Adsorptive separation of Ce, Co, Ru, Sb and Sr ions using inorganic ion exchangers

A dissertation presented by

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Declaration

I, Nosipho Mercy Nzama, student number u16394382 hereby declare that this dissertation, "*Purification of irradiated uranium from fission products and actinides using inorganic ion exchangers*", is submitted in accordance with the requirements for the Master's degree at University of Pretoria, is my own original work and has not previously been submitted to any other institution of higher learning. All sources cited or quoted in this dissertation are indicated and acknowledged with a comprehensive list of references.

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Nosipho Mercy Nzama

08 August 2019

Dedication

I dedicate this research to my beautiful mother Zanele and my sisters Nonjabulo and Amahle.

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Abstract

Ion exchange and adsorption (can both be referred to as 'sorption') are widely used as purification and concentration methods in the nuclear industry. Various mathematic models have been developed to describe the mechanisms of sorption using the kinetics and equilibrium data. In this study, the ion exchange and adsorption capability and efficacy of various inorganic sorbent materials to remove contaminants were investigated with the intent of applying the process in the purification of post reactor uranium for reuse and cleaning of research reactors pool water. The contaminants studied are Ce, Co, Ru, Sb and Sr ions. The sorbent materials candidates investigated are antimony pentoxide, CoTreat®, IONSIV R9120B, activated carbons, alumina, titania, manganese oxide and SrTreat®.

The sorption of Ce and Sr on antimony pentoxide was determined to be a slow sorption process. The sorption kinetics data obtained for Sr removal by antimony pentoxide conformed to the pseudo-second order kinetic model, with the sorption process reaching completion after 78 hours contact time. The considerably slow kinetics makes the sorbent material a less suitable candidate.

At fixed solid/aqueous ratio, various parameters affecting sorption of Co on CoTreat® were studied which include initial Co concentration, contact time, solution pH and temperature. The sorption capacity of CoTreat® for Co ions was identified to increase with increasing contact time and with increasing initial Co concentration. The Co sorption was halted at pH < 2. The sorption of Co on CoTreat® reaction can be approximated to first order reversible kinetics at high initial concentrations of Co while the sorption kinetics followed the pseudo-second order kinetics at low initial concentrations of Co. The examination of the thermodynamic parameters revealed that the sorption of Co on CoTreat® is an endothermic process and is spontaneous in the studied temperature range. The equilibrium isotherm data was analysed using the Langmuir, Freundlich and Dubinin-Radushkevich equations. The sorption of Co on CoTreat® followed the Langmuir isotherm model. The Dubinin-Radushkevich parameters revealed that the sorption process is driven by ion exchange. Slow kinetics were obtained for the Co removal by IONSIV R9120B sorption process, therefore making the sorbent material not a good candidate for practical application.

The sorption capacities of manganese oxide for Ru removal from aqueous solutions was investigated at different initial concentrations of Ru. The fitting of the Langmuir and Freundlich sorption models to the equilibrium data was investigated. The equilibrium data for the Ru sorption on manganese oxide followed the Freundlich isotherm. The monolayer sorption capacity was determined to be 0.90 mg/g at 30 °C. The pseudo-first order and the pseudo-second order kinetic models were used to fit the kinetic experimental data. The sorption of Ru on manganese oxide follows the pseudo-second order kinetic model. The temperature dependent data revealed that the sorption process is an endothermic and spontaneous ion exchange process. Poor sorption capacities were determined for Ru removal by activated carbons.

The maximum sorption of Sb on titania was obtained at 0.1 M nitric acid medium. Kinetics studies revealed that the sorption process followed pseudo-second order kinetics. The equilibrium data was evaluated using the Langmuir and Freundlich isotherm models, and well fitted the Freundlich isotherm. The obtained negative values of $\Delta G°$ and positive value of ΔH° advocate that Sb sorption on titania is a spontaneous and endothermic process.

The effect of the experimental parameters: contact time, initial concentration of metal ion and solution pH were investigated for Sb removal by alumina. The sorption capacity increased with increasing contact time and initial Sb concentration. The sorption data could be explained by the pseudo-first order kinetic model and the Langmuir isotherm.

The sorption data on Sr removal by SrTreat® revealed that the sorption capacity increases with increasing initial Sr concentration. The sorption of Sr ions on SrTreat® was halted at pH < 2, and the kinetics data obtained at high initial Sr concentration can be approximated to the pseudo-second order kinetics.

The dynamic sorption studies revealed that efficacy of the studied sorbent materials to remove the target contaminants drastically declined in the presence of uranium ions.

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List of abbreviations

AA	Atomic absoprtion
AGR	Advanced gas cooled reactor
CARBEX	Carbonate extraction
CMP	Dihexyl-N,N-diethylcarbomyl-methylphoshonate
CMPO	Octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide
DBBP	Di-butyl butyl phosphonate
DDPA	Monododecyl phosphoric acid
DEHPA/D2EHPA	Di-2-ethylhexyl phosphonic acid
D-R	Dubinin-Radushkevich
HDPA	Heptadecyl phosphoric acid
ICP-OES	Inductively coupled plasma – optical emission spectroscopy
JAERI	Japan Atomic Energy Research Institute
LWR	Light-water reactor
Necsa	South African Nuclear Energy Corporation
NPP	Nuclear power plant
NTP	Nuclear Technology Products
PE	Polyethylene
Purex	Plutonium Uranium Redox Extraction
SNF	Spent nuclear fuel
SX	Solvent extraction
T	Temperature
TBP	Tributyl phosphate
THORP	Thermal Oxide Reprocessing Plant

TOPO	Trioctyl phosphine oxide
UK	United Kingdom
Urex	Uranium extraction
USA	United States of America
UV-Vis	Ultraviolet-visible

List of symbols

b	Langmuir isotherm constant (mL/mg)
β	D-R isotherm constant (mol^2/kJ^2)
C	concentration of sorbate in the column effluent at breakthrough (mg/L)
c_e	concentration of adsorbate at equilibrium (mg/L or ppm)
c_i	initial concentration of adsorbate (mg/L or ppm)
C_0	concentration of column feed adsorbate (mg/L)
c_t	concentration of adsorbate in the liquid phase at contact time t (mg/L or ppm)
$\Delta G°$	Gibb's free energy change (kJ/mol)
$\Delta H°$	enthalpy change (kJ/mol)
$\Delta S°$	entropy change (kJ/(mol K))
D_f	decontamination factor
E	mean free energy of sorption (kJ/mol)
ε	D-R isotherm constant
k_d	distribution coefficient (mL/g)
k_f	Freundlich isotherm constant relation to the intensity of sorbent (mg/g)(dm^3/g)^n
k_1	pseudo-first order rate constant (min^{-1} or hr^{-1})
k_2	pseudo-second order rate constant (g/mg min or g/mg hr)
M	mass of sorbent material (g)
n	Freundlich isotherm relating to sorption capacity
q_e	amount of adsorbate in the adsorbent at equilibrium (mg/g)
Q	column sorption capacity (mg/g)
Q_0	maximum monolayer adsorption capacity (mg/g)
q_s	theoretical isotherm saturation capacity (mg/g)

q_t	amount of adsorbate in the adsorbent at contact time t (mg/g)
r^2	squared correlation coefficient
R	gas constant (8.3144598 J/(mol K))
R_L	separation factor
V	initial volume of sorbate solution (mL)
V_b	volume processed at the breakthrough (L)

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Research outputs

Publication in peer-reviewed journal:

Nzama, N., Stassen, L. and Crouse, P., (2019), "Batch studies on adsorptive removal of Co ions by CoTreat® in acidic media," *Journal of Radioanalytical and Nuclear Chemistry*, 322(2), 605-611.

Chapter 1: General introduction

1.1 Background

NTP a subsidiary to Necsa, supplies the important medical radioisotope ^{99}Mo. During each production run, target plates containing enriched uranium are subjected to an alkaline dissolution process to extract ^{99}Mo. During the dissolution process, the uranium and fission products precipitate as mixed hydrated oxides forming a residue. This residue is currently stored in stainless steel containers in a hot cell at NTP's ^{99}Mo production facility. This material contains ~44 % commercially valuable enriched uranium. It is in Necsa's best interest to recover uranium from the residue through its purification from the fission products and transuranium elements.

Various dissolution processes for uranium oxides have been researched (Casas *et al*, 2009; Chung *et al*, 2010; Kim *et al*, 2009a; Kim *et al*, 2009b; Lambert, 1964; Rao *et al*, 2008; Smith *et al*, 2009a; Smith *et al*, 2009b; Tomioka *et al*, 2001). The most efficient alkaline medium reported utilizes ammonium carbonate (Smith *et al*, 2009a; Smith *et al*, 2009b). In a previous Necsa project where the U residue was characterized, the U leached and purified using inorganic ion exchangers in an ammonium carbonate media, satisfactory results were obtained (Stassen & Suthiram, 2015; Stassen & Suthiram, April 2013; Stassen *et al*, 2010; Stassen *et al*, 2014).

Necsa chose the ammonium carbonate route because of its favourable features such as no gas emissions and lower volatile fission products released during the dissolution process making the process less hazardous compared to the nitric acid media reprocessing. Also, due to low solubility of many fission products in ammonium carbonate, a carbonate dissolution processing of the U residue can likely give an acceptably pure product (Stassen & Suthiram, 2015).

In the nuclear field, both acidic and alkaline dissolution have been utilized effectively. In the processing of uranium ores, acidic leaching is predominantly used. For ores containing high lime-content, the alkaline leach process is usually employed (Aly & Hamza, 2013; Edwards & Oliver, 2000; Seidel, 1981; Woods, 2016). Australian uranium ores from Koongara, Naburlek and the Ranger deposits in the Northern territory could be leached easily in dilute sulphuric acid, whereas calcrete ores from Yeelime and Lake Way in Western Australia were leached in carbonate media (Ring, 1979). The uranium ore mill at Dolni Rozinka and the Langer Heinrich uranium mine in Namibia both utilize alkaline leaching to extract uranium from its ores (Marsh, 2009; Toman & Jezova, 2007).

The well-known method for processing of irradiated uranium is the PUREX process, which utilizes nitric acid and TBP as the extractant. This method is currently used in China, France, India, Japan, Russia and in the United Kingdom (Herbst *et al*, 2011). Unfortunately, due to the co-extraction of plutonium in the PUREX process it cannot be practised at Necsa due to proliferation issues. Various modified PUREX methods are studied and employed in order to prevent plutonium recovery such as the UREX process (Regalbuto, 2011). Recently in Russia, laboratory experiments were conducted to process simulant uranium-containing SNF using the CARBEX process, giving good purification values (Stepanov *et al*, 2011). Even though there has not been work done on the CARBEX process beyond lab work, based on this recent development the process is a promising alternative to the PUREX process.

1.2 Problem statement

The production of ^{99}Mo, the mother nuclide of ^{99m}Tc which is one of the most widely used isotopes in nuclear medicine today (WNA, 2019), is undertaken at a Necsa subsidiary company NTP Radioisotopes SOC Limited. Like most other production facilities NTP uses an alkaline process to dissolve irradiated uranium/aluminium (U/Al) alloy target plates, and the ^{99}Mo is then extracted from the solution (IAEA, 1998). During dissolution a residue precipitates which contains most of the unburnt enriched uranium, and a process has been developed at Necsa to recover the uranium by dissolution in ammonium carbonate with hydrogen peroxide as oxidant, and then purify it from its fission products and plutonium, though solubility differences in carbonate and using inorganic ion exchangers. The end product (partially purified U) obtained through the carbonate process contained a few problematic radionuclide contaminants remaining at levels above their specification values for U to be reused in target plates. These are ^{60}Co, ^{106}Ru/^{106}Rh, ^{125}Sb, ^{90}Sr, ^{134}Cs and ^{144}Ce/Pr. A summary of the decontamination factors (DF) for uranium from the problematic nuclides obtained using the carbonate process is given in Table 1-1, and the further DFs required to get these nuclides within their specification levels for uranium to be reused in new ^{99}Mo target plates

Table 1-1 Decontamination factors (DF) obtained for the problematic nuclides in carbonate process

Nuclide	Bq/g U in residue	Specification (Bq/g U)	DF required	Bg/g after purification in carbonate	Wt.% in U	Further DF required
^{60}Co	7.90 x 10^4	100	790	7.62 x 10^3	1.79 x 10^{-8}	76
^{90}Sr	9.99 x 10^8	5000	2.0x10^5	2.51 x 10^5	4.98 x 10^{-7}	50
^{106}Ru	4.22 x 10^7	12000	3500	6.45 x 10^5	2.14 x 10^{-6}	54
^{125}Sb	1.35 x 10^7	12000	1100	8.53 x 10^5	1.09 x 10^{-7}	71
^{144}Ce	2.79 x 10^8	12000	2.3 x 10^4	2.32 x 10^5	1.91x10^{-7}	19

There are potential inorganic exchangers that would be efficient for removal of these problematic nuclides in nitric acid media (Ali *et al*, 2010; Girardi *et al*, 1970; Harjula *et al*, 1999; Mukhopadhyay & Lahiri, 2007; Qadeer, 2013; Tusa *et al*, 2007). A new approach is therefore proposed for complete purification of the uranium, which includes U purification in a carbonate medium as the first step followed by the conversion from a carbonate medium to a nitric acid medium using steam stripping. In this step the ammonium carbonate solution (at pH 9) is heated to just below boiling point, leading to volatilization of NH_3 and CO_2 and lowering of the pH until uranium starts precipitating as $UO_3 \cdot 2H_2O$, which is then filtered off and dissolved in nitric acid. Subsequently, the partially purified U would be further purified by ion exchange. Therefore a research project investigating U purification in nitric acid media using ion exchanger could provide solutions to improve the ammonium carbonate process. Inorganic ion exchangers are ideal for use in the nuclear field because of their exceptional properties which include good selectivity, high thermal and radiation resistance and good compatibility with final waste storage materials (Clearfield, 2000).

The radionuclides mentioned above are also some of the problematic radionuclides found in cooling water circuits of research reactors such as Necsa's SAFARI reactor, which are continuously removed using ion exchange resins. Ion exchange resins are reported to be used in the water purifying system at the TRIGA PUSPATI reactor of Nuclear Malaysia (Zalina *et al*, 2010) and the clean-up of the cooling water of the IEA-R1 research reactor located at the Institute for Nuclear and Energy Research in Sao Paulo (Taddei *et al*, 2013).

1.3 Aims and objectives

The main aim of this research is to investigate the purification of U in neutral to acidic media using inorganic ion exchangers, after it has been leached from the ^{99}Mo waste residue and purified through the carbonate process. The decontamination factors from its contaminants are required to be within the specification levels for re-use as ^{99}Mo target plates.

If the development work carried out in this project is successful, it would lead to the establishment of a full-scale processing facility to recover enriched uranium from the large stockpile of this irradiated residue from the ^{99}Mo production process at NTP. The availability of the recovered uranium for re-manufacturing of ^{99}Mo target plates would ensure the sustainability of NTP's isotope production business far into the future, and would be of enormous strategic importance to NTP since it would make the company independent of international enriched uranium suppliers, with all the political ramifications surrounding importation of enriched uranium.

The secondary aim of this study is to investigate the removal of problematic radionuclides from reactor water cooling circuits using inorganic ion exchangers. If the inorganic ion exchangers studied in this research project can remove the problematic radionuclides from neutral to slightly acidic solutions, they could be a viable replacement for the organic resins which have complicated waste handling requirements.

For the aims of this research project to be fulfilled, the following questions have to be addressed:

- What are the mechanistic characteristics of the inorganic ion exchangers concerning their capability of removing contaminants? This will require detailed research on the efficacies of the ion exchangers in the chosen media and under various experimental conditions. This includes the determination of the following parameters: rate of exchange/adsorption, surface properties, thermodynamic parameters of sorption, selectivity of the sorbent material, decontamination factors and breakthrough curves of the problematic nuclides.
- Based on the decontamination factors achieved, is the U recovery and purification process plausible for implementation? This requires studying the separation of U from its contaminants in a dynamic setting.

1.4 Thesis structure

The research of this project's objectives is given in thesis based on the structure given below:

Chapter 1: General introduction. This chapter presents the motivation behind this research project and how the project will be executed.

Chapter 2: Literature review. This chapter gives an overview of the nuclear waste reprocessing techniques and the processes in the purification of uranium specifically. It also gives a detailed description of how the efficacy of ion exchangers can be described, and how to interpret the parameters that can be derived from the kinetics and equilibria models. The known behaviour and operating mechanisms of the ion exchangers are presented as well.

Chapter 3: Experimental details presents the experimental materials, methods and strategies employed in this research project.

Chapter 4: Batch sorption studies. This chapter gives detailed descriptions of the operating mechanisms of the ion exchangers to determine their efficacies to remove the problematic nuclides from solution.

Chapter 5: Dynamic sorption studies presents the behaviour of the ion exchangers in a dynamic setting and the quantified separation of the problematic nuclides from U.

Chapter 6: Conclusions and recommendations. This chapter presents the overall results and possible future work to improve the results.

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Chapter 2: Literature review

2.1 Reprocessing of spent nuclear fuel (SNF)

Reprocessing refers to the physical and chemical treatment of SNF to separate its constituents (Murray & Holbert, 2015). These constituents include various valuable elements that are present at higher concentrations in SNF than in natural sources (Nash & Nilsson, 2015). There are several advantages of reprocessing which include:

- Reclaim of fissile nuclides ^{239}Pu and ^{235}U from spent fuel thus making them available for recycling (Bruno & Ewing, 2006).
- Isolation of useful fission products that can be used industrially e.g. ^{85}Kr, ^{90}Sr, ^{137}Cs (Murray & Holbert, 2015).
- Reclaim of scarce elements of economic and strategic value e.g. Ru, Pd and Rh (Murray & Holbert, 2015).
- Generation of lower waste volumes to dispose of, thus delaying the filling of waste repository sites (Murray & Holbert, 2015; Choppin, 2006).

The main concern with reprocessing is that separated Pu isotopes present a potential nuclear weapons proliferation risk.(Choppin, 2006) Therefore it is crucial to develop a proliferation resistant technology that would make plutonium inaccessible to weapon material production.

Even though commercial reprocessing of spent fuel is banned in the United States, other countries have operational reprocessing facilities to ensure a sustainable fuel supply by reusing the separated uranium in new nuclear fuel. The largest commercial reprocessing facilities for bulk used nuclear fuel are located in France and in the United Kingdom.(Nash & Nilsson, 2015) In France, three large reprocessing plants have been constructed and commissioned namely UP-1, UP-2 and UP-3. UP-1 located in Marcuoule reprocesses defence waste and uses PUREX (Plutonium Uranium Redox Extraction) chemistry. UP-2 and UP-3 both located in the La Hague site reprocess fuel. The latter was built exclusively to reprocess foreign fuel from other countries that lack such reprocessing technologies.(Nash & Nilsson, 2015) In the UK, two plants are operated in the Sellafield sites namely the Magnox reprocessing plant and the Thermal Oxide Reprocessing Plant (THORP). The plant reprocesses fuel from the Magnox reactors and the THORP plant reprocesses oxide fuel from light-water reactors (LWRs) and advanced gas cooled reactors (AGRs).(Nash & Nilsson, 2015) Other known reprocessing plants are the Mayak plant and the Rokkasho-mura plant located in Russia and Japan respectively.(Nash & Nilsson, 2015)

Most reprocessing plants utilize the plutonium and uranium recovery process by extraction (PUREX) where the organic solvent is tributyl phosphate (TBP) diluted with kerosene.(Nash & Nilsson, 2015; Murray & Holbert, 2015) The plutonium extracted through this process is converted into an oxide that can be used as part of (or all) the fuel of a reactor (Murray & Holbert, 2015; Nash & Nilsson, 2015); thus Pu would be less accessible. A number of alternative processes are under research or development. These include the uranium extraction (UREX) process and molten salt systems (Murray & Holbert, 2015; Choppin, 2006).

2.2 Uranium purification

When uranium has been leached from SNF, it undergoes a purification process. Two of the most promising methods for U purification are solvent extraction (SX) and the use of ion exchangers.

2.2.1 Uranium purification through solvent extraction

Solvent extraction is used in concentration and purification of metal ions. This technique involves use of two immiscible solvents (the aqueous leaching solution and an organic solvent). Organic solvents utilized in this technique are capable of bonding with solute ions. The efficacy of the technique strongly depends on a number of factors which include extractant, pH of the aqueous phase, immiscible solvent, etc. The general procedure for solvent extraction of uranium is: an aqueous solution is mixed with an extractant such as TBP or an alkyl amine in a carrier or solvent (e.g. kerosene) sometimes with an added modifier such as a long chain alcohol to increase solubility of the extracted species and prevent third-phase formation (Aly & Hamza, 2013; Murray & Holbert, 2015). The uranium ions migrate from the aqueous leach solution into the organic solvent by agitation. After the exchange of uranium in solution has occurred, the pregnant SX liquor must be stripped. The choice of stripping agent depends on the organic solvent used (Aly & Hamza, 2013). A number of ligand systems are studied for the extraction of U. These include organic phosphate oxides (Mathur *et al*, 2001; Nash & Choppin, 1997), Schiff bases (Salmon *et al*, 2006a), crown ethers (Rogers *et al*, 1987) and calixarenes (Salmon *et al*, 2006b; Shinkai *et al*, 1987).

