El-Sourougy, N. Abdel Moneim and H.F. Aly. Preparation, characterization and utilization of potassium nickel hexacyanoferrate for the separation of cesium and colbat from contaminated waste water. J. Radioanal. Nucl. Chem. 237 (1-2): 97-102, 1998

112. M.Y. Miah, K. Volchek, W. Kuang and F.H. Tezel. Kinetic and equilibrium studies of cesium adsorption on ceiling tiles from aqueous solutions. J. Hazard. Mater. 183, 712–717, 2010

113. S.P. Mishra, D. Tiwari, S.K. Prasad, R. S. Dubey and M. Mishra. Inorganic ion-exchangers in radioactive waste management Part XVI: Uptake of some metal phosphates (stannic and zirconium) for ^{134}Cs. *J. Radioanaly. Nucl. Chem., 268(2): 191–199, 2006*

114. A.F. Seliman, Y.F. Lasheen, M.A.E. Youssief, M.M. Abo-Aly and F.A. Shehata. Removal of some radionuclides from contaminated solution using natural clay: bentonite. J Radioanal. Nucl. Chem. 300:969–979, 2014

115. R.R. Sheha and E. Metwally. Equilibrium isotherm modeling of cesium adsorption onto magnetic materials. J. Hazard. Mat. 143: 354–361, 2007

116. B. Ma, S. Oh, W.S. Shin and S.J. Choi. Removal of Co^{2+}, Sr^{2+} and C^{s+} from aqueous solution by phosphate-modified montmorillonite (PMM). Desalination 276: 336–346, 2011

117. H. Mimura , M. Kimura, K. Akiba and Y. Onodera. Selective Removal of Cesium from Sodium Nitrate Solutions by Potassium Nickel Hexacyanoferrate- Loaded Chabazites. Solvent extraction and ion exchange, 34:1, 17-28, 1999

118. A.K. Vipin, B. Hu and B. Fugetsu. Prussian blue caged in alginate/calcium beads as adsorbents for removal of cesium ions from contaminated water. J. Hazard. Mat. 258– 259: 93– 101, 2013

119. I. Smiciklas, S. Dimovic and I. Plecas. Removal of Cs^{+}, Sr^{2+} and Co^{2+} from aqueous solutions by adsorption on natural clinoptilolite. Appl. Clay Sci. 35: 139–144, 2007

120. N.Y. Kremlyakova and V.M. Komarevsky. Sorption of alkaline and alkaline-earth radionuclides on zirconium phosphate sorbent Termoxid-3A from aqueous solution. J. Radioanal. Nucl. Chem. 218 (2): 197-200, 1997

121. J. Mizera, G. Mizerová, V. Machovic̑ and L. Borecká. Sorption of cesium, cobalt and europium on low-rank coal and chitosan. Water Research 41:620 – 626, 2007

122. K.M. Abd El-Rahman, A.M. El-Kamash,1 M.R. El-Sourougy and N.M. Abdel-Moniem. Thermodynamic modeling for the removal of Cs+, Sr2+, Ca2+ and Mg2+ ions from aqueous waste solutions using zeolite A. *J. Radioanaly. Nucl. Chem., 268(2): 221–230, 2006*

123. S. Wang, Y. Boyjoo, A. Choueib and Z.H. Zhu. Removal of dyes from aqueous solution using fly ash and red mud. Water Research 39: 129–138, 2005

124. B.E. Johnson, P.H. Santschi, R.S. Addleman, M. Douglas, J. Davidson, G.E. Fryxell and J.M. Schwantes. Optimization and evaluation of mixed-bed chemisorbents for extracting fission and activation products from marine and fresh waters. Analytica Chimica Acta 708: 52– 60, 2011

125. S.M. Yakout and H.S. Hassan. Adsorption Characteristics of Sol Gel-Derived Zirconia for Cesium Ions from Aqueous Solutions. Molecules *19*:9160-9172, 2014 doi:10.3390/molecules19079160

126. G.S. Murthy, M.V. Sivaiah, S.S. Kumar, V.N. Reddy, R.M. Krishna and S. Lakshminarayana. Adsorption of cesium on a composite inorganic exchanger zirconium phosphate . ammonium molybdophosphate. J. Radioanal. Nucl. Chem. 260 (1):109-114, 2004

127. S.C. Tsai, T.H. Wang, M.H. Li, Y.Y. Wei and S.P. Teng. Cesium adsorption and distribution onto crushed granite under different physicochemical conditions. J. Hazard. Mat. 161: 854–861, 2009

128. I.M. El-Naggar, E.S. Zakaria, I.M. Ali, M. Khalil and M.F. El-Shahat. Kinetic modeling analysis for the removal of cesium ions from aqueous solutions using polyaniline titanotungstate. Arabian J. Chem. 5, 109–119, 2012

129. F. Han, G.H. Zhang and P. Gu. Removal of cesium from simulated liquid waste with countercurrent two-stage adsorption followed by microfiltration. J. Hazard. Mat. 225– 226: 107– 113, 2012