Organic phosphate oxide have been used since the 1900's in the uranium extraction process. The commonly used organo phosphorus compounds are Tributyl phosphate (TBP) (Mathur *et al*, 2001), Di-2-ethylbexyl phosphonic acid (DEHPA or D2EHPA) (Singh *et al*, 2001), Trioctyl-phosphine oxide (TOPO) (Kulkarni, 2003; Singh *et al*, 2001), Didecyl phosphoric acid (DDPA) (Mathur *et al*, 2001), Heptadecyl phosphoric acid (HDPA), Dialkyl pyrophosphoric acid, Octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO), Glycerophosphate

(Koban & Bernhard, 2004), Dihexyl-N,N-diethylcarbomyl-methylphosphonate (CMP) and Di-butyl butyl phosphonate (DBBP) (Singh *et al*, 2001).

2.2.2 Uranium purification through ion exchange

Ion exchange (also known as solid phase extraction) is a reversible process in which ions are exchanged between the solution and the ion exchange resin. It is an important technique for uranium recovery in both alkaline and acidic leaching (Aly & Hamza, 2013; Woods, 2016). There are various types of ion exchangers that are studied and reported to be good candidates in purification and preconcentration of trace metals.

Ion exchange has been successfully developed to effectively recover uranium from its ores. After the uranium has been leached, the pregnant solution is passed through columns of resins where it is selectively adsorbed onto resin (Woods, 2016). Ion exchangers mostly used in this application are synthetic polymers made of an organic structural framework with functional groups attached to it. Examples of the mostly used functional groups are: -COOH (weak acid), $-SO_3H$ (strong acid), NH_2RCl (weak base), NR_3Cl (strong base) etc (Aly & Hamza, 2013). The uranium in the uranium ore leachates is present in anionic forms (e.g. carbonate, sulfate) thus uranium ion exchange is an anionic exchange process (Woods, 2016). This technique has been applied in a Western Australian mine where an ion exchange resin contain a quaternary amine functionality (strong base) was used to purify and concentrate a uranium alkaline leachate (Dunn *et al*).

For the Necsa research project on U recovery of the ^{99}Mo residue, adsorbents or exchangers that capture contaminants and allow U to be eluted is preferred. Organic resins are an unfavourable choice given their poor radiation resistance, poor mechanical stability and requiring additional modification prior to immobilization in solid matrices for final waste disposal. Therefore inorganic exchangers were a superior option for this application.

Various inorganic exchangers have been utilized in the treatment of radioactive liquid waste. Good examples of such are zeolites, sodium titanates, silicotitanates, hexacyanoferrates and metal oxide. Zeolites are used in the removal of ^{90}Sr and ^{137}Cs in low-salts solutions e.g. floor drain waters in nuclear power plants (Lonin *et al*, 2015; Nikashina *et al*, 1986). They can only be use in neutral pH conditions due to the dissolution of aluminium at extreme pH. Insoluble transition metal hexacynoferrates are known for their effectiveness in the removal of radioactive caesium in high concentrations of alkali metals (Harjula *et al*, 1994; Mimura *et al*, 1997). A brief overview of the inorganic ion exchangers/adsorbents selected to be investigated in this study for uranium purification in nitric acid media will be given below.

Hydrous metal oxides:

Cationic and anionic exchange sorption by oxides and hydrous oxides are reported to occur by displacement of hydrogen and hydroxide ions from the exchanger/sorbent. The ion exchange properties of metal hydroxides are attributable to the amphoteric reactions of the hydroxyl groups contained in their structure with two dissociation modes given by equations (1) and (2), where (1) is favoured by low pH promoting anionic exchange properties and (2) is favoured by high pH promoting cationic properties (Fuller, 1971). The hydrous metal oxides tested in this study are alumina, titania, manganese oxide, antimony pentoxide and CoTreat®.

$$M\text{–}OH \leftrightharpoons M^+ + OH^- \tag{1}$$

$$M\text{–}OH \leftrightharpoons M\text{–}O^- + H^+ \tag{2}$$

At the pH point of zero-point charge (pH_{ZPC}), the concentration of surface anionic and cationic sites is equal. At $pH > pH_{ZPC}$ the surface is anionic and exchanges cations, while at $pH < pH_{ZPC}$ the surface is cationic and exchanges anions (Wang *et al*, 2006).

The composition of alumina lies between the various crystalline aluminium trihydroxides ($Al(OH)_3$), and the various crystalline aluminas (Al_2O_3) (Steigman, 1982). Values for the pH_{ZPC} for alumina varying between 8.98 (Trivedi & Axe, 1999) and 7.5 (Wang *et al*, 2006) are given in the literature.

Fuller (1971) reports that at $pH < 6$, hydrated alumina exhibits anionic exchange properties and at $pH > 9$ it exhibits cationic exchange behaviour. Therefore under acidic conditions (applicable to this study), alumina should act as an anionic exchanger. pH titration studies on hydrated Al_2O_3 suggests that the material is a ter-function anionic exchanger. The proposed dissociation reaction explaining this behaviour of alumina as a base is given in (3) (Fuller, 1971).

$$Al(OH)_3 \leftrightharpoons Al(OH)_2^+ + OH^- \leftrightharpoons AlOH^{2+} + 2OH^- \leftrightharpoons Al^{3+} + 3OH^- \tag{3}$$

Hydrous TiO_2 is reported to be a ter-functional cation exchanger by Fuller (1971). Values in the literature for the pH_{ZPC} vary from 5.2 for the rutile mineral (Koretsky, 2000), to 4.5 for TiO_2 nanoparticles (Lajayer *et al*, 2018). Therefore, under very acidic conditions, TiO_2 should act as an anionic exchanger and in mildly acidic conditions as a cation exchanger. Study by Mukhopadhyay & Lahiri (2007) revealed that titania is a good adsorbent for ^{125}Sb with fast adsorption kinetics.

The study also reports alumina to have good adsorption capability for ^{125}Sb as well, with a maximum of ≈ 78% at 0.5 M HNO_3.

The ion exchange properties and structure of hydrous antimony pentoxide ($Sb_2O_5 \cdot 4H_2O$) are well documented in literature. Hydrous antimony oxide (also known as antimonic acid) has a high affinity for Sr in acidic conditions. The material has a well-defined crystal structure that can be correlated to its cationic exchange capacity with a theoretical value of 5.1 meq/g. Three crystalline phases are known to exist, one of which has the pyrochlore structure type that has a cubic unit cell of ≈10.3 Å and a space group of *Fd3m*. The pyrochlore structure has a 3-dimensional structure built from corner sharing of SbO_6 groups, forming a 3-dimensional SbO_6 network. The water and proton molecules are located in the cavities and tunnels of the framework structure (Baetsle & Huys, 1968; Belinskaya & Militsina, 1980; Fuller, 1971; Slade *et al*, 1996). Girardi *et al* (1970) reports complete ^{144}Ce (II) and ^{85}Sr (II) retention on hydrated antimony pentoxide in 1 M HNO_3 medium.

Hydrous MnO_2 or so-called Manox, has higher acidity than alumina; values for the pH_{ZPC} for Manox varying between 4.5 (Correa & Jiménez-Becerril, 2004) and 2.6 (Trivedi & Axe, 1999) are given in the literature. It therefore exhibits cation-exchange behaviour almost exclusively. Girardi *et al* (1970) reports partial retention of Ru and complete retention of Sb on hydrated manganese oxide at 0.1 M HNO_3 (at 65 °C) and 14 M HNO_3 media respectively.

CoTreat®, a titanium oxide based commercial product, effective in removing radiocobalt has been tested in the THORP feed pond plant (Sellafield, UK) as a precoat to Funda filters for the removal of ^{60}Co from light water reactor (LWR) fuel (Harjula *et al*, 2004a; Harjula *et al*, 2004b; Harjula *et al*, 2003; Harjula *et al*, 2000b). This material has been used to effectively remove ^{60}Co in nuclear power plant (NPP) waters (Harjula *et al*, 1999). The ion exchange of ^{57}Co on CoTreat® in the H^+ form is given by the reaction equation (4) (Harjula *et al*, 2010).

$$Co^{2+} + 2\overline{H}^{+} \leftrightharpoons \overline{Co}^{2+} + 2H^{+} \qquad (4)$$

No pH_{zpc} values for CoTreat was found in literature, but because it is a titania-based product, it is expected to be similar to that of TiO_2 given above.

Titanosilicate:

A sodium titanosilicate with an ideal formula of $Na_2Ti_2O_3(SiO_4) \cdot 2H_2O$ was developed in 1993 (Anthony *et al*, 1993; Anthony *et al*, 2000). The structure has a tetragonal until cell with approximate cell dimensions of a = b = 7.8 Å and c ≈ 12.0 Å. Half of the sodium ions are located inside the tunnels formed by the TiO_6 octahedra and the SiO_4 tetrahedra (Poojary *et al*, 1994). The other half (which is the exchangeable sodium) is in the framework between the silicate groups (Poojary *et al*, 1996). The affinity of the material is highly influenced by the presence of competitive ions and the alkalinity or acidity of the solution (Clearfield *et al*, 2000).

Crystalline titanosilicate has been studied to be one of the most promising compounds in the treatment of nuclear waste solutions. (Sylvester *et al*, 1999) reported sodium titanosilicate to be the best material in the removal of Sr from simulated Hanford Tank Wastes. A commercial titanosilicate, IONSIV R9120B supplied by Honeywell UOP is investigated in this study. This exchanger is report to exhibit high sorption capacity at short contact times for caesium (UOP LLC, 2012). However, this exchanger was tested for its adsorption characteristics for Co in this study. Ali *et al* (2010) reported that titanosilicate effectively removes ^{60}Co, ^{22}Na and ^{134}Cs from aqueous solutions.

Sodium titanates:

This material is reported to be effective in Sr removal (Lehto & Clearfield, 1987). Most sodium titanates belong to the group Na_2TiO_{2n+1} or Na_4TiO_{2n+2}. Most sodium titanates are layered compounds. The layers are constructed of octahedra sharing edges with exchangeable Na^+ ions located between the layers (Clearfield & Lehto, 1988). The pH_{ZPC} value of magnesium titanate is reported to be 7.12 (Gopal & Elango, 2010) and that of sodium titanate is expected to be similar. At acidic pH values, sodium titanate should therefore act as an anion exchanger. A commercial sodium titanate, SrTreat® is investigated in this study. The exchanger is highly effective in the removal of radioactive Sr. It has been used in the nuclear industry for the purification of process waters in Russia (Lehto *et al*, 1999) and for Sr removal in waste simulants at the Japan Atomic Energy Research Institute (JAERI) (Harjula *et al*, 2000a) and at the Hanford site, USA (Lehto & Harjula, 1999).

Activated carbons:

Activated carbons can be produced from almost any carbonaceous material. This adsorbent material is widely used because of its high adsorptive capacity, selectivity and low cost (Aly & Hamza, 2013). The adsorptive characteristics of these materials are attributable to their high surface area, high degree of surface reactivity and favourable pore size distribution (Qadeer, 2005). The materials are reported to be effective in the removal of toxic metal ions and contaminants from waste solutions (Daifullah *et al*, 2004; Dave *et al*, 2009; Kannan & Veemaraj, 2010; Khalkhali & Omidvari, 2005; Kobya, 2004; Qadeer & Khalid, 2005; Qadeer & Rehan, 2002; Qadeer & Akhtar, 2005; Iqbal & Ashiq, 2007). Perrich (2018) reported that van der Waals forces are the bases for the mechanism of adsorption of wastewater contaminants from waste solutions. The ash contents of the activated carbon, the degree of carbonization and method of activation are grouped with the parameters that greatly influence the material's adsorption properties (Iqbal & Ashiq, 2007). Activated carbon and activated charcoal are used in this study to capture Ru. (Qadeer, 2013) reported that activated charcoal is effective in removing Ru from an acidic solution, optimally in 3 M HNO_3. According to Shah *et al* (2015), the pH_{ZPC} of activated carbon is in the region of 6.4 - 7.4. Therefore, in any acidic pH region, it will act as an anion exchanger.

The above stated materials are good potential candidates in the removal of the problematic nuclides (Ce, Co, Sr, Ru and Sb) and are worth studying. There is inadequate literature on the mechanistic insights of these materials in nitric acid media. Chapter 3 and 4 present detailed results on the mechanisms of ion exchange and adsorption onto these materials.

2.3 Characterisation of ion exchange and adsorption

Adsorption and ion exchange processes are forms of sorption. Adsorption is the attachment of solute to a solid material. The solid material is referred to as the adsorbent and the bound metal ions are referred to as the adsorbate. In theory, adsorption can occur at any solid-fluid interface, e.g. liquid-solid interface and gas-solid interface. There are two distinct types of adsorption namely chemisorption and physisorption. The chemisorption process is caused by formation of chemical bonds between the surface of the adsorbent and the adsorbate. Because of this, chemisorption is usually irreversible such that extreme conditions are required for the chemisorbed species to be removed. Differently, physisorption involves the interaction of molecules with the surface of the adsorbent through van der Waals interactions. The process is generally reversible in nature. Irregularly, both chemisorption and physisorption may occur on the same surface concurrently, a layer of adsorbent may be physically adsorbed on top of a chemisorbed layer (Al-Anber, 2011). The general adsorption reaction involves 3 steps:

(i) Transfer of adsorbate from the bulk solution to the adsorbent surface
(ii) Migration of adsorbate into pores
(iii) Interaction of the adsorbate with the interior surface sites of pores

Ion exchange refers to the exchange of ions of the same charge between a solid ion exchanger and the electrolyte solution (M.D. *et al*, 2008). When the functional groups of the solid matrix are negatively charged, cations will be exchanged. For a solid matrix containing positively charged functional groups, anions are exchanged (IAEA, 2002). An ion exchange reaction between ion X (charge z_x) and Y (charge z_y) maybe represented as equation (5), where the superscript bars refer to the ions in the solid ion exchanger (Harjula, 2000).

$$z_y X^{Z_x} + z_x \bar{Y}^{z_y} \leftrightharpoons z_x Z^{Z_y} + z_y \bar{X}^{z_x} \quad (5)$$

Often, ion exchange and adsorption are grouped together as sorption due to the vast number of common features the two processes share. Sorption behaviour is generally described by kinetics and equilibrium isotherms (Chabani *et al*, 2006). To design an ion exchange purification technology, it is very important to study the efficacy of the chosen ion exchangers and their mechanisms.

Various parameters can be used to measure the efficacy of a sorbent material. The most commonly used are:

(i) Distribution coefficient (k_d), which can be mathematically written as equation (6) (Sylvester *et al*, 1999), where c_i (mg/L) is the initial concentration of the adsorbate solution, c_e (mg/L) is the equilibrium or final concentration of adsorbate in solution, V (mL) is the initial volume of the adsorbate solution and M (g) is the mass of the sorbent material. In a batch process, the measured k_d value can be used to calculate the amount of sorbent material required to obtain a certain decontamination of a certain amount of liquid (IAEA, 2002). The higher the $\mathrm{k_d}$ value, the more effective the sorbent material is.

$$k_d\left(\frac{\mathrm{mL}}{\mathrm{g}}\right) = \frac{c_i - c_e}{c_e} \times \frac{V}{M} \quad (6)$$

(ii) % Sorption, which can calculated using equation (7) (Al-Anber, 2011), where c_i and c_e are as stated above.

$$\%\ \mathrm{Sorption} = \frac{c_i - c_e}{c_i} \times 100 \quad (7)$$

(iii) Metal ions sorbed or exchanged on sorbent material (q_e) can be determined using equation (8) (Al-Anber, 2011)

$$q_e(\frac{\text{mg}}{\text{g}}) = (c_i - c_e) \times \frac{V(\text{mL})}{M\ (\text{g})} \tag{8}$$

2.3.1 Sorption operations

Both ion exchange and adsorption can be carried out by either batch or column operation.

- **Batch operation**: The batch operation is the simplest method for operating sorption processes and is normally used in research because it is simple to construct and operate. Also, a large number of experiments can be conducted in parallel and the process can be easily customized for specific treatment problems. In batch operation, a measured amount (*M*) of sorbent material is mixed with a given volume (*V*) of adsorbate solution (of know concentration). The mixture is allowed to equilibrate for a specific length of time with stirring (Harjula, 2000). When the reaction is complete, the solid and the liquid phases are separated by conventional separation techniques such as centrifugation, decantation or filtration. The optimum agitation speed, contact time, pH and temperature are used in this technique. During the sorption process, the reaction vessel or container must be covered to avoid evaporation (Al-Anber, 2011). The disadvantages of the batch process are that manual operation may be complicated to handle at large scale, the separation of the solid and liquid phase and that the sorbent material can be used once through only (IAEA, 2002).
- **Column operation**: In a column operation, a solution containing unfavourable ions (X) is passed through a column containing an exchanger in the Y form. The X ions are taken up by the exchanger while the Y ions are released into the effluent. The Y ions are constantly being removed from the system. At the beginning, the column effluent is free of X ions, but when a given amount of the solution has passed through, X ions starts to emerge in the effluent. The plot of concentration of X in the effluent vs the effluent volume is called the breakthrough curve. The same principle applies to adsorption, the adsorbate solution is allowed to percolate through the column containing the adsorbent at a specific flow rate (Harjula, 2000). The sorption capacity (*Q*) can be determined using equation (9) (Al-Anber, 2011), where C_0 (mg/L) is the concentration of the feed adsorbate solution, *C* (mg/L) is the concentration of the adsorbate in the column effluent at breakthrough, *M* (g) is the mass of the adsorbent and V_b (L) is the volume processed at the breakthrough of the adsorbate. From column operation, high decontamination factors

(*Df*s) can be achieved. The decontamination factor can be calculated using equation (10) (Alfassi & Wai, 1991), where C_0 and C are as described previously.

$$Q\left(\frac{\mathrm{mg}}{\mathrm{g}}\right) = \frac{C_0 - C}{M} \times V_b \tag{9}$$

$$D_f = \frac{C_0}{C} \tag{10}$$

2.3.2 Factors influencing sorption

The factors that affect the sorbent material capacity to remove metal ions in solution include (i) surface area, (ii) solution pH, (iii) presence of competing ions, (iv) solution temperature, (v) contact time, and (vi) initial concentration of sorbate. The influence of these factors is described below.

(i) Surface area: The sorption capacity of a material is generally proportional to its surface area. An increase in the surface area results to an increase in the sorption capacity of the sorbent material (Al-Anber, 2011; Kadirvelu & Jyotsna).

(ii) Solution pH: The dependence of sorption capacity on pH is due to the changes in the surface chemical characteristics and distribution of sorbate species of ions with varying solution pH. In general cationic species removal is directly proportional to solution pH, whereas the uptake of anionic species increases with decreasing pH. The latter is mainly due to electrostatic repulsion (Al-Anber, 2011; Kadirvelu & Jyotsna).

(iii) Presence of competing ions: The presence of competing ions can alter the sorption capacity of a sorbent material from that observed in a mono-component system. The extent of the competition depends on the affinity of the sorbent material for the sorbate ions, number of surface sites and the concentration of the competing ions (Kadirvelu & Jyotsna).

(iv) Temperature effect: Adsorption is a spontaneous and exothermic process. Therefore, an increase in temperature will result in the reduction in the equilibrium adsorption capacity whereas lower temperatures will favour an increased adsorption capacity. Ion exchange can be an endothermic process. For an endothermic process, an increase in solution temperature would result in an increased sorption capacity (Kadirvelu & Jyotsna).

(v) Contact time or residence time: The longer the contact time means the more complete the sorption process will be. To provide insight into the sorption process, it is important to determine the required contact time for the sorption process to be completed or reach equilibrium (Al-Anber, 2011).

(vi) Effect of initial concentration: At high levels, fewer available sorption sites are available. Therefore the sorption efficiency decreases with increasing initial concentration of sorbate (Al-Anber, 2011).

2.3.3 Kinetic models of sorption

Sorption can be described by kinetics and equilibrium models. Thermodynamic data only give information about the final state of the system whereas kinetics mostly deals with the rates of changes of chemical properties (Azizian, 2004). In designing a sorption treatment technology, it is important to be able to predict the rate at which the contaminants are removed from aqueous solutions. Studying the sorption kinetics provides insights into the reaction pathways and mechanisms of sorption reactions (Ho & McKay, 1999; Qiu *et al*, 2009).

The widely used kinetics models for sorption processes in solutions is the pseudo-first order and the pseudo-second order kinetic models which will be discussed below.

(i) Pseudo-first order kinetic model: Lagergren presented a first order rate equation for the sorption of solutes from liquid solutions, which is based on the solid phase capacity. The pseudo-first order equation is given in equation (11) (Ho & McKay, 1998), where q_e (mg/g) is the sorption capacity at equilibrium, q_t (mg/g) is the sorption capacity at time t, k_1 (min^{-1}) is the pseudo-first order ate constant.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{11}$$

Integration of (11) for the boundary conditions $t = 0$ to $t = t$, and $q = 0$ to $q = q$, gives equation (12), which can be rearranged to equation (13).

$$\ln\frac{(q_e - q_t)}{q_e} = -k_1 t \tag{12}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{13}$$

The pseudo-first order kinetic model has been used to describe sorption kinetic systems in literature (Banerjee *et al*, 1997; Hameed & El-Khaiary, 2008b; Hameed & El-Khaiary, 2008a; Sharma *et al*, 1990; Singh *et al*, 1988; Tan *et al*, 2008; Trivedi *et al*, 1973).

(ii) Pseudo-second order kinetic model: The rate law for this model is given by equation (14) (Ho & McKay, 1998).

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{14}$$

Integration of equation (14) for the boundary conditions $t = 0$ to $t = t$, and $q = 0$ to $q = q$, gives equation (15), where q_e, q_t are as described previously and k_2 (g/(mg min)) is the pseudo-second order rate constant. Equation (15) can be re-arranged to give a linear form (16).

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{15}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{16}$$

The pseudo-second order kinetic model has been applied in various sorption systems (Anirudhan & Radhakrishnan, 2008; Cheng *et al*, 2008; Ho & McKay, 1999; Ho & McKay, 2000; Petroni *et al*, 2004; Yan & Viraraghavan, 2003; Hameed, 2008).

2.3.4 Sorption isotherm models

An isotherm (also known as equilibrium data) is a curve describing the relationship between the amount of adsorbate retained on adsorbent and the adsorbent's residual concentration at equilibrium (Ali *et al*, 2010; Chabani *et al*, 2006; Ncibi, 2008). The equilibrium state is reached when the capacity of the sorbent material is reached and the rates of sorption and desorption are equal (Al-Anber, 2011). The physicochemical parameters combined with the underlying thermodynamic parameters that can be derived from the isotherms give insight into the sorption mechanism, surface properties and the affinity of the exchangers (Bulut *et al*, 2008). The models mostly used to describe experimental isotherm data are the Langmuir, Freundlich and the Dubinin-Radushkevich (D-R) isotherm models. A brief description of the models is given below.

(i) Langmuir isotherm (Foo & Hameed, 2010): This empirical model assumes monolayer adsorption and that adsorption can occur at a fixed number of sites. The adsorption sites are assumed to be identical and equivalent. The mathematical description of the Langmuir model is given by the non-linear equation (17) and linear equation (18) where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), c_e is the concentration of adsorbate at equilibrium (mg/L), Q_0 is the maximum monolayer adsorption capacity (mg/g) and b is the Langmuir isotherm constant (mL/mg).

$$q_e = \frac{Q_0 b c_e}{1 + b c_e} \tag{17}$$

$$\frac{c_e}{q_e} = \frac{1}{bQ_0} + \frac{c_e}{Q_0} \tag{18}$$

From the Langmuir constant b, a dimensionless constant known as the separation factor (R_L) can be derived using equation (19), where c_i (mg/L) is the initial concentration of the adsorbate.

$$R_L = \frac{1}{1 + b c_i} \tag{19}$$

The R_L value indicates that the adsorption nature to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

(ii) Freundlich isotherm: This empirical model is used to describe non-ideal, reversible adsorption. The model can be applied to multilayer adsorption, with non-uniform adsorption sites. The stronger binding sites are occupied first (Foo & Hameed, 2010). The mathematical description of the model is given by the non-linear equation (20) and linear equation (21) where q_e and c_e are as described previously, k_F (mg/g)(dm^3/g)^n and $1/n$ are the Freundlich isotherm constants relating to sorption capacity and intensity of adsorption respectively (Ali *et al*, 2010).

$$q_e = k_f {c_e}^{1/n} \tag{20}$$

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \tag{21}$$

The slope of the linear curve ($1/n$) ranges between 0 and 1 (Foo & Hameed, 2010). A $1/n$ value greater than 1 indicates cooperative adsorption, a term referring to the molecules influencing one another's adsorption. For example, a molecule adsorbed at high pressures may contribute its energy to improve the adsorption site next to it of lower energy. In doing so, it does not influence its own adsorption. A value less than 1 indicates chemisorption and favourable adsorption (Chabani *et al*, 2006; Foo & Hameed, 2010; Halsey, 1948). The closer the value of $1/n$ is to 0, the more heterogeneous the sorption surface is (Foo & Hameed, 2010).

(iii) Dubinin-Radushkevich (D-R) isotherm: This empirical model is more general than the Langmuir and Freundlich isotherm models. It is normally used to distinguish between physical and chemical adsorption of solute (Donat *et al*, 2005). The mathematical description of the model is given by the non-linear equation (22) and linear equation (23) where c_e and q_e are as described previously, q_s (mg/g) is the theoretical isotherm saturation capacity, β (mol^2 / kJ^2) is the activity coefficient related to mean sorption energy and ε (given by equation (24)) is the Polanyi potential (Foo & Hameed, 2010).

$$q_e = (q_s)e^{-\beta\varepsilon^2} \text{ (nonlinear)} \tag{22}$$

$$\ln q_e = \ln q_s - \beta\varepsilon^2 \text{ (linear)} \tag{23}$$

$$\varepsilon = RT\ln(1 + \frac{1}{c_e}) \tag{24}$$

From the slope of the linear curve, the mean free energy of sorption energy E can be calculated by equation (25). The value of E can be used to categorise the sorption process as either physisorption, ion exchange or chemisorption based on the limits given in Table 2-1 (Al-Anber, 2011; Inglezakis & Zorpas, 2012).

$$E = \frac{1}{\sqrt{-2\beta}} \tag{25}$$

Table 2-1 Adsorption energy parameter limit relative to the nature of sorption (Inglezakis & Zorpas, 2012)

Nature of sorption	Adsorption energy (kJ/mol)
Physisorption	< 8
Ion exchange	8-16
Chemisorption	> 16

2.3.5 Thermodynamic parameters

The thermodynamic parameters enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of sorption can be derived from the linear Arrhenius equation (26)(Khan *et al*, 1995), where k_d is the distribution coefficient at equilibrium, R is the gas constant and T is the temperature in Kelvin. Based on the sign of $\Delta H°$, the sorption process can be considered an endothermic or exothermic process. Based on the value of $\Delta H°$, the sorption process can be inferred to be either physisorption ($\Delta H° < 80$ kJ/mol), ion exchange ($\Delta H° < 40$ kJ/mol) or chemisorption ($\Delta H° > 80$ kJ/mol)(Inglezakis & Zorpas, 2012). The Gibbs free energy of sorption can be determined from equation (27). Based on the value and sign of $\Delta G°$, the sorption process can be deemed a spontaneous or a non-spontaneous process.

$$\ln k_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{26}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{27}$$

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Chapter 3: Experimental details

3.1 Materials

The materials that were used in this study are Sb_2O_5 (Sigma Aldrich®, Alfa Aesar), CoTreat® (Fortum), Activated charcoal granules (ACE chemicals), Al_2O_3 (UNILAB, Sigma Aldrich® (weakly acidic)), MnO_2 (MERCK), Activated carbon (SUTCLIFFE SPEAKMAN & Co. Ltd), Manox A (R.A.N (Recherche Appliquee du Nord), SrTreat® (Fortum), IONSIV™R9120-B (UOP Honeywell), TiO_2 (R.A.N (Recherche Appliquee du Nord), U_3O_8 (Nufcor (Pty) Ltd), atomic absorption (AA) standards for Ce, Co, Ru, Sb, Sr (Laboratory consumables & chemical supplies CC) and 70% Nitric acid (ACE platinum line), NaOH (Sigma Aldrich®) and NaCl (MERCK). Due to the safety hazards associated with working with radioactive nuclide solutions, inactive standard solutions were used.

3.2 Analytical instrumentation

The analytical techniques used in this study are inductively coupled plasma – optical emission spectroscopy (ICP-OES) and ultraviolet-visible (UV-Vis) spectroscopy. The respective instruments utilized are Spectro Arcos and UV-Vis spectrophotometer (Perkin Elmer Lambda 1050).

The ICP-OES technique is based on the measurement of light emitted by elements in a sample that was introduced into the plasma as an aerosol produced in the nebulizer or spray chamber system. The function of the high temperature plasma is to vaporize solvent, vaporize the salt particles to gas, dissociate the gas molecules into atoms, excitation and ionization of the atoms. Each element has a characteristic spectrum of emission lines. The intensity of the emitted light is related to the concentration of the analyte in the sample and to the number of atoms in the plasma (Postawa & Hayes).

The UV-Vis spectroscopy technique is based on the absorption of energy in the form of ultraviolet or visible light. The Bouguer-Lambert-Beer law states that the absorbance (A) of a sample is related to the concentration of absorbing species (C) and the path length (l). The law equation is presented in (28), where I_0 is the intensity of incident light, I is the transmitted intensity and ε is the extinction coefficient (Förster, 2004).

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon\, C\, l \tag{28}$$

In this study a UV-Vis spectrophotometer was used to analyse samples for U, using the carbonate method (described in Appendix B) which is based on the intense yellow colour produced by the $[UO_2(CO_3)OOH]^{3-}$ complex which absorbs visible light at 450 nm.

3.3 Methods

3.3.1 Quantifying adsorption and ion exchange (batch studies)

Ion exchange and adsorption can be measured using a batch method where a known amount of sorbent material is contacted with an element solution of known concentration and volume. In all the batch experiments in this study, the ratio of adsorbent amount (g) to solution (mL) was 1:100. The solutions were prepared prior to the conduction of each experiment by dilution of the certified standards. Where applicable, the pH was adjusted to the desirable pH by dilution using ultrapure water.

The sorbent-element pairs studied in this research are presented in Table 3-1.

Table 3-1 Studied sorbent materials and their respective target elements

Sorbent material/exchanger	Element
Activated charcoal	Ru
Activated carbon	Ru
Al_2O_3	Sb
Sb_2O_5	Ce, Sr
CoTreat®	Co
IONSIV™R9120-B	Co
MnO_2, Manox A	Ru
SrTreat®	Sr
TiO_2	Sb

3.3.2 Investigating the sorption extent over time

A known mass of sorbent material was transferred to a reaction vessel (50mL polyethylene (PE) bottle (Plastpro Scientific (Pty) Ltd) followed by the addition of nuclide solution of known concentration (ppm) and volume. Immediately after the solution was added, the reaction vessel was closed and then incubated at 30 °C in a Labex platform incubator shaker shaking at 250 rpm.

After the desired contact time was reached, the reaction vessel was removed from the incubator. The aqueous phase was then separated from the solid phase by centrifugation at 4000 rpm for 10 minutes followed with filtration using 0.2 µm nylon syringe filters (Separation Science SA (Pty) Ltd). In the case of the CoTreat® and SrTreat exchangers, the phase separation was achieved by ultracentrifugation at 30000G using the Thermo Scientific™ Sorvall™ LYNX 6000 superspeed centrifuge. Ultracentrifugation is required for these two exchangers because they get slightly peptized, which mean that if the liquid and solid phase separation is not carried properly a minor amount of the exchanger will be left in the aqueous phase. In such a case, the ICP-OES analytical technique will read both the free metal ions and the colloid-bound metal ions left due to improper phase separation, thus giving incorrect k_d results. Ultrafiltration is another effective method for the complete removal of colloidal exchanger fragments.

The resultant solutions after phase separation were analysed using ICP-OES.

The study of the effect of pH on adsorption/ion exchange was conducted as described above, with element solutions of varying pH. The contact time was kept constant and was unique for each element-sorbent pair. The sorbent-element pairs for which the pH study was not conducted are presented in Appendix A, accompanied by the suitable reasoning for the elimination of the pairs.

3.3.3 Measuring sorption equilibrium

The ion exchange and adsorption equilibria can be described by construction of sorption isotherms, which are curves relating the amount of element retained on sorbent material to the element residual concentration. For each sorbent-element pair, the sorbent material was exposed to element solutions of different concentrations. The exchangers and element solutions were kept in contact until equilibrium was reached (equilibrium time predetermined for each element-sorbent pair). By ICP-OES analysis, the residual concentration and amount of element retained on sorbent at equilibrium was determined for each initial element concentration. The sorbent-element pairs for which this study was not conducted is given in Appendix A, accompanied by the appropriate reasoning.

3.3.4 Determination of thermodynamic parameters

The thermodynamic parameters of sorption can be determined by studying the effect of temperature on the amount of element retained on the exchanger at equilibrium. For this experiment, the sorbent was kept in contact with an element solution of known concentration until equilibrium was reached (equilibrium time predetermined). The experiments were conducted at 30, 45 and 60 °C. The list of the sorbent-element pairs for which the temperature study was not conducted is given in Appendix A, accompanied by the relevant reasoning.

3.3.5 Investigating the effect of temperature on the sorption kinetics

The effect of temperature on the sorption kinetics was studied by determining the sorption extent over time at different temperatures at a fixed element concentration. The studied temperatures are 30, 45 and 60 °C. This experiment was only conducted for the CoTreat®-Co and titania-Sb pairs due to limited resources.

3.3.6 Selectivity of the sorbent materials

The selectivity of the sorbent materials was studied by preparing a mixture of the problematic elements Co, Ce, Ru, Sb, and Sr at equal concentrations. The mixture was then exposed to a sorbent material at 30 °C solution temperature. After the chosen contact time, the liquid and solid phase separation was achieved by centrifugation followed by filtration or ultracentrifugation in CoTreat® and SrTreat® exchangers' experiments. The resultant solutions were analysed for all the contaminants by ICP-OES. The list of the sorbent-element pairs for which this experiment was not conducted is given in Appendix A.

3.3.7 Preparing the uranium stock solution

10 g of U_3O_8 was weighed and transferred to a four-necked round bottom flask. The setup is shown in Figure 3-1. The reflux condenser condensed the water vapour, preventing water loss. The thermocouple (Heidolph) was used to maintain the solution temperature. 100 mL of 1 M HNO_3 was added to the U_3O_8 powder. The dissolution reaction was conducted at 60 °C and the solution was stirred continuously at 500 rpm for 2 hours. When the reaction was completed, the solution was filtered (Whatman 2.5 µm particle retention filter paper) to remove any undissolved material. The resultant U solution was transferred to a 1 L volumetric flask and diluted with ultrapure water. The target pH for the feed solutions containing U was achieved by addition of 1 NaOH or 1 M HNO_3.

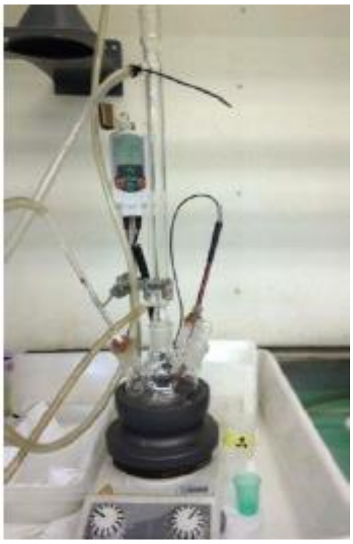

Figure 3-1 Experimental set up for the dissolution of U_3O_8 to prepare a U stock solution

3.3.8 Co sorption on column packed with CoTreat®

A weighed amount of 3.98 g of CoTreat® material was placed in a beaker and washed with tap water to remove dust particles. After most of the dust was removed, the material was slurried into the plastic column (TRISKEM) to a height equivalent to a 5 mL volume. A piece of cotton wool was place at the bottom of the column's reservoir in order to prevent the packed bed from being disturbed when the feed solution was passed through the column. After the packing, the column was washed with 50 mL of HNO_3 (pH 2.46) to remove dust and fine particles left after packing and also equilibrate the column to be at the same acid pH as the feed solution. The feed solution contained 10 ppm Co, with a total volume of 240 mL. The feed solution was passed through the column at a flow rate of ≈1mL/min. The flow rate was controlled with polycarbonate flow valves (TRISKEM). Fractions of 20 mL were continuously collected. After the feed was depleted, the column was washed with 30 mL of HNO_3 (pH 2.46). The concentration of Co in the effluent fractions was measured by ICP-OES analysis.

For the experiment conducted in the presence of U, the feed solution had a volume of 264 mL and contained 5360 ppm U and 4 ppm Co. The collected 50 mL fractions were analysed for U using the UV-Vis spectrophotometer. Samples of the collected fractions were sent to Pelindaba Analytical Laboratories (PAL) for Co analysis using ICP-OES.

3.3.9 Ru sorption on column packed with Manox A

The exchanger was slurried into the column to a height equivalent to a volume of 5 mL. After the packing, the column was washed with 50 mL of HNO_3 (pH 2.56) to remove dust and fine particles left after packing and also equilibrate the column to be at the same acid pH as the feed solution. The feed solution contained 8 ppm Ru and 6234 ppm U, with a total volume of 253 mL. The feed solution passed through the column at a flow rate less than 1mL/min. Fractions of 50 mL were continuously collected. After the feed was depleted, the column was washed with 30 mL of HNO_3 (pH 2.56). Samples of the collected fractions were sent to PAL for Co and U analysis by ICP-OES. The UV-Vis spectrophotometer was not used for U analysis in this case because the dark colour of Manox A was interfering with U detection resulting in false absorbance readings.

3.3.10 Sb sorption on column packed with titania

A weighed amount of 5.55 g of titania material was slurried into the column. After the packing, the column was washed with 50 mL of 0.1 M HNO_3 to remove dust and fine particles left after packing and also equilibrate the column to be at the same acid pH as the feed solution. The feed solution contained 10 ppm Sb, with a total volume of 239 mL. The feed solution was passed through the column at a flow rate of ≈1mL/min. Fractions of 20 mL were continuously collected. After the feed was depleted, the column was washed with 30 mL of 0.1 M HNO_3. The concentration of Sb in the effluent fractions was measured by ICP-OES.

For the experiment conducted to determine if the U is sorbed on titania, the feed solution had a volume of 248 mL and contained 6754 ppm U. The collected 50 mL fractions were analysed for U using UV-Vis.

For the experiments conducted in presence of both Sb and U, the feed solution had a volume of 250 mL and contained 5900 ppm U and 4 ppm Sb. Immediately after the feed solution was depleted, the column was washed with ≈60 mL HNO_3 (pH 0.96). The collected 50 mL fractions were analysed for U using the UV-Vis. Samples of the collected fractions were sent to PAL for Sb analysis using ICP-OES.

3.3.11 Sr sorption on column packed with SrTreat®

A 3.13 g weighed amount of SrTreat® material was placed in a beaker and washed with 29 g/L NaCl to remove dust particles. After most of the dust was removed, the material was slurried into the column to a height equivalent to a 5 mL volume. After the packing, the column was washed with 50 mL of HNO_3 (pH 2.45) to remove dust and fine particles left after packing and also equilibrate the column to be at the same acid pH as the feed solution. The feed solution contained 10 ppm Sr (pH 2.47), with a total volume of 239 mL. The feed solution was passed through the column at a flow rate of ≈1mL/min. Fractions of 20 mL were continuously collected. After the feed was depleted, the column was washed with 30 mL of HNO_3 (pH 2.45). The concentration of Sr in the effluent fractions was measured by ICP-OES.

For the experiment conducted in presence of U, the feed solution had a volume of 260 mL and contained 5910 ppm U and 4 ppm Sr. After the feed was depleted, the column was washed with ≈195 mL of HNO_3 (pH 2.47). This column was washed with excessive solvent (in comparison to the other experiments) in order to make sure that the uranium deposits (that were visible to the naked eye) on the column were due to sorption, rather than suspension. The collected 50 mL fractions were analysed for U using the UV-Vis. Samples of the collected fractions were sent to PAL for Sr analysis with ICP-OES.

3.4 Experimental design

A complete experimental matrix with the list of experiments conducted in this study is presented in Appendix A.

References

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Postawa, A. and Hayes, C. (2013), "8.5 Inductively Coupled Plasma Sprectometry," *Best Practice Guide on the Control of Iron and Manganese in Water Supply*, IWA Publishing, 65.