130. A.I. Bortun, S.A. Khainakov, L.N. Bortun, E. Jaimez, J.R. García, A. Clearfield, Synthesis and characterization of a novel layered tin(IV) phosphate with ion exchange properties, Mater. Res. Bull. 34: 921–932, 1999

131. E.H. Borai, R. Harjula, L. malinen, A. Paajanen, Efficient removal of cesium from low-level radioactive liquid waste using natural and impregnated zeolite minerals, J. Hazard. Mater. 172: 416–422, 2009

132. C. Thammawong, P. Opaprakasit and P. Tangboriboonrat and P. Sreearunothai. Prussian blue-coated magnetic nanoparticles for removal of cesium from contaminated environment. J. Nanopart. Res.15:1689, 2013

133. B. Hu, B. Fugetsu, H. Yu and Y. Abe. Prussian blue caged in spongiform adsorbents using diatomite and carbon nanotubes for elimination of cesium. J. Hazard. Mater. 217– 218: 85– 91, 2012

134. H.Y. Zhang, R.S. Wang, C.Sh. Lin and X.Y. Zhang. A new economical zirconyl molybdopyrophosphate for the removal of 137Cs and 90Sr from HLLW. J. Radioanal. Nucl. Chem., 247 (3): 541.544, 2001

135. A. Hanafi. Adsorption of cesium, thallium, strontium and cobalt radionuclides using activated carbon. J. At. Mol. Sci. 1 (4): 292-300, 2010. doi: 10.4208/jams.100809.112309

136. L.N. Oji, K.B. Martin and D.T. Hobbs. Development of prototype titanate ion-exchange loaded-membranes for strontium, cesium and actinide decontamination from aqueous media. J. Radioanal. Nucl. Chem., 279(3): 847–854, 2009

137. J. Vejsada, E. Jelínek, Z. Řanda, D. Hradil and R. Přikryl. Sorption of Cesium on smectite-rich clays from the Bohemian Massif (Czech Republic) and their mixtures with sand. Appl. Radiat. Isot. 62: 91–96, 2005

138. C. Poinssot, B. Baeyens and M.H. Bradbury. Experimental and modelling studies of caesium sorption on illite. Geochimica et Cosmochimica Acta, 63 (19/20): 3217–3227, 1999

139. H. Kazemian, H. Zakeri and M.S. Rabbani. Cs and Sr removal from solution using potassium nickel hexacyanoferrate impregnated zeolites. *J. Radioanal. Nucl. Chem. 268(2): 231–236, 2006*

140. A.D.L. Al-Attar and R. Harjula, Uptake of radionuclides on antimony silicate. J.Radioanal. Nucl. Chem. 260: 199–203, 2004

141. D.V. Ca and J.A. Cox. Solid Phase Extraction of Cesium from Aqueous Solution Using Sol-Gel Encapsulated Cobalt Hexacyanoferrate. Microchim. Acta. 147, 31–37, 2004

142. K. Morimoto, K. Tamura, Y. Umemura, H. Sato and A. Yamagishi. Capture of Radioactive Nuclear Wastes from Sea Water by Use of Clay Minerals. Chem. Lett. 40, 867-869, 2011

143. A. Leusch, Z.R. Holan, B. Volesky. Solution and particle effects on the biosorption of heavy metals by seaweed biomass. Appl. Biochem. Biotechnol. 61, 231–249, 1996

144. Dongjiang Yang, Sarina Sarina, Huaiyong Zhu,* Hongwei Liu, Zhanfeng Zheng, Mengxia Xie, Suzanne V. Smith, and Sridhar Komarneni. Capture of Radioactive Cesium and Iodide Ions from Water by Using Titanate Nanofibers and Nanotubes. Angew. Chem. Int. Ed. 50: 10594 –10598, 2011

145. N.V. Levit and E.W. Teather. Acoustically absorbent ceiling tile having barrier facing with diffuse reflectance, US Patent Application 20090173570, 2009

146. M.A. Baig. Ceiling tile construction, US Patent Application 20080216936, 2008

147. A.F. Seliman, E.H. Borai, Y.F. Lasheen, M.M. Abo-Aly, T.A. DeVol and B.A. Powell. Mobility of radionuclides in soil/groundwater system: Comparing the influence of EDTA and four of its degradation products. Environ. Pollut. 158: 3077-3084, 2010

148. A. Bhatnagar, W. Hogland, M. Marques and M. Sillanpää. An overview of the modification methods of activated carbon for its water treatment applications. Chem. Engr. J. 219: 499–511, 2013

149. V.K. Gupta, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Suhas, low-cost adsorbents: growing approach to wastewater treatment – a review, Cri. Rev. Environ. Sci. Technol. 39: 783–842, 2009

150. K. Vijayaraghavan and Y.S. Yun. Bacterial biosorbents and biosorption. Biotechnol. Advances 26: 266–291, 2008