Chapter 4: Batch sorption studies

4.1 Ce removal by antimony pentoxide (Sb_2O_5)

Lanthanides exist in significant amounts in spent nuclear fuel with maximum mass yields of neodymium and cerium. ^{144}Ce is one of the problematic nuclides to be investigated in this study. In order to achieve the objective of designing an ion exchange purification technology for U recovery from ^{99}Mo waste, it is crucial to identify and study inorganic adsorbents capable of removing Ce in nitric acid media. In literature, it is reported that ^{114}Ce can be removed by solvent extraction from a mixture of rare earth fission products (Butler & Ketchen, 1961). Also, the material Y Zeolite is reported to exhibit high affinity for the exchange of Ce^{3+} ions in aqueous media (Keane, 1996). The inorganic sorbent material that was available for this study is antimony pentoxide. Girardi *et al* (1970) reported that Ce is completely retained on a column packed with hydrated antimony pentoxide at 1 M nitric acid media.

4.1.1 Effect of contact time on the Ce sorption capacity of antimony pentoxide

To evaluate the efficacy of antimony pentoxide to remove Ce in solution, a batch study was conducted according to the method described in 3.3.2. The results are presented in Figure 4-1.

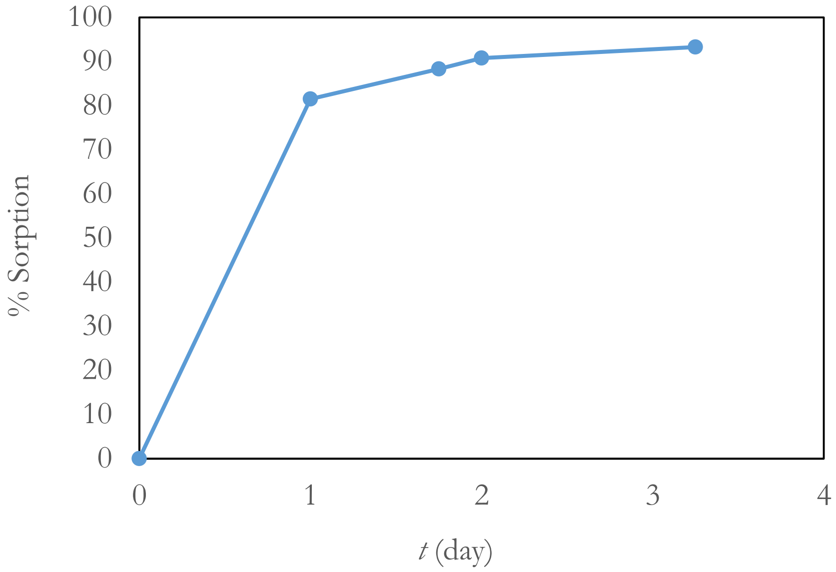

Figure 4-1 Time variation curve for percentage Ce removal by antimony pentoxide at 30 °C and initial concentration of 5 ppm, 1 M HNO_3

From the curve it can deduced that at 78 hours contact time, the saturation or equilibrium point is approached. Based on the initial concentration of Ce, 0.468 mg Ce is retained on antimony pentoxide after 78 hours contact time which is equivalent to 93.26 % Ce sorbed. This is a significant amount, however the kinetics are considerably slow. Thus this material is not a good candidate for this research. Additional experimental work could not be conducted on this material due to material shortage.

When material supplied by a different commercial supplier (Alfa Aesar) was used, it gave contradicting results (given in Table 4-1) to the results obtained from the Sigma Aldrich product. The article by Zhang *et al* (2014) presents work showing that the sorption properties are dependent on the preparation method of the exchanger. Therefore the discrepancy in the results may be explained by that the two products have different sorption characteristics due to their different properties attributed to their preparation methods which may be different in the two commercial suppliers.

Table 4-1 Sorption results of Ce removal by antimony pentoxide supplied by Alpha Aesar

Time (day)	% Sorption
0	0
0.5	0
4	0

4.2 Co removal by CoTreat®

The activation product ^{60}Co remains at levels higher than required for the U leached from the post-reactor waste to be re-used as target plates. The inorganic exchangers CoTreat® and IONSIV R9120B were studied for their potential to remove Co from solution.

The inorganic exchanger material, CoTreat® is a commercial product based on titanium dioxide, tailored for the removal of radiocobalt in aqueous solutions. It is reported to be effective in the removal of activation products ^{54}Mn, ^{59}Fe, ^{65}Zn and ^{63}Ni from NPP waters (Harjula *et al*, 2010). XRD and XRF analysis was done on the CoTreat®, the results are included in Appendix A.

4.2.1 The effect of solution pH on Co removal by CoTreat®

The effect of solution pH on the sorption capacity of CoTreat® for Co was studied using the method described in 3.3.2 within a narrow pH range of 0.5-2.6. The results obtained are presented in Figure 4-2, which reveals that a solution pH of 2 and greater is required for optimum Co sorption on CoTreat®. It is surprising that the exchanger possesses such efficacy in the ultra-acidic pH range, given that Tusa *et al* (2007) reported that the best results are obtained from pH 6-8. The results obtained prove that the CoTreat® exchanger is highly effective in removing Co from acidic aqueous solutions. The pH of 2.6 was chosen for subsequent experiments.

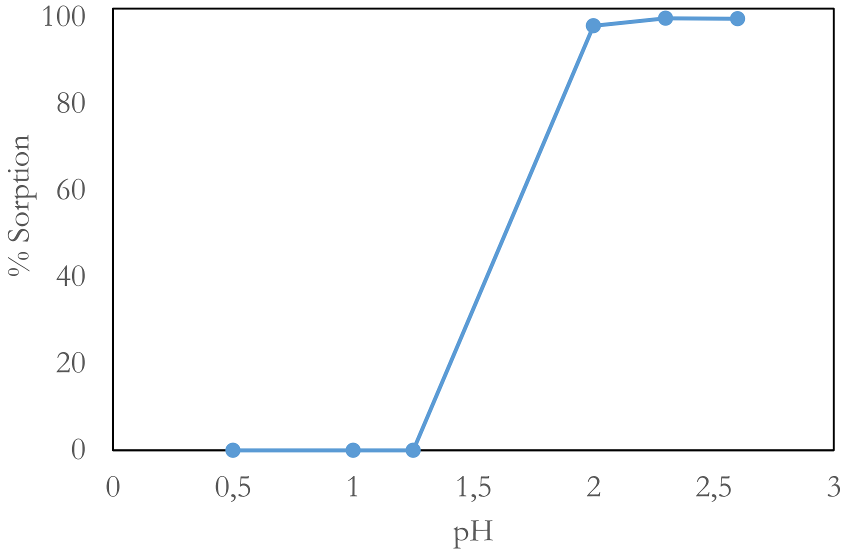

Figure 4-2 The sorption extent of CoTreat® for Co in varying nitric acid pH

4.2.2 Sorption kinetic modelling of Co removal by CoTreat®

One of the ways to assess the performance of a sorbent material is determining the kinetic aspects of the sorption reaction. From the kinetic analysis, various mechanistic factors can be determined. The batch method used to describe the exchange of Co on CoTreat® is described in 3.3.2. The experiment was conducted at four Co concentrations i.e. 5, 10, 30 and 40 ppm. The contact times selected were 5, 10, 30, 60, 120, 180 and 240 minutes. The pH of the Co solutions was adjusted to 2.6. The results obtained are presented in Figure 4-3. From the plot, it can be deduced that the CoTreat® exchanger is an efficient exchange material for Co removal in acidic solutions. A sharp initial rise can be observed at the lower Co concentrations (5 and 10 ppm) followed by complete Co removal after 10 and 30 minutes contact time respectively. A slower initial rise can be observed for the higher Co concentration (30 and 40 ppm) followed by complete saturation after 4 hours contact time. The uptake rate decreases with increasing initial concentration of Co. At the concentrations 5, 10 and 30 ppm, complete Co removal from solution was attained, whereas at 40 ppm initial Co concentration, partial Co removal (~77 %) was obtained after 4 hours contact time. This is due to the saturation of exchanger material. At lower concentrations, adequate sorption sites were available for complete removal of the Co ions in solution.

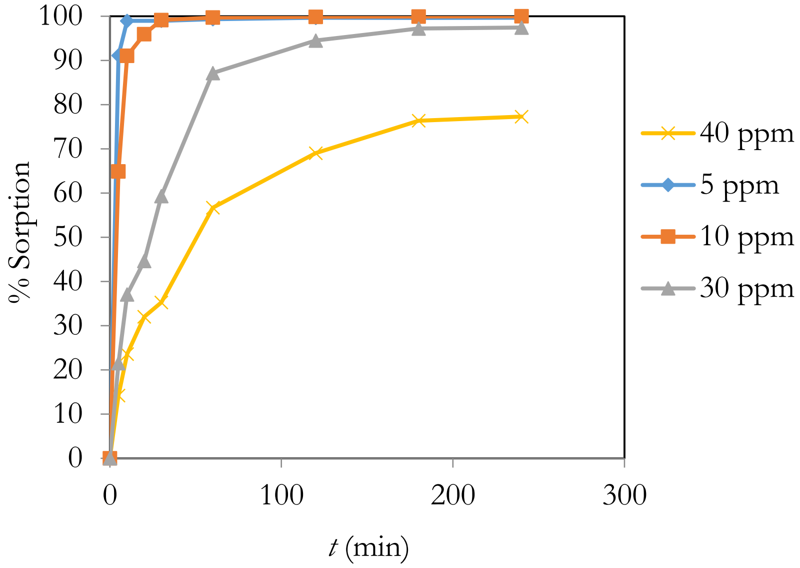

Figure 4-3 Time variation of percentage removal of Co by Co Treat® at various concentrations of Co (30 °C, pH 2.6)

The time dependent data was fitted to the well know adsorption kinetic models viz. the pseudo-first order and the pseudo-second order kinetic models (described in 2.3.3). For initial Co concentrations 5 and 10 ppm, non-linear plots of log (q_e-q_t) vs t (not shown) was obtained, thus demonstrating the non-validity of the pseudo-first order kinetic model at these two concentrations. When the kinetic results for the initial Co concentrations 5 and 10 ppm were fitted to the pseudo-second kinetic model equation, good linear fits were obtained (Figure 4-4). The kinetic parameters derived from the fittings are given in Table 4-2, it can de deduced that the rate of ion exchange decreases with increasing element concentration as expected. Moreover, the calculated values of q_e (mg/g) gave a better agreement with the experimental values of q_e (mg/g) along with a good correlation coefficient ($r^2 \approx 0.999$). Therefore the exchange of Co ions on CoTreat® could be said to conform to the pseudo-second order kinetic model at the 5 and 10 ppm concentrations of Co ions.

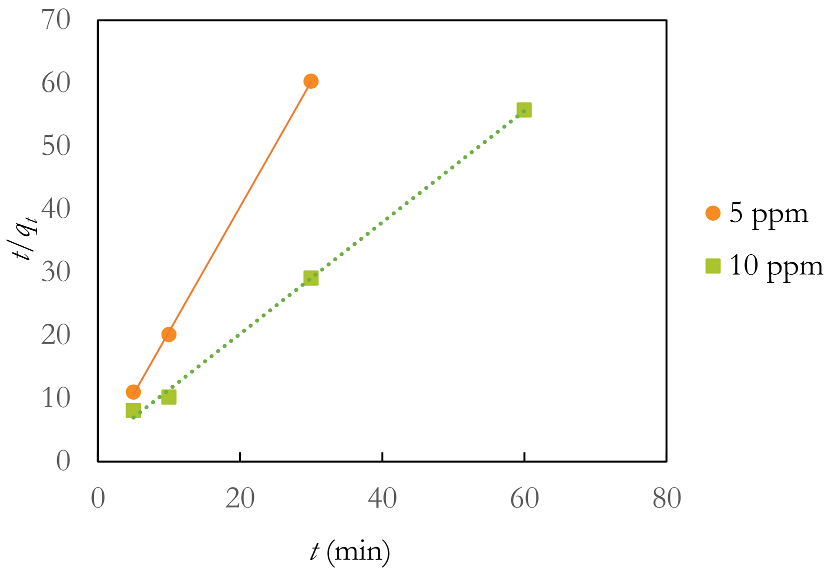

Figure 4-4 Pseudo-second-order kinetic model for Co removal by CoTreat® (pH 2.6)

Table 4-2 Calculated values of the pseudo-second order kinetic model constants for Co removal by the CoTreat® exchanger

Co ions solution concentration (mg/L)	5	10
k_2 (g/mg min)	5.37	0.31
q_e (mg/g)(calculated)	0.50	1.13
r^2	0.999	0.998
q_e (mg/g) (experimental)	0.51	1.09

The contrary was determined for the data obtained at 30 and 40 ppm Co concentrations. The pseudo-first order kinetic model treatment of the data gave good linear fits displayed in Figure 4-5, whereas the pseudo-second order kinetic model fittings gave non-linear curves (not shown), proving the non-validity of the kinetic model at the Co concentration of 30 and 40 ppm. The kinetic parameters derived from the pseudo-first order model are given in Table 4-3. From the calculated results, it can be deduced that the rate of exchange of Co ions on CoTreat® decreases with increasing Co ions concentration. Also, the pseudo-first order kinetic model could be said to be the best kinetic model to describe the mechanism of Co exchange on CoTreat® at the studied concentrations, given the good agreement between the calculated and experimental q_e (mg/g) values and the high correlation coefficient values.

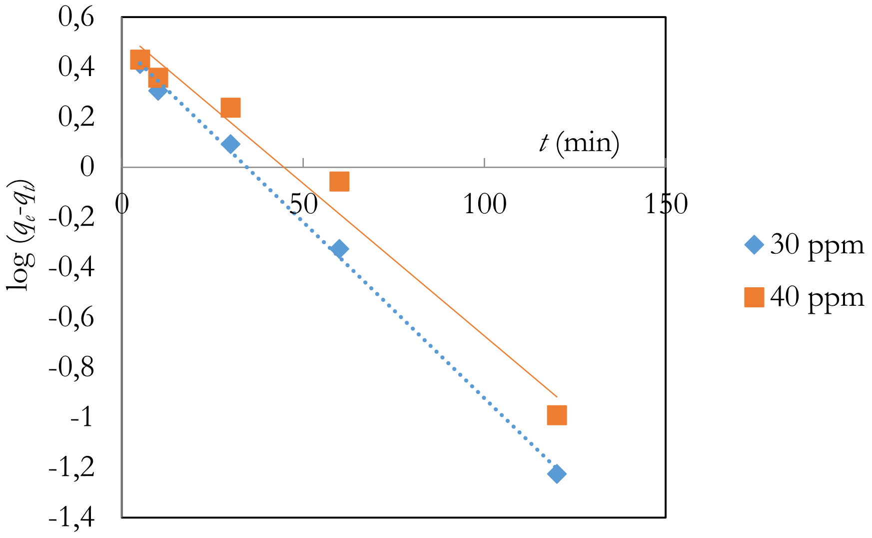

Figure 4-5 Pseudo-first order kinetic model for Co removal by CoTreat® (pH 2.6)

Table 4-3 Calculated values of the pseudo-first order kinetic model constants for Co exchange on CoTreat®

Co ions solution concentration (mg/L)	30	40
k_1 (min^{-1})	0.03	0.03
q_e (mg/g)(calculated)	3.06	3.50
r^2	0.998	0.976
q_e (mg/g) (experimental)	3.26	3.31

Overall, the kinetic data reveals that the mechanism of the exchange of Co on CoTreat® can be explained by the pseudo-second order kinetic model at lower concentrations and conforms to the pseudo-first order kinetic model at higher concentrations. Fundamentally at higher Co concentrations, the mechanism becomes independent of the Co ions in solution. These results are unusual, but not incorrect. In the work done by Azizian (2004), theoretical derivations showed that the sorption process obeys pseudo-first order model at higher initial concentrations of solute, while it conforms to the pseudo-second order kinetic model at lower concentrations of solute. The theoretical predictions presented in this paper were in close agreement with experimental data.

4.2.3 Sorption isotherm modelling of equilibrium data of Co on CoTreat®

Sorption isotherms are curves relating the amount of solute adsorbed (q_e) to residual concentration (c_e). Isotherms are crucial in describing the interaction of solutes and exchangers in order to optimize their function (Chabani *et al*, 2006; Ncibi, 2008; Ali *et al*, 2010).

The fitting of the equilibrium data to the Freundlich isotherm model gave a non-linear plot (Figure 4-6) suggesting that the model cannot be used to explain the mechanism of Co removal by CoTreat® in the studied concentration range.

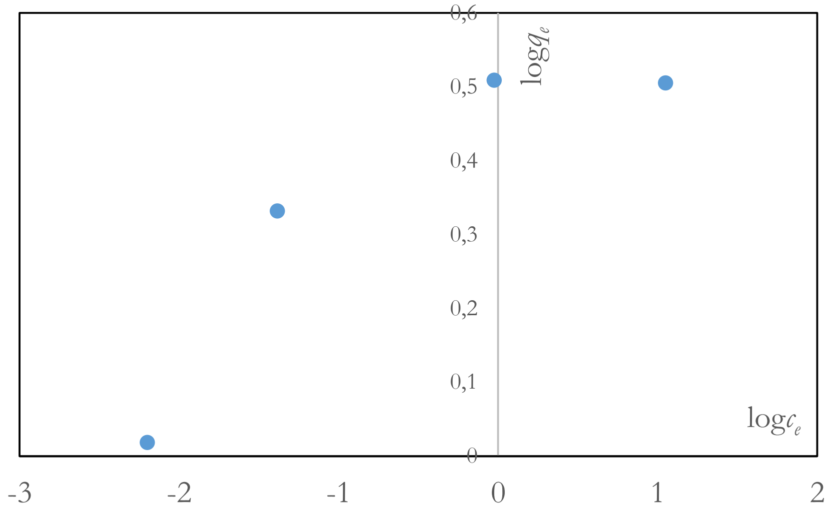

Figure 4-6 Freundlich isotherm of Co on CoTreat

The fitting of the equilibrium data to the Langmuir isotherm model yielded a linear plot presented in Figure 4-7. The correlation coefficient was found to be 1. The Langmuir isotherm model is applicable to homogeneous surface sites with equivalent binding sites. The adsorption capacity (Q_0) was determined to be 3.20 mg/g which is in close proximity to the saturation q_e determined in kinetics data (4.2.2) which was 3.31 mg/g. The value of b calculated from the plot in Figure 4-7 was determined to be 107.6 ml/mg. The Langmuir constant b was used to calculate the separation factor (R_L). The calculated values of R_L were less than 1 for all the Co concentrations studied, thus indicating that the exchange of Co on CoTreat® is a favourable process.

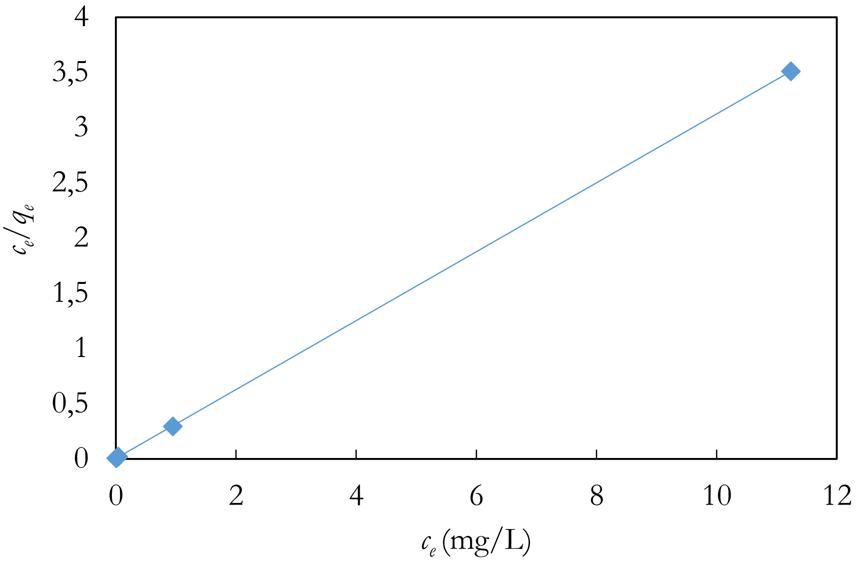

Figure 4-7 Langmuir isotherm of Co on CoTreat®

The D-R isotherm model is normally used to identify the nature of the sorption reaction either as ion exchange, physical or chemical adsorption based on the value of the sorption energy (*E*) (Inglezakis & Zorpas, 2012). A good linear fit (Figure 4-8) was obtained when the equilibrium data was fitted to the D-R isotherm model. From the plot, the value of β can be calculated, from which the value *E* (kJ/mol) can be determined. The *E* value for the exchange of Co on CoTreat® was calculated to be 8.45 kJ/mol, which suggest that the mechanism of Co removal by CoTreat® conforms to ion exchange.

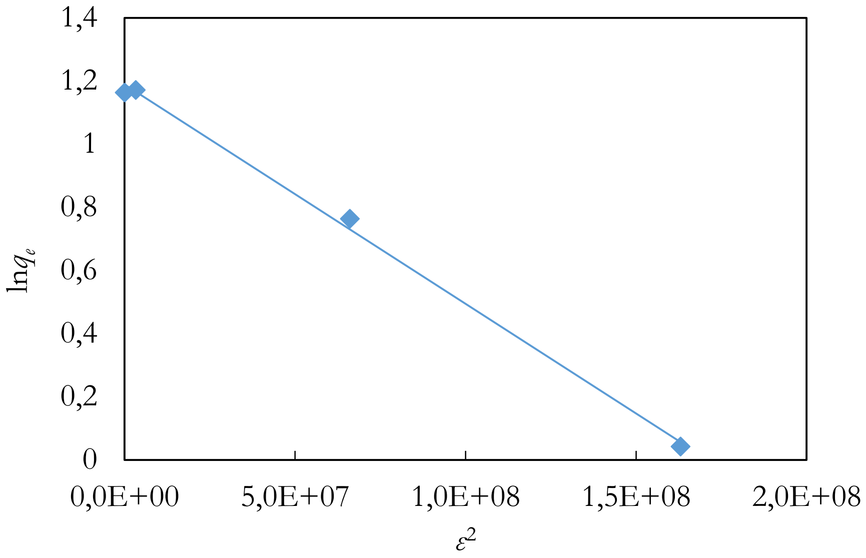

Figure 4-8 D-R isotherm of Co on CoTreat®

4.2.4 Effect of temperature on the sorption extent and determination of thermodynamic parameters for the Co sorption on CoTreat®

The thermodynamic parameters can be determined by studying the effect of temperature on the equilibrium distribution coefficient (k_d). The experimental method for this study is given in 3.3.4. The temperature was varied from 30–60 °C, while the other parameters were kept constant (Co concentration: 10 ppm, pH 2.6). The results are presented in Figure 4-9, showing that the amount of Co exchanged increases from 1.03 to 1.15 mg/g when the temperature is increased from 30-60 °C. The increase in the amount of Co removed at higher temperatures may be due to the creation of new active sites or acceleration of some slow reaction steps. The sorption enthalpy ($\Delta H°$) can be calculated from the slope of the linear plot of $\log k_d$ vs $1/T$ (Figure 4-9). The value was estimated to be +32.52 kJ/mol, indicating the removal of Co by CoTreat® is an endothermic ion exchange process. The calculated values of $\Delta S°$ and $\Delta G°$ are presented in Table 4-4. $\Delta G°$ is negative at all the studied temperatures, indicating that the exchange of Co ions with Na^+ and H^+ on the CoTreat® surface is spontaneous. These results agree with those obtained from sorption isotherms (4.2.3) which also supported that Co removal by CoTreat® is a favourable process.

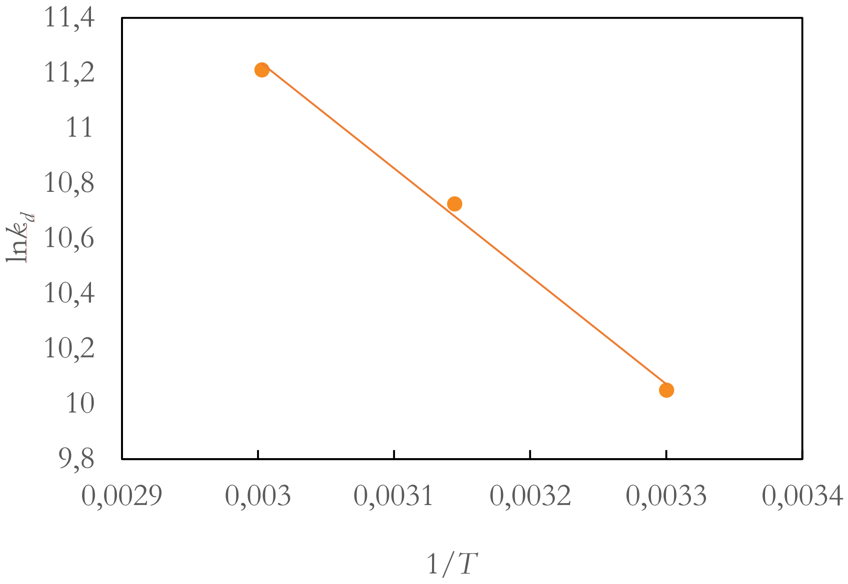

Figure 4-9 Effect of solution temperature on the distribution coefficient of Co on CoTreat® (pH 2.6)

Table 4-4 Thermodynamic parameters for Co sorption on CoTreat®

Temperature (°C)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)
30	-25.37	0.19
45	-28.24	
60	-31.10	

4.2.5 Selectivity of CoTreat®

The selectivity experiment was conducted as described in 3.3.6. The sorbate solution contained 2 ppm of Co, Ce, Ru, Sb, Sr. The adsorbate solution was contacted with the CoTreat® exchanger for 3 hours. The results are presented in Figure 4-10, showing that under the experimental conditions described above, the CoTreat® does not specifically target only Co but it effectively removes significant amounts of other problematic ions as well. For the purpose of this research project, these results are good in a way that there is a possibility that one sorbent material can be used to remove all the problematic nuclides at one. The results also give new information which was not previously known that CoTreat® can effectively remove Ce, Ru, Sb and Sr.

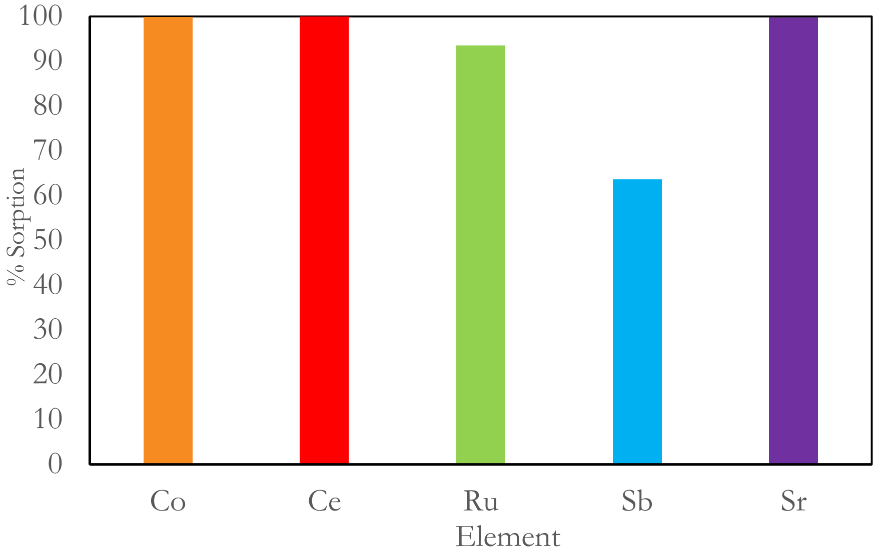

Figure 4-10 The soption extent of Co, Ce, Ru, Sb and Sr on CoTreat® (3 hours contact time, 2 ppm element concentration, pH 2.6)

4.3 Co removal by IONSIV R9120B

IONSIV R9120B is a selective media based on crystalline titanosilicate. This exchanger was utilized in this study for determining Co removal efficacy. A study of the sorption kinetics was conducted the method described 3.3.2. The results obtained are given in Figure 4-11. The results reveal a poor sorption capacity. After 66 hours contact time, only 50 % of Co was moved from solution. Also it can be seen that the sorption reaction is slow, rendering the material not a good candidate for this study. The pH of the Co solutions used was arbitrarily selected since there was no data obtainable on the exchange of Co on the IONSIV R9120B exchanger material. Additional experimentation on this material could not be conducted due to material shortage.

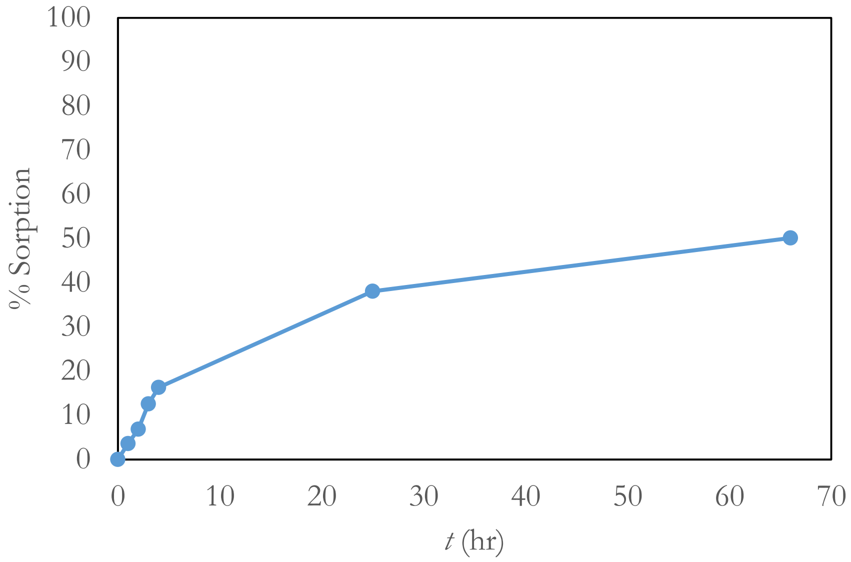

Figure 4-11 Time variation for percentage Co removal by IONSIV R9120B ([Co] = 5 ppm, pH 2.6)

4.4 Ru removal by activated carbons

The ruthenium radioisotopes i.e. ^{108}Ru ($t_{1/2}$ = 40 days) and ^{106}Ru ($t_{1/2}$ = 386 days) remain in significant amounts in waste solutions generated in chemical processing laboratories for post-reactor waste. This study utilized activated carbon, activated charcoal and manganese oxide to study Ru removal from aqueous solutions with intent to use the process to purify post reactor waste to recover U.

4.4.1 Effect of nitric acid solution on Ru removal by activated carbons

The effect of acid media concentration on the sorption capacity of activated carbons was studied using the method described in 3.3.2. Activated charcoal was used for this study. The results obtained are presented in Figure 4-12, which reveal that maximum sorption capacity is obtainable in 3 M HNO_3. This optimum acid concentration was used in the experimentation reported by Qadeer (2013) and was chosen for subsequent experiments.

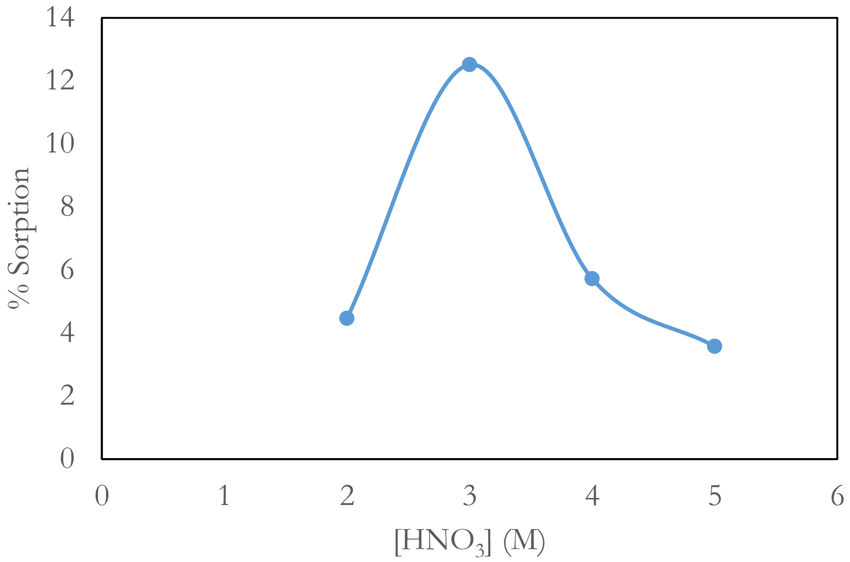

Figure 4-12 The sorption extent of Ru by activated charcoal in varying concentrations of nitric acid

4.4.2 Effect of contact time on the sorption capacity of activated carbons for Ru

The kinetics of Ru removal by activated carbon (Sutcliffe, Speakman & Co. Ltd) and activated charcoal (ACE chemicals) are given in Figure 4-13. From the results, both materials have slow kinetics. After 4 hours contact time, the sorption extent was determined to be 0.50 and 0.52 mg/g for the activated carbon and activated charcoal respectively. The activated charcoal was observed to have a faster sorption rate than the activated carbon. The two materials gave poor results in comparison to the results obtained by Qadeer (2013). Qadeer (2013) states that after an hour contact time between 50 ppm Ru ions and activated charcoal (M/S British Drug House), ≈58 % Ru ions are sorbed at 23 °C in 3 M HNO_3. For the two carbon materials studied in this research, it was determined that 2.84 % and 7.16 % of Ru ions were sorbed by activated charcoal and activated carbon respectively at 30 °C in 3 M HNO_3 after 1 hour contact time. The discrepancy in the results may be due to the fact that the activated carbon materials might have different properties due to their different material sources. Also, it may be due to the temperature difference at which the experiments were conducted. If Ru sorption on activated carbons is governed by physisorption only (as reported by (Perrich, 2018)) which is an exothermic process, then an increase in temperature would cause a decrease in sorption capacity.

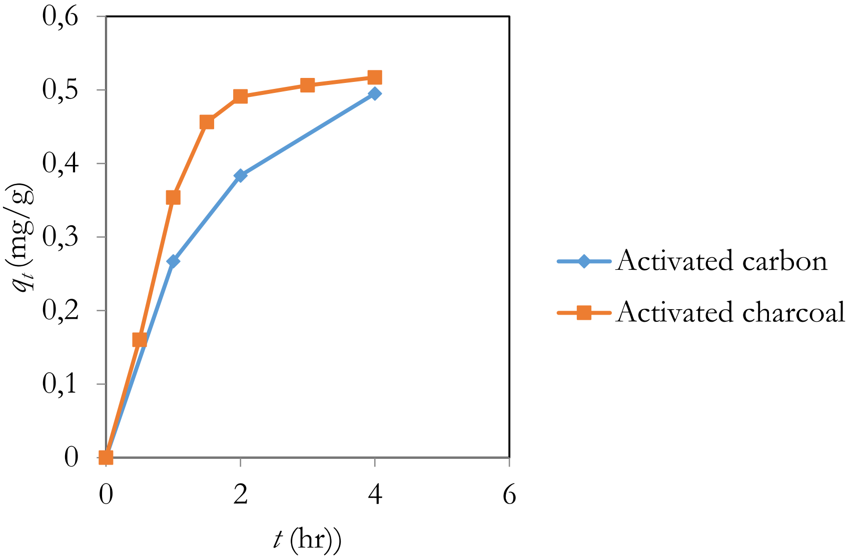

Figure 4-13 Time variation of the Ru retained on two activated carbon materials ([Ru] = 50 ppm, 3 M HNO_3, 30 °C)

4.5 Ru removal by manganese oxide

4.5.1 Effect of solution pH on Ru removal by manganese oxide

The effect of the acidity of the medium was studied using the method described in 3.3.2. The selected HNO_3 concentrations were 0, 0.5, 1, 2 and 4 M. The results obtained are presented in Figure 4-14, which show that the maximum sorption capacity in ultrapure water. Subsequent experiments were conducted in ultrapure water.

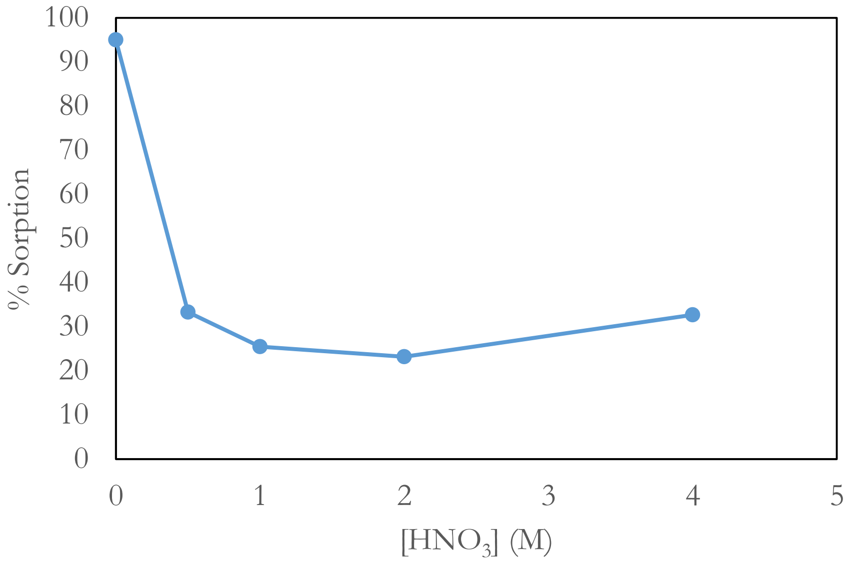

Figure 4-14 The sorption extent of Ru on manganese oxide at different acid concentrations

4.5.2 Sorption kinetic modelling of Ru removal by manganese oxide

The kinetics of Ru removal by manganese oxide was determined using the method described in 3.3.2. The results obtained are presented in **Error! Reference source not found.** and Figure 4-15. The results show that the sorption rate decreases with increasing initial concentration of Ru, which is expected given that there is less available sorption sites relative to the amount of available Ru ions in solution at high concentrations. Also, it can observed that the amount of Ru sorbed at equilibrium (q_e) increases with increasing initial Ru ions concertation. This trend is due to the fact that there is more Ru ions in solution available to be sorbed at high concentrations.

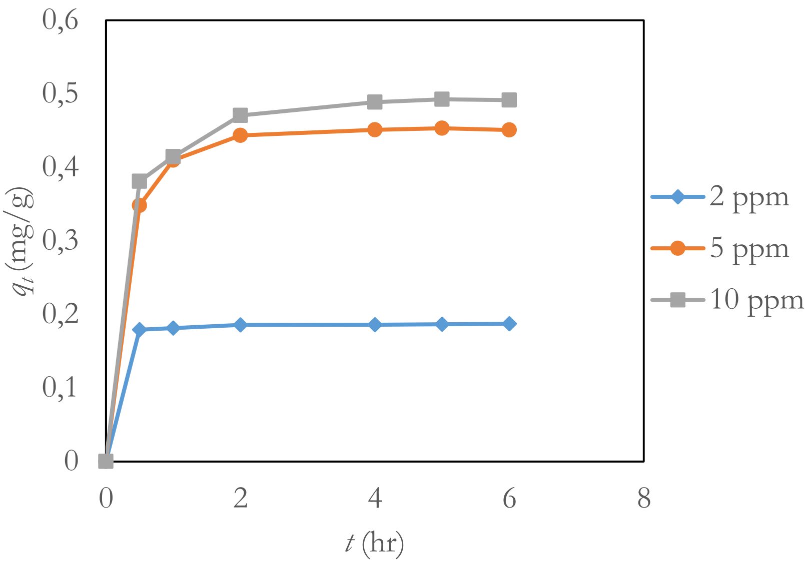

Figure 4-15 Time variation of the amount of Ru retaimed on manganese oxide at various concentrations of Ru (30 °C, Media: ultrapure water)

The time dependent data was fitted to the pseudo-first order kinetic model. The linear plots obtained are presented in Figure 4-16. The linear plots have good correlation coefficients given in Table 4-5 along with the kinetic parameters derived from the kinetic model. There is a substantial discrepancy between the calculated and experimental q_e values. This finding invalidates the validity of the pseudo-first order kinetic model in explaining Ru removal by manganese oxide.

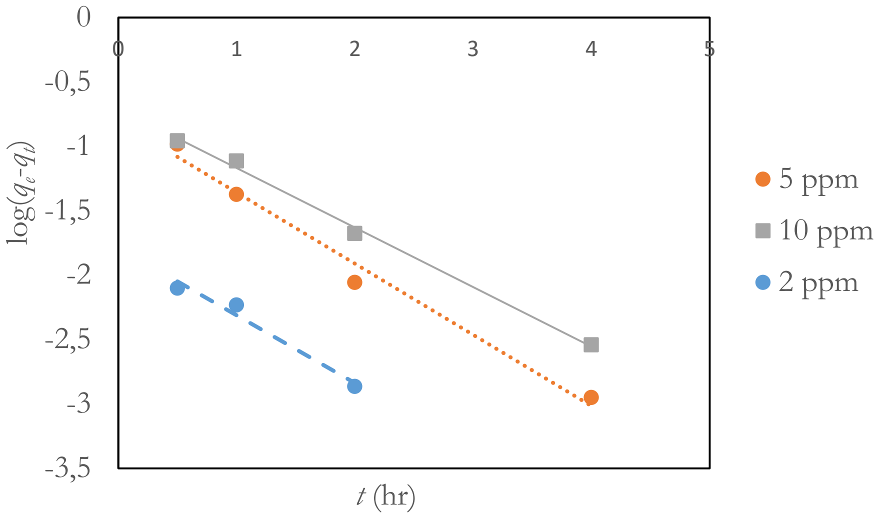

Figure 4-16 Pseudo-first order kinetic model for Ru removal by manganese oxide

Table 4-5 Calculated values of the pseudo-first order kinetic model constants for Ru removal by manganese oxide

Ru ions solution (mg/L)	2	5	10
k_1 (hr^{-1})	1.21	1.27	1.06
q_e (mg/g) (calculated)	0.02	0.16	0.20
r^2	0.970	0.984	0.996
q_e (mg/g) (experimental)	0.19	0.45	0.49

When the time dependent data was fitted to the pseudo-second kinetic model, good linear plots were obtained at all the studied Ru concentrations. The results are presented in Figure 4-17 and the kinetic parameters derived from the kinetic model are presented in Table 4-6. Judging by the correlation coefficients values obtained and the good agreement between the calculated and experimental q_e values, the pseudo-second kinetic model can be used to explain Ru removal by manganese oxide.

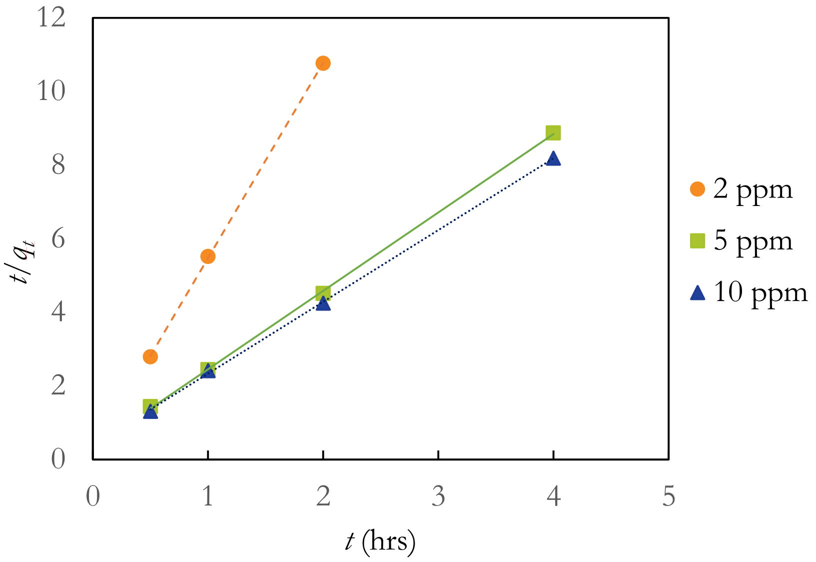

Figure 4-17 Pseudo-second order kinetic model for Ru removal by manganese oxide

Table 4-6 Calculated values of the pseudo-second order kinetic model constants for Ru removal by manganese oxide

Ru ions solution (mg/L)	2	5	10
k_2 (g/mg hr)	170.58	14.06	9.86
q_e (mg/g) (calculated)	0.19	0.47	0.51
r^2	0.999	0.999	0.999
q_e (mg/g) (experimental)	0.19	0.45	0.49

Overall, the sorption kinetics of manganese for Ru are moderately fast, rendering manganese oxide a good candidate for Ru removal from aqueous acidic solutions.

4.5.3 Sorption isotherm modelling of equilibrium data of Ru on manganese oxide

The sorption equilibrium of Ru sorption on manganese oxide was studied using the method described in 3.3.3. The four initial Ru concentrations selected were 2, 5, 15 and 20 ppm.

The equilibrium data was fitted to the Langmuir isotherm model, giving a good liner plot (r^2 = 0.990) presented in Figure 4-18. The good fitting of the equilibrium data into the Langmuir isotherm model suggests that the model can be used to explain the mechanisms of Ru removal by manganese oxide. Therefore Ru sorption on manganese oxide involves monolayer adsorption with an adsorption capacity (Q_0) of 0.902 mg/g. The value of the Langmuir constant b was calculated to be 3.62 ml/mg. From the calculated b value, the R_L was determined to be less than 1 at all the studied Ru concentrations, which suggests that the sorption of Ru on manganese oxide is a favourable process.

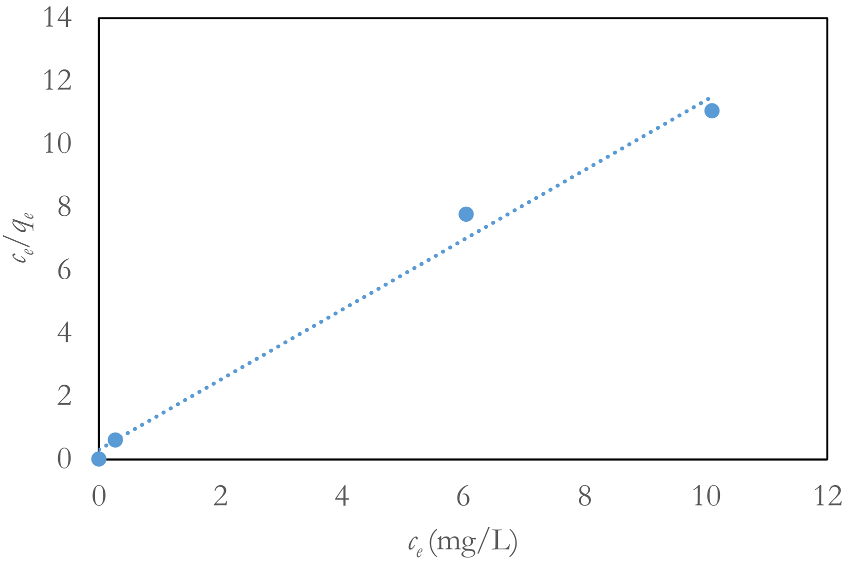

Figure 4-18 Langmuir isotherm of Ru on manganese oxide

The equilibrium data was also fitted to Freundlich isotherm model. A good linear plot (r^2 = 0.9982) presented in Figure 4-19 was obtained from the fitting, which suggests that the manganese sorption sites are heterogeneous. The Freundlich constant k_f was determined to be 0.58 and $1/n$ was calculated to be less than 1 which suggests that favourable sorption.

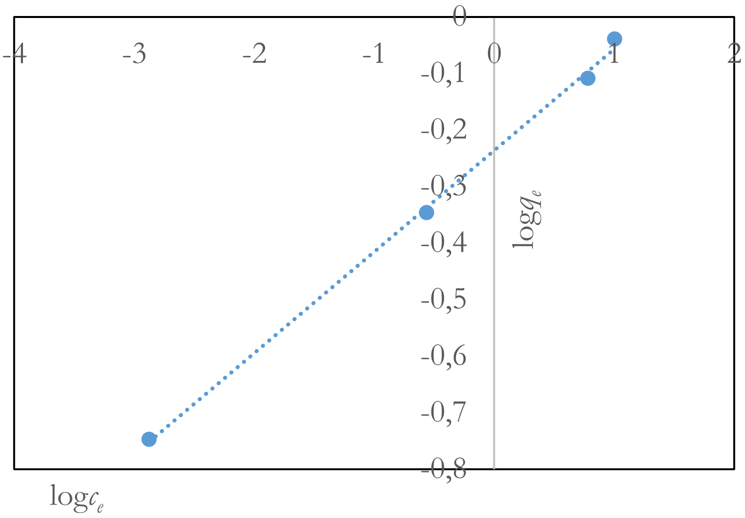

Figure 4-19 Freundlich isotherm of Ru on manganese oxide

The equilibrium data could not be fitted to the D-R isotherm model, therefore the sorption energy could not be determined.

In summary, the good fitting of the equilibrium data to both the Langmuir and Freundlich isotherm suggests that the mechanism of Ru sorption on manganese oxide involves formation of a monolayer followed by a multilayer i.e. the overall mechanism is non-uniform, however the manganese oxide surface possess Langmuir behaviour. In most published material, in a situation where the equilibrium data fits both the Langmuir and Freundlich isotherms, the mechanism of sorption is explained by the isotherm model with a better fitting (higher correlation coefficient). In this study, the Freundlich isotherm model had the best fit. Even so, the monolayer adsorption capacity obtained from the Langmuir isotherm model is still applicable.

4.5.4 Effect of temperature on the sorption extent and determination of thermodynamic parameters for Ru sorption on manganese oxide

The effect of temperature was on the sorption of Ru on manganese oxide was studied using the method described in 3.3.4. The results obtained are presented in Figure 4-20, which shows that the equilibrium distribution coefficient (k_d) increases with increasing temperature from 1647 to 2727 mL/g. The increase in the sorption extent with increasing temperature may be due to creation of new active sites or acceleration of some slow reaction steps. From the linear plot of $\ln k_d$ vs $1/T$, the sorption $\Delta H°$ was calculated to be +14.10 kJ/mol which indicates that the Ru removal by manganese oxide is an endothermic ion exchange process. The calculated values of $\Delta S°$ and $\Delta G°$ are presented in Table 4-7. $\Delta G°$ is negative at all the studied temperatures, indicating that the ion exchange of Ru on manganese oxide is spontaneous. These results agree with those obtained from the sorption isotherms 4.5.3, which supported that Ru exchange on manganese oxide is a favourable process.

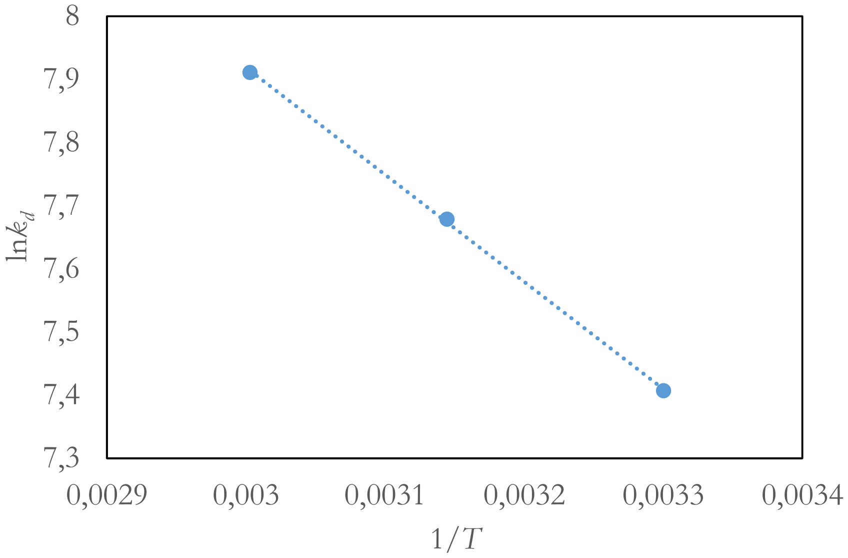

Figure 4-20 Effect of temperature on the equilibrium distribution coefficient of Ru on manganese oxide

Table 4-7 Thermodynamic parameters for Ru sorption on manganese oxide

Bulk temperature (°C)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)
30	-18.67	0.11
45	-20.29	
60	-21.91	

4.5.5 Selectivity of manganese oxide

When designing an ion exchange or adsorption purification technology, it is important to study the selectivity of the sorbent material for their target nuclides. The selectivity of manganese oxide was studied using the method described in 3.3.6. The results obtained are presented in Figure 4-21, which reveals that manganese oxide targets Ru and Sb ions. A lesser but significant sorption capacity of manganese oxide for Ce ions was observed too. Co and Sr ions are not retained at all. The affinity for Ce and Sb ions displayed by manganese oxide was not unexpected. Girardi *et al* (1970) has reported the sorptive properties of manganese oxide for Ce and Sb.

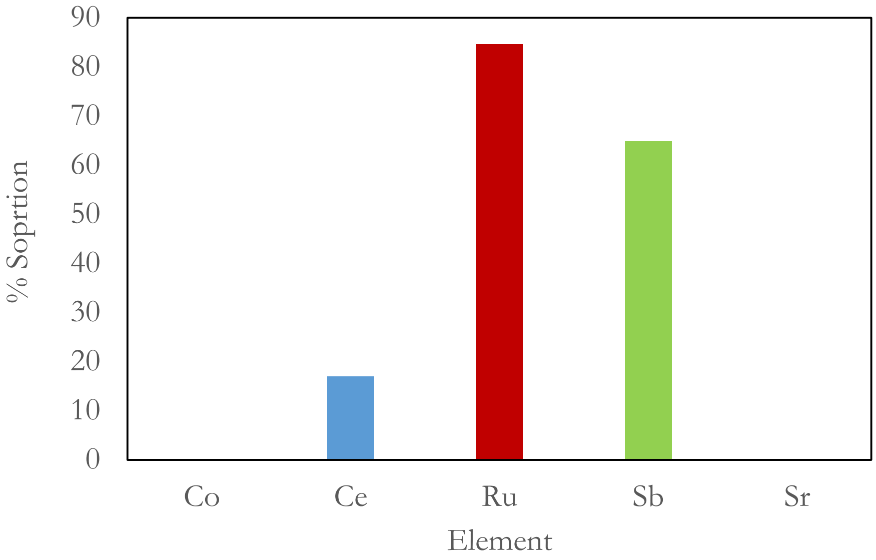

Figure 4-21 The sorption extent of Co, Ce, Ru, Sb and Sr on manganese oxide (6 hours contact time, 2 ppm element concentration)

4.6 Sb removal by alumina

The long-lived ^{125}Sb radioisotope ($t_{1/2}$ = 2.75 y) is one of the contaminants to be investigated in this study. The knowledge of preconcentration and isolation of long lived nuclides is useful in radioactive waste management and reprocessing. In literature, it is reported that ^{125}Sb can be adsorbed on various inorganic sorbent material surfaces which include titania, alumina (Mukhopadhyay & Lahiri, 2007), Fe_2O_3 (Ambe, 1987), MnO_2 (Girardi *et al*, 1970), hydrous zirconium oxide (Shivakamy *et al*, 2013) and zirconium phosphate oxide (Souka & Abdel-Rehim, 1974). This study intends to investigate Sb removal by titania, alumina and manganese oxide.

4.6.1 Effect of solution pH on Sb removal by alumina

The solution pH is one of the major factors which affect sorption. In order to design an ion exchange purification scheme, it is crucial to determine the solution pH required for optimum efficacy of the sorbent materials. The pH effect on Sb removal by alumina was investigated using the method described in 3.3.2. The acid concentrations studied were 0, 0.1, 0.5, 1 and 3 M HNO_3. The alumina material was kept in contact with 5 ppm Sb solutions for 5 hours. The results obtained are presented in Figure 4-22. From the results, it can inferred that the highest sorption efficacy can be obtained in ultrapure water. Contrary to the results given by Mukhopadhyay & Lahiri (2007) which gave an optimum nitric acid concentration of 0.5 M. The discrepancy in the results may be due to that the alumina material used in this study has a different acidity to the one used in the study by Mukhopadhyay & Lahiri (2007), thus possessing different surface properties. Subsequent tests were conducted were conducted in ultrapure water.

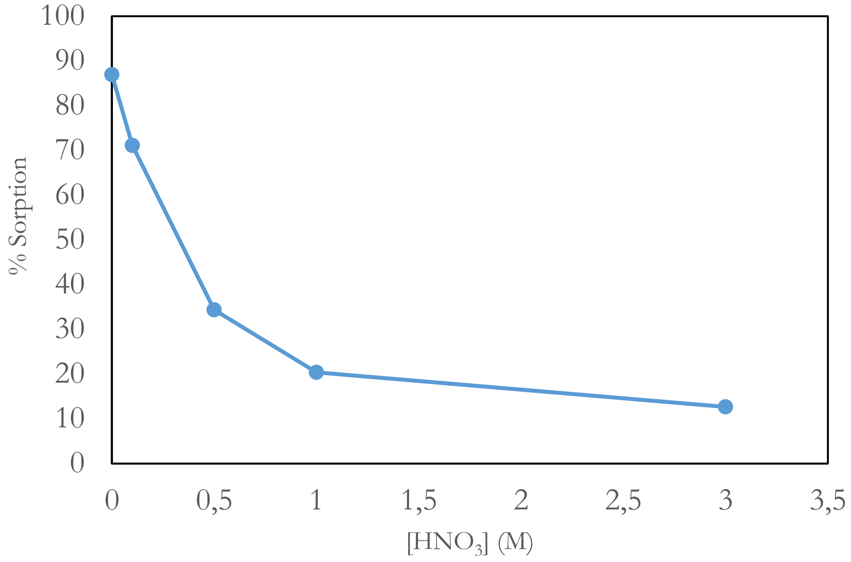

Figure 4-22 The sorption extent of Sb on alumina at different concentrations of nitric acid

4.6.2 Sorption kinetic modelling of Sb removal by alumina

Determining the kinetics parameters is one way of determining the sorption efficacy of a sorbent material for its target contaminant. The batch method described in 3.3.2 was used to determine the sorption kinetics of Sb on alumina. The experiment was conducted using an aqueous solution containing a Sb concentration of 5 ppm. The contact time points selected were 0.25, 1, 2, 3 and 5 hours. The results obtained are presented in Figure 4-23. From the plot, a sharp initial rise can be observed after 15 minutes contact time followed by a slow steady increase thereafter. The equilibrium state can be estimated to be reached after 3 hours contact time.

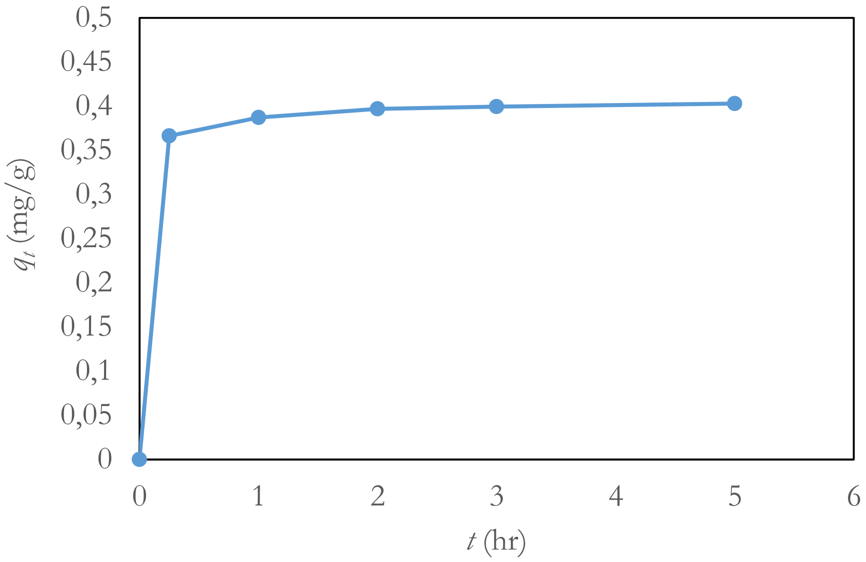

Figure 4-23 Time variation of the amount of Sb retained on alumina ([Sb] = 5 ppm, 30 °C, Media: ultrapure water)

The time dependent data was fitted to the two sorption kinetic models viz. the pseudo-first and pseudo-second order kinetic models. Both models gave good linear plots (Figure 4-24 and Figure 4-25) with good correlation coefficients.

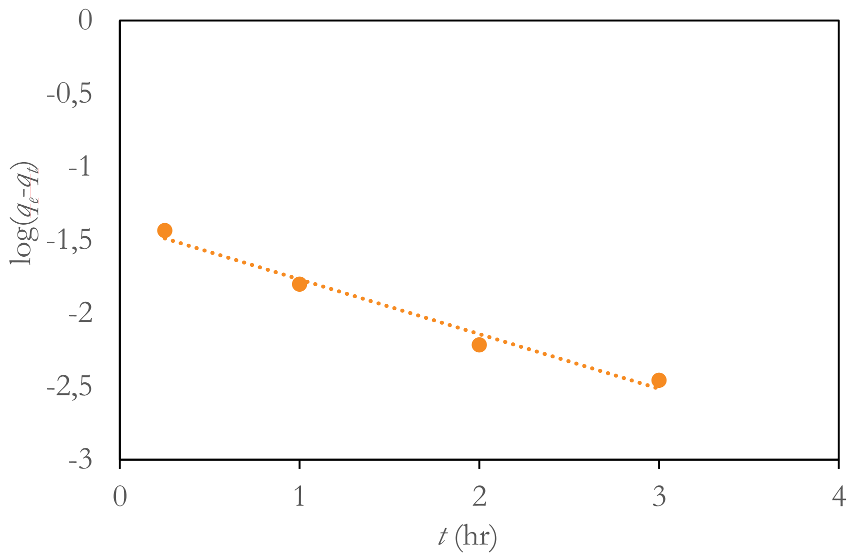

Figure 4-24 Pseudo-first order kinetic model for Sb removal by alumina

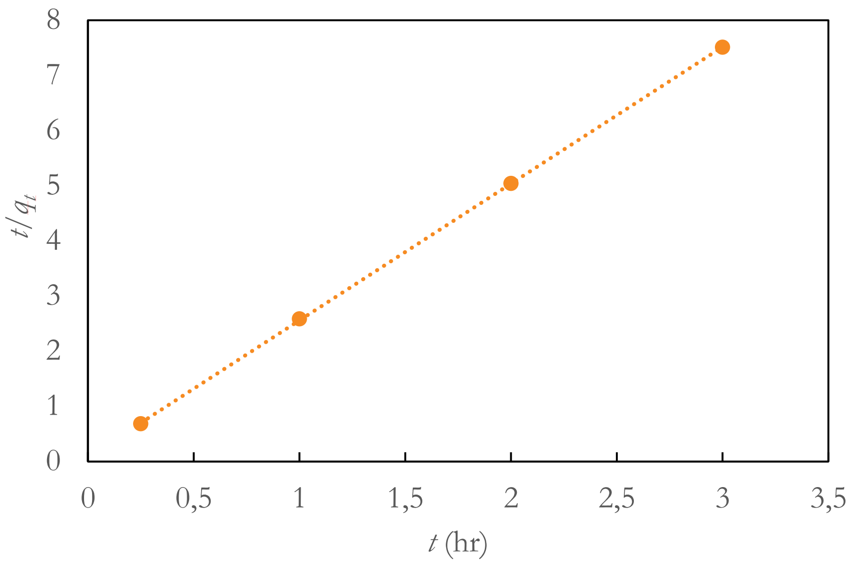

Figure 4-25 Pseudo-second order kinetic model for Sb removal by alumina

The pseudo-first order rate of sorption (k_1), and the calculated and experimental q_e values are presented in Table 4-8. The non-conformity of the calculated and experimental q_e values indicates that the sorption kinetics of Sb on alumina cannot be explained by the pseudo-first order kinetic model.

Table 4-8 Calculated values of the pseudo-first order kinetic model constants for Sb removal by alumina

Sb ions solution concentration (mg/L)	5
k_1 (hr^{-1})	0.86
q_e (mg/g) (calculated)	0.04
r^2	0.979
q_e (mg/g) (experimental)	0.40

The pseudo-second order rate of sorption (k_2), and the calculated and experimental q_e values are given in Table 4-9. The close agreement of the calculated and experimental q_e values and the good correlation coefficient of 1 supports that the kinetics of Sb sorption on alumina can be explained by the pseudo-second order kinetic model at the studied Sb concentration and experimental conditions.

Table 4-9 Calculated values of the pseudo-second order kinetic model constants for Sb removal by alumina

Sb ions solution concentration (mg/L)	5
k_2 (g/mg hr)	76.6
q_e (mg/g) (calculated)	0.40
r^2	1
q_e (mg/g) (experimental)	0.40

Overall, the sorption kinetics of Sb on alumina are moderately fast with high equilibrium Sb sorption capacity (≈85 %); therefore rendering alumina a possible sorbent material for Sb removal from aqueous solutions.

4.6.3 Sorption isotherm modelling of equilibrium data of Sb on alumina

The equilibrium data for Sb removal by alumina was obtained using the batch method described in 3.3.3. The selected initial concentrations of Sb ions selected were 2, 5, 10, 15 and 20 ppm.

The equilibrium data was fitted to the Langmuir isotherm model, which gave a good linear plot ($r^2 = 0.986$) presented in Figure 4-26, which suggests monolayer adsorption. The adsorption capacity (Q_0) was determined to be 1.40 mg/g. The value of the Langmuir constant b was calculated to be 0.524 mL/mg, which was used to calculate the R_L values. The calculated R_L values were less than 1 for all the studied Sb concentrations, which indicates that Sb sorption on alumina is a favourable process.

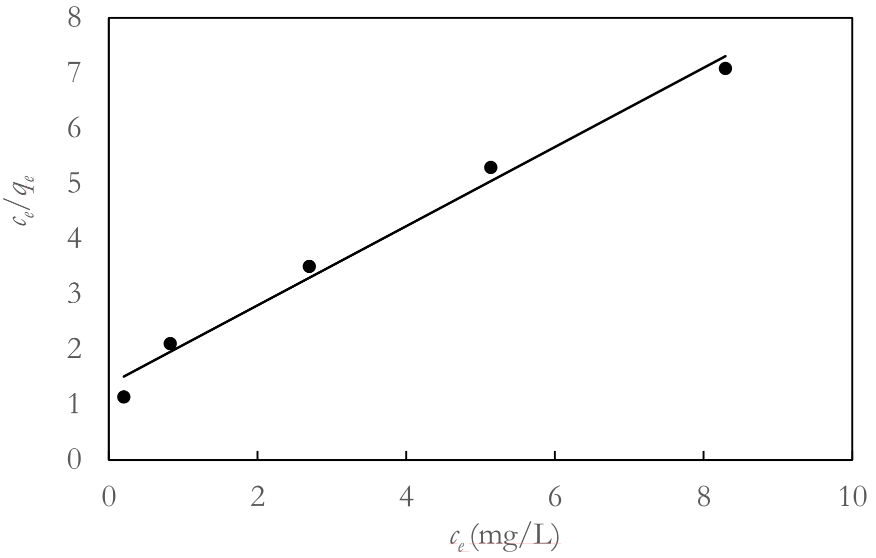

Figure 4-26 Langmuir isotherm of Sb on alumina

The equilibrium data was also fitted to the Freundlich isotherm model. A good linear plot (r^2 = 0.9935) was obtained is presented in Figure 4-27, which supports that alumina sorption sites are heterogeneous. The Freundlich constant k_f was determined to be 0.422. The $1/n$ values was determined to be less than 1, which suggest that the sorption of Sb on alumina is a favourable process.

The equilibrium data could not be fitted to the D-R isotherm model. Therefore, the sorption energy *(E)* could be determined to disguise the sorption process as either a chemisorption, physisorption or ion exchange.

Given that the equilibrium data fits the Freundlich isotherm model better than the Langmuir, it supports that the overall mechanism of Sb sorption on alumina is non-uniform and may include multi-layer formation. The good fit obtained from the Langmuir isotherm suggests alumina sorption sites possess Langmuir behaviour.

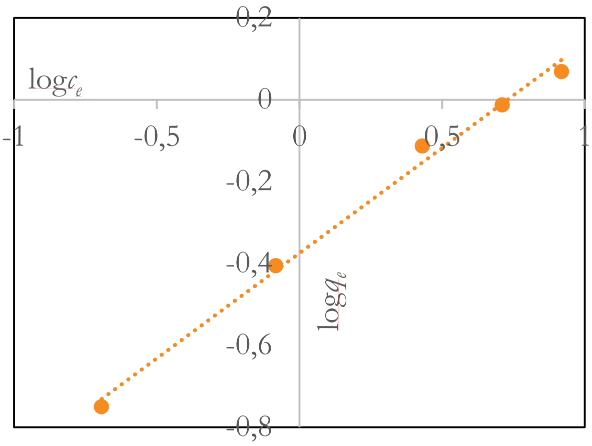

Figure 4-27 Freundlich isotherm of Sb on alumina

4.6.4 Effect of pH on sorption kinetics of alumina for Sb

The paper published by Mukhopadhyay & Lahiri (2007) provided that the optimum nitric acid solution is 0.5 M. For the alumina utilized in this study, ultrapure water containing no nitric acid was the optimum medium. Before this was discovered, a kinetics study was already conducted at the recommended 0.5 M nitric acid concentration. It is worthwhile to evaluate the differences in the sorption kinetics at the two nitric acid concentrations. The obtained time dependent data for Sb removal by alumina in 0.5 M HNO_3 is presented in Figure 4-28.

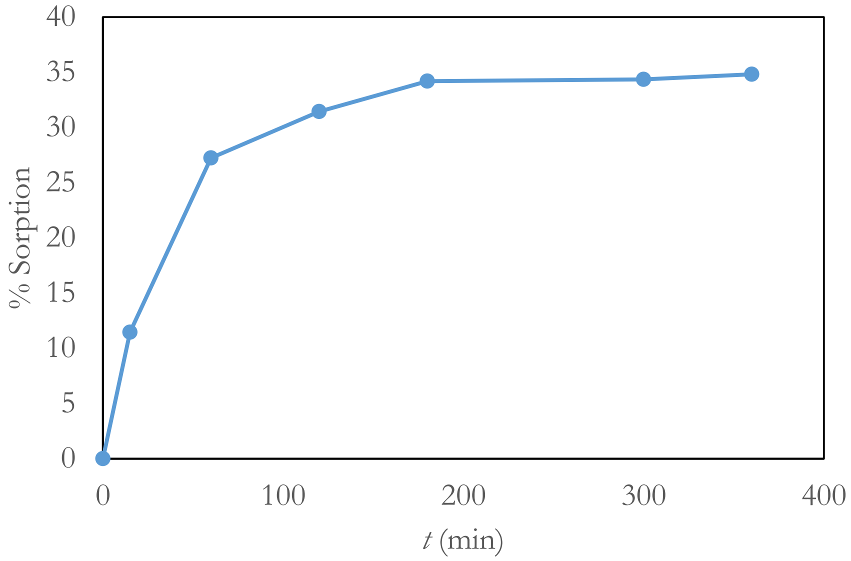

Figure 4-28 Time variation of Sb removal by alumina in 0.5 M HNO_3 (30 °C, [Sb] = 5 ppm)

The time depend data was fitted to the pseudo-first order kinetic model, giving an unsatisfactory linear plot (not shown). When the data was fitted to the pseudo-second order kinetic model, a good linear plot (presented in Figure 4-29) was obtained. The kinetic parameters derived from the kinetic model are presented in Table 4-10. Judging by the good correlation coefficient and the agreement between the calculated and experimental q_e values, the pseudo-second order kinetic model can be used to explain the sorption of Sb on alumina at the studied nitric acid concentration. In comparison to the sorption kinetics obtained in 4.6.2, the kinetics of Sb sorption on alumina in 0.5 M HNO_3 are considerably slower with a k_2 value of 6.80 g/(mg hr) (equivalent to 0.113 g/(mg min)) which is way lower that the k_2 value of 76.58 g/(mg hr) obtained in ultrapure water. It is worth noting that in both acid concentrations, the sorption of Sb on alumina conforms to the pseudo-second kinetic model.

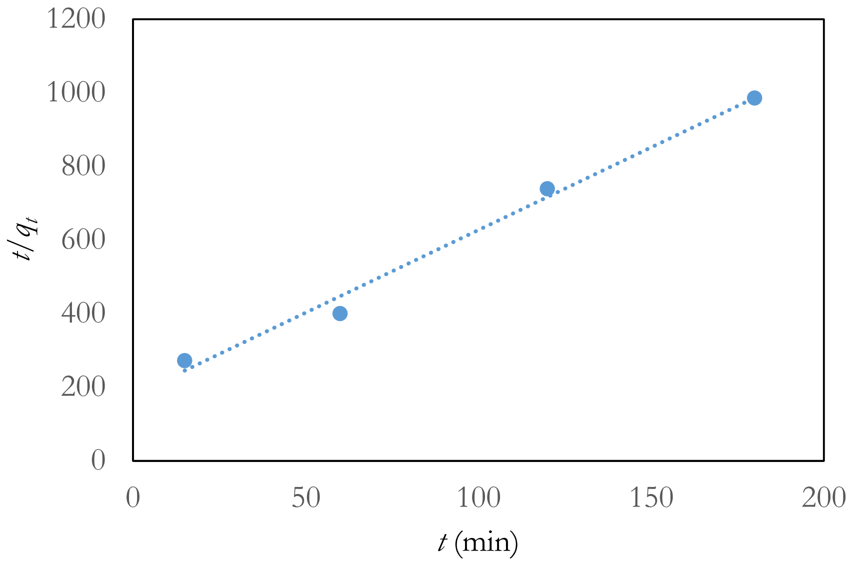

Figure 4-29 Pseudo-second kinetic model for Sb removal alumina in 0.5 M HNO_3

Table 4-10 Calculated values of the pseudo-second order kinetic model constants for Sb sorption on alumina in 0.5 M HNO_3

Sb ions solution concentration (mg/L)	5
k_2 (g/mg min)	0.11
q_e (mg/g) (calculated)	0.22
r^2	0.989
q_e (mg/g) (experimental)	0.18

4.6.5 Selectivity of alumina

The selectivity of alumina was investigated using the batch method described in 3.3.6. The sorbate solution contained 2 ppm of Co, Ce, Ru, Sb, Sr. The sorbate solution was contacted with alumina for 3 hours. The results are presented in Figure 4-30, showing that the sorption efficacy of alumina for Sb is negatively influence by the presence of other cations in comparison to the results obtained for a mono-component system. Also, the results show that alumina has an affinity (to some extent) for Ru and Ce ions.

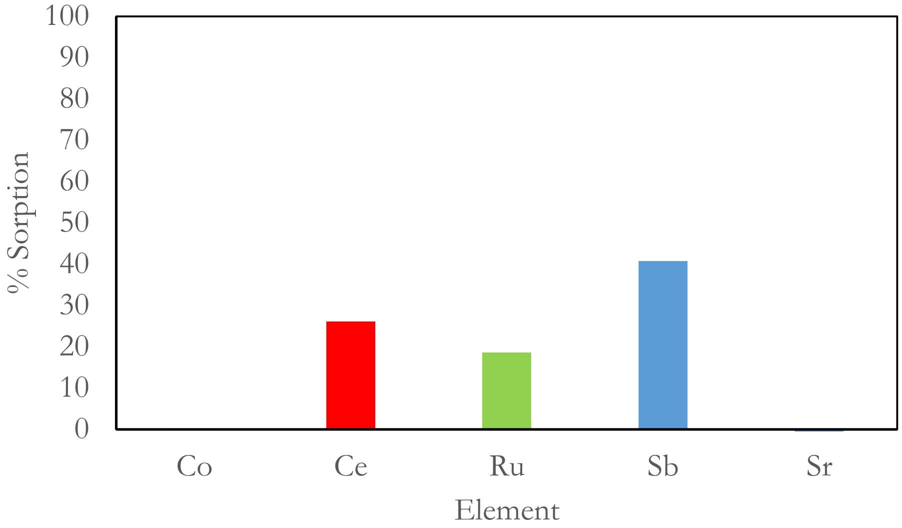

Figure 4-30 The sorption extent of Co, Ce, Ru, Sb and Sr on alumina (3 hours contact time, 2 ppm element concentration)

4.6.6 Sorption of Sb on a different commercial alumina

A sample of activated alumina (Sigma-Aldrich, weakly acidic, 58 Å pore size) was used in this experiment. It was of interest to study this material's sorption potential for Sb because visually the material seem coarser (i.e. more crystalline) than the alumina supplied by UNILAB, which was more of a powder.

The sorption extent of the Sigma Aldrich product was determined using the method described in 3.3.2. The sorbate solution used contained 5 ppm Sb ions. The results obtained are presented in Table 4-11, which shows that almost complete Sb removal was obtained after 15 minutes contact time. Therefore the Sigma product is superior than the one supplied by UNILAB.

Table 4-11 Sorption results for Sb removal by alumina supplied by (Sigma Aldrich)

Time (hr)	% Sorption
0.25	98.78
1	99.55

4.7 Sb removal by titania

4.7.1 Effect of solution pH on Sb removal by titania

The effect of pH on the sorption capacity of titania was studied using the batch method described in 3.3.2. The Sb containing solution was kept in contact with titania for 10 minutes. The nitric acid concentrations selected were 0, 0.01, 0.1, 0.5 and 1 M. The results for this experiment are presented in Figure 4-31. Titania showed good sorption capacity (except at in ultrapure water), giving a peak at 0.1 M HNO_3. The work done by Mukhopadhyay & Lahiri (2007) gave the same results that support that 0.1 M HNO_3 is the optimum concentration for Sb sorption on titania in nitric acid media. Subsequent experiments were conducted at this optimum acid concentration.

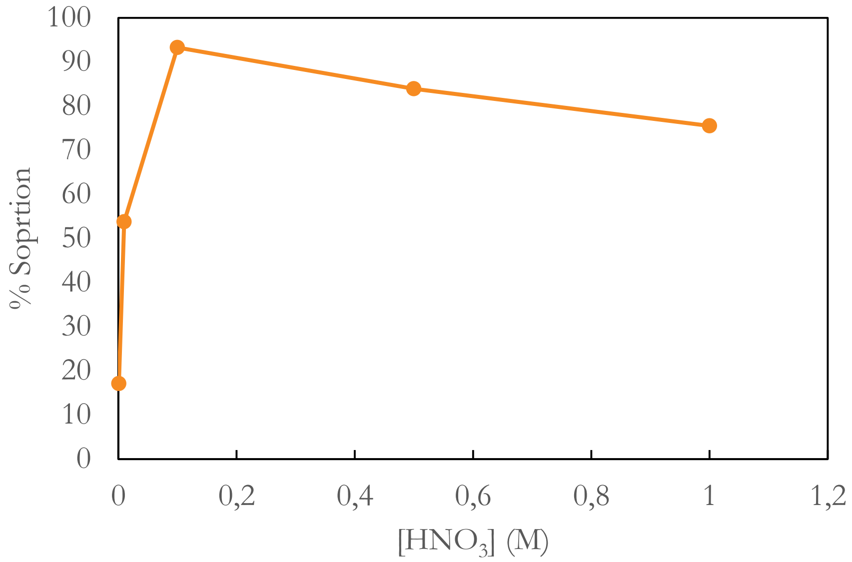

Figure 4-31 The extent of Sb removal by titania in varying concentrations of nitric acid

4.7.2 Sorption kinetic modelling of Sb removal by titania

The sorption kinetics of Sb removal by titania were investigated using the batch method described in 3.3.2 at three different Sb concentrations (5, 10 and 15 ppm). The chosen contact times were 5, 10, 25, 20, 30, 60 and 90 minutes. The results obtained are given in Figure 4-32. From the results, it can deduced that the reaction reached completion or equilibrium after 60 minutes contact time at all the studied concentrations. Also from these results, more Sb ions are removed (*q*) from solution with increasing initial Sb concentration. This is due to there being more Sb ions available to be sorbed at high concentrations; therefore the amount of Sb sorbed at equilibrium will be higher at high concentrations compared to amount sorbed at low concentrations.

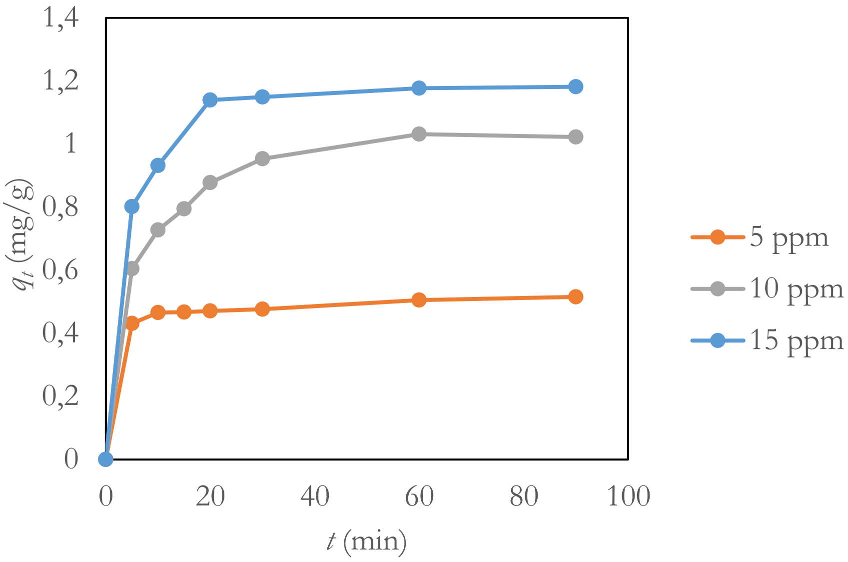

Figure 4-32 Time variation of Sb removal by titania at various Sb concentrations (0.1 M HNO_3, 30 °C)

The time-dependent data was fitted to the pseudo-first and pseudo-second order kinetic models. A plot obtained when the data was fitted to the pseudo-first order kinetic model is given in Figure 4-33 and the parameters derived from the plots are presented in Table 4-12. The values of the correlation coefficients obtained and the discrepancies between the calculated and the experimental q_e values invalidates the relevancy of the pseudo-first order kinetic model in explaining the mechanism of Sb removal by titania.

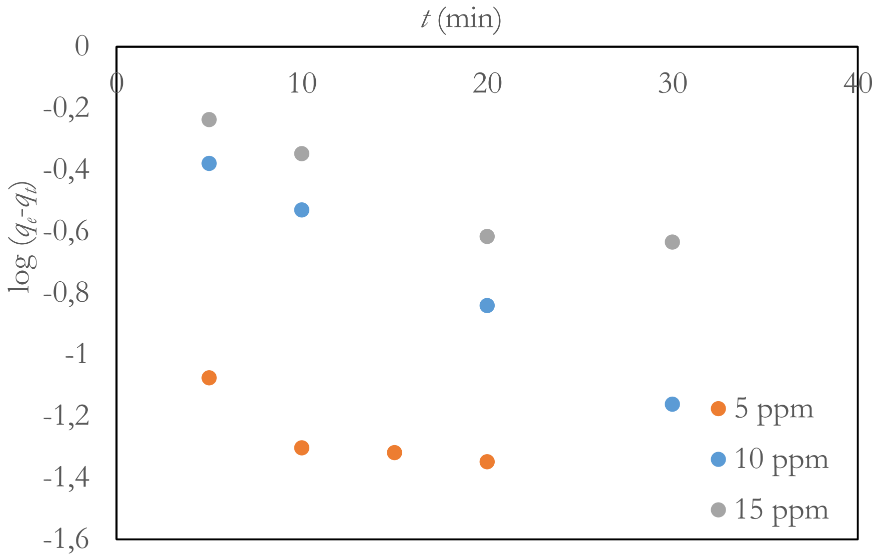

Figure 4-33 Pseudo-first order kinetic model for Sb removal by titania (0.1 M HNO_3, 30 °C)

Table 4-12 Calculated values of pseudo-first order kinetic model constants for Sb removal by titania

Sb ions solution (mg/L)	5	10	15
k_1 (min^{-1})	0.04	0.072	0.04
q_e (mg/g) (calculated)	0.09	0.60	0.65
r^2	0.7382	0.999	0.888
q_e (mg/g) (experimental)	0.51	1.02	1.38

When the data was fitted to the pseudo-second order kinetic model, a linear plot (presented in Figure 4-34) was obtained. The kinetic parameters derived from the kinetics plot are given in Table 4-13. Good correlation coefficients were obtained from the linear kinetics plots and the calculated q_e values gave a good agreement to the experiment q_e values. From these findings, it can be reasoned that the kinetics of Sb removal by titania can be explained by the pseudo-second kinetic model. Overall that results show that titania is a good sorbent material for Sb removal from aqueous solutions due to its fast sorption kinetics.

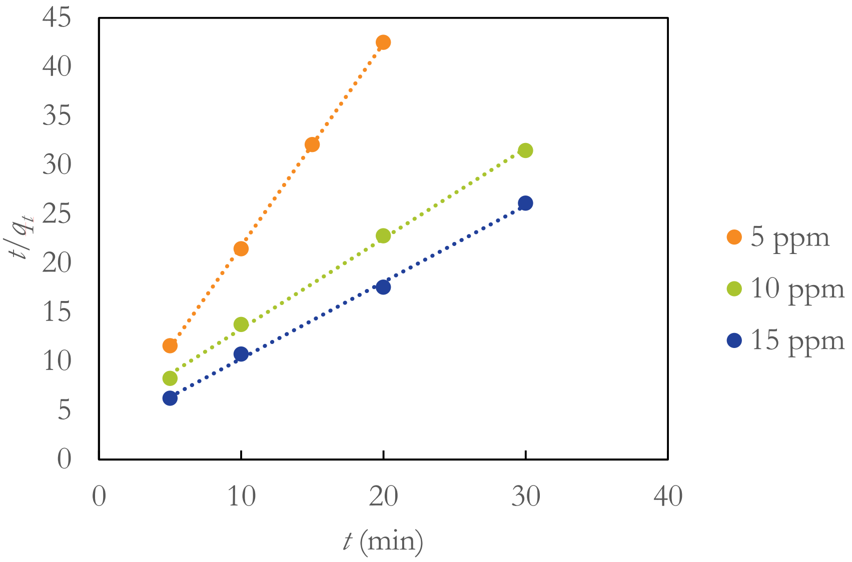

Figure 4-34 Pseudo-second order kinetic model for Sb removal by titania (0.1 M HNO_3, 30 °C)

Table 4-13 Calculated values of pseudo-second order kinetic model constants for Sb removal by titania

Sb ions solution (mg/L)	5	10	15
k_2 (g/mg min)	3.96	0.21	0.24
q_e (mg/g) (calculated)	0.48	1.08	1.28
r^2	0.999	0.998	0.998
q_e (mg/g) (experimental)	0.51	1.02	1.38

4.7.3 Sorption isotherm modelling of equilibrium data of Sb on titania

The equilibrium data for Sb removal by titania was obtained using the batch method described in 3.3.3. The selected initial concentrations of Sb selected are 2, 5, 10, 15 and 20 ppm.

The data was fitted to the D-R isotherm, giving a linear plot (not shown) with a poor correlation coefficient. The linear plot could therefore not be used to estimate the sorption energy.

The equilibrium data was fitted to the Langmuir isotherm model, which gave a linear plot presented in Figure 4-35. The obtained r^2 value of 0.957, suggests that the data fit the model, therefore titania possess Langmuir behaviour.

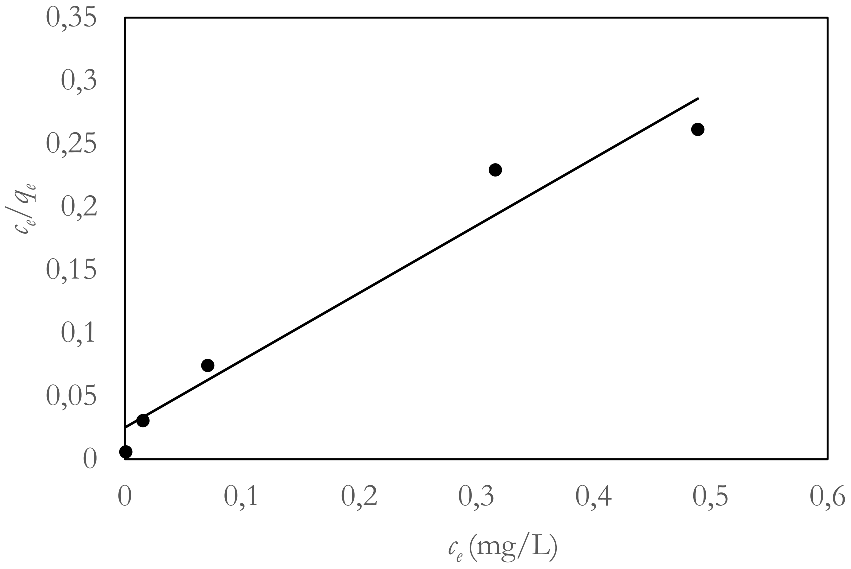

Figure 4-35 Langmuir isotherm of Sb on titania

The equilibrium data was also fitted to the Freundlich isotherm model. A good linear plot (r^2 = 0.9939) was obtained and is presented in Figure 4-36, which supports that titania sorption sites are heterogeneous. The Freundlich constant k_f was determined to be 2.377. The $1/n$ value was determined to be less than 1, which suggest that the sorption of Sb on titania is a favourable process.

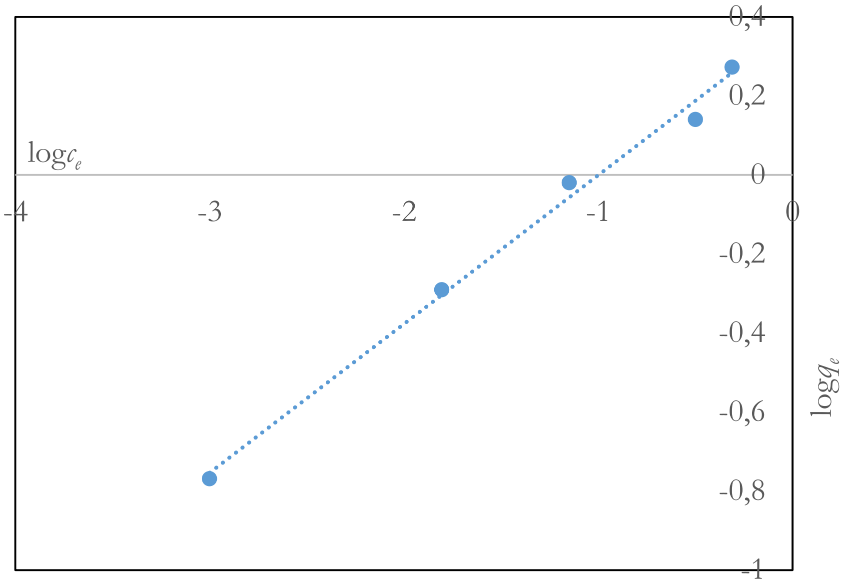

Figure 4-36 Freundlich isotherm of Sb on titania

Given that the equilibrium data fits the Freundlich isotherm model the best, it can be deduced that the overall mechanism of Sb sorption on titania is heterogeneous and may involve formation of a monolayer layer followed by multilayer.

4.7.4 Effect of temperature on the sorption extent and determination of thermodynamic parameters for Sb sorption on titania

The thermodynamic parameters of the sorption of Sb by titania were determined using the method described in 3.3.4. The temperature was varied from 30–60 °C, while the other experimental conditions were kept constant (Sb ions concentration: 5 ppm, 0.1 M HNO_3). The results obtained are given in Figure 4-37, which show that the equilibrium distribution coefficient is directly proportional to temperature. The equilibrium distribution coefficient increase from 2441 to 8001 mL/g when the temperature is increased from 30–60 °C. The increase in the sorption extent with increasing temperature may be due to creation of new active sites or acceleration of some slow reaction steps. From the linear plot of $\ln k_d$ vs $1/T$, the sorption $\Delta H°$ was calculated to be +33.13 kJ/mol, which indicates that the Sb removal by titania is an endothermic ion exchange process. The calculated values of $\Delta S°$ and $\Delta G°$ are presented in Table **4-14**. The calculated $\Delta G°$ values are negative at all the studied temperatures, indicating that the Sb sorption titania is a spontaneous process. These results correlate with the sorption isotherm results (in section 4.7.3) which suggested that Sb sorption on titania is a favourable process.

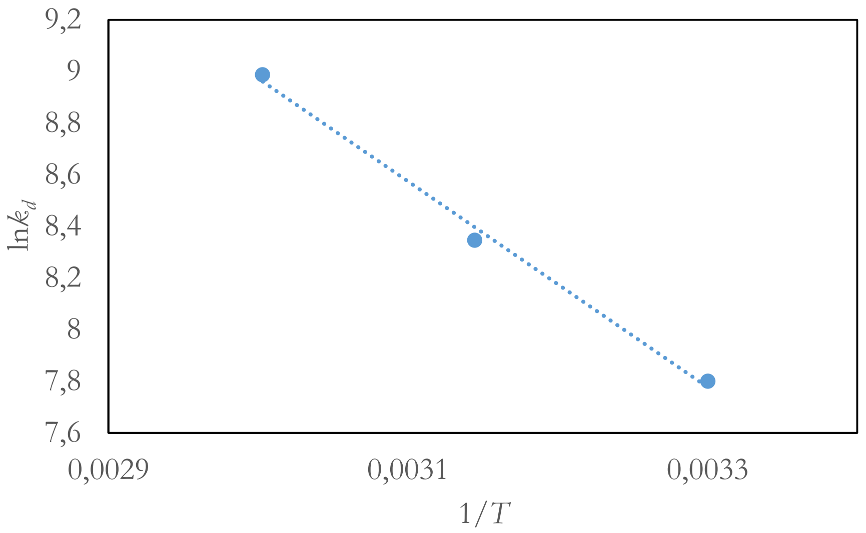

Figure 4-37 Effect of solution temperature on the dustribution coefficient of Sb on titania

Table 4-14 Thermodynamic parameters for Sb sorption titania

Bulk temperature (°C)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)
30	-19.59	
45	-22.20	0.17
60	-24.81	

4.7.5 Effect of temperature on the sorption kinetics of Sb on titania

Section 4.7.4 revealed that the equilibrium k_d is directly proportional to temperature. This section looks into the investigation of the effect of temperature on the sorption kinetics. The experiment was conducted using the method described in 3.3.5. The results obtained at 45 °C are presented in Figure 4-38.

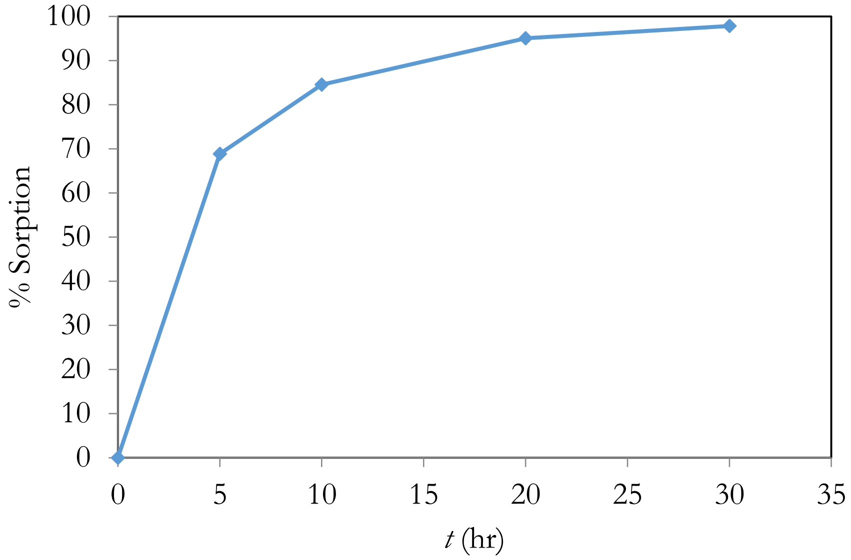

Figure 4-38 Time variation of percentage removal of Sb by titania at 45 °C ([Sb] = 10 ppm, 0.1 M HNO_3)

The time dependent data was fitted to the pseudo-first order kinetic model which gave a poor linear plot (not shown) invalidating the applicability of the kinetic model of the kinetic model at the stated experimental conditions. The time dependent data was also fitted to the pseudo-second order kinetic model. The resultant linear plot is presented in Figure 4-39. The kinetic parameters derived from the kinetic model are given in Table 4-15. The good correlation coefficient in conjunction with the good agreement between the calculated and experiment q_e indicates that the pseudo-second kinetic model can be used to explain Sb sorption by titania at the studied temperature. In comparison to the kinetics obtained at 30 °C, the sorption rate is higher. Given that the kinetics experiment was performed at only two temperatures, it cannot be concluded that the sorption rate increases with increasing temperature. However it is plausible that the increase in equilibrium sorption capacity with increasing bulk temperature (determined in section 4.7.4) may be due to the acceleration of some reaction steps. Additional experimentation is needed to make determine a more definitive relation between the sorption kinetics and bulk temperature for this sorbent-element pair.

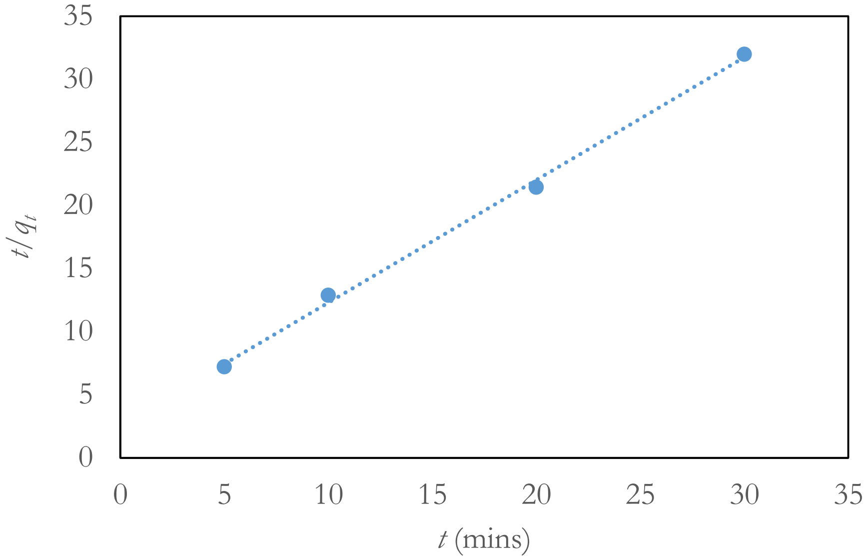

Figure 4-39 Pseudo-second order kinetic model for Sb removal by titania at 45 °C

Table 4-15 Calculated values of pseudo-second order kinetic model constants for Sb exchange on titania

Sb ions solution concentration (mg/L)	10
k_2 (g/mg min)	0.37
q_e (mg/g) (calculated)	1.03
r^2	0.998
q_e (mg/g) (experimental)	0.95

4.7.6 Selectivity of titania

The selectivity of titania was investigated using the method described in 3.3.6. The sorbate solution containing 5 ppm of Co, Ce, Ru, Sb and Sr ions was contacted with titania for 10 minutes in 0.1 M HNO_3. The results obtained from this experiment are given in Figure 4-40, which reveal that the affinity of titania for Sb ions is not influenced by the presence of other ions in solution. Also from the results, it can be gathered that titania is capable of removing Ru from aqueous solutions. Overall these results show that titania is highly selective for Sb.

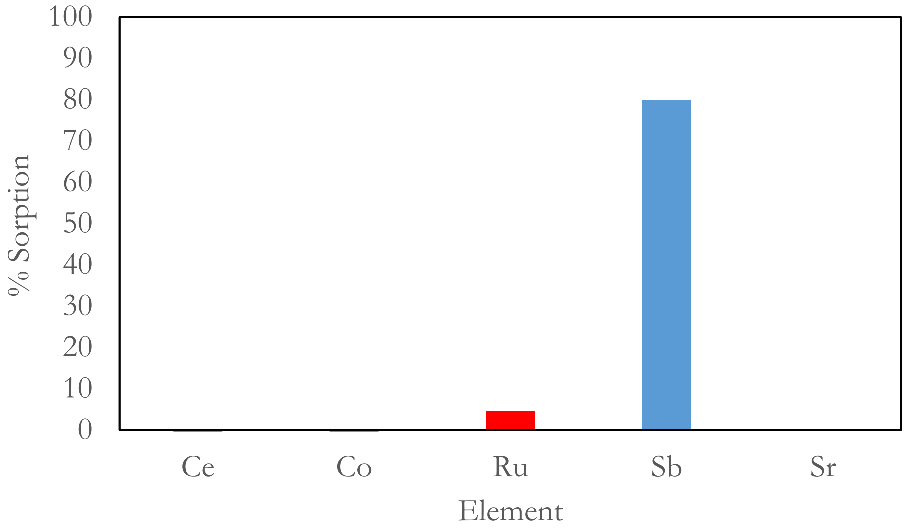

Figure 4-40 The sorption extent of Co, Ce, Ru, Sb and Sr on titania (10 minutes contact time, 5 ppm element concentration, 0.1 M HNO_3)

4.8 Sr removal by antimony pentoxide

Girardi *et al* (1970) reports that complete retention of ^{85}Sr(II) on antimony pentoxide is obtained in 1 M HNO_3. The extent of Sr retention on antimony pentoxide was investigated in this study using the method described in 3.3.2. The results obtained are presented in Figure 4-41, which show the reaction reaches completion after 78 hours contact time.

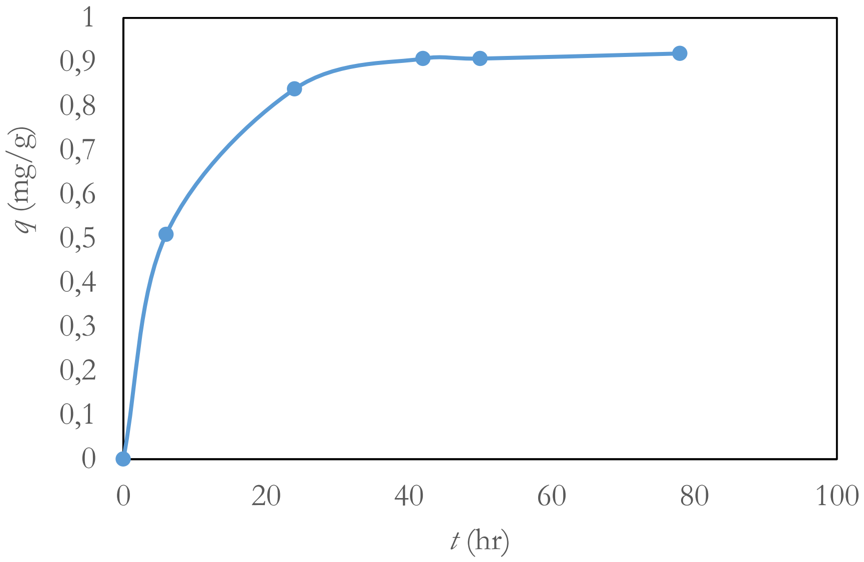

Figure 4-41 Time variation of percentage removal of Sr by antimony pentoxide (30 °C, [Sr] = 10 ppm, 1 M HNO_3)

The time dependent data was fitted to the pseudo-first order kinetic model, giving a good linear plot presented in Figure 4-42. The kinetic parameters derived from the model are present in Table 4-16. The discrepancy between the calculated and experimental q_e values suggests that the pseudo-first order kinetic model cannot be used to explain the Sr removal by antimony pentoxide.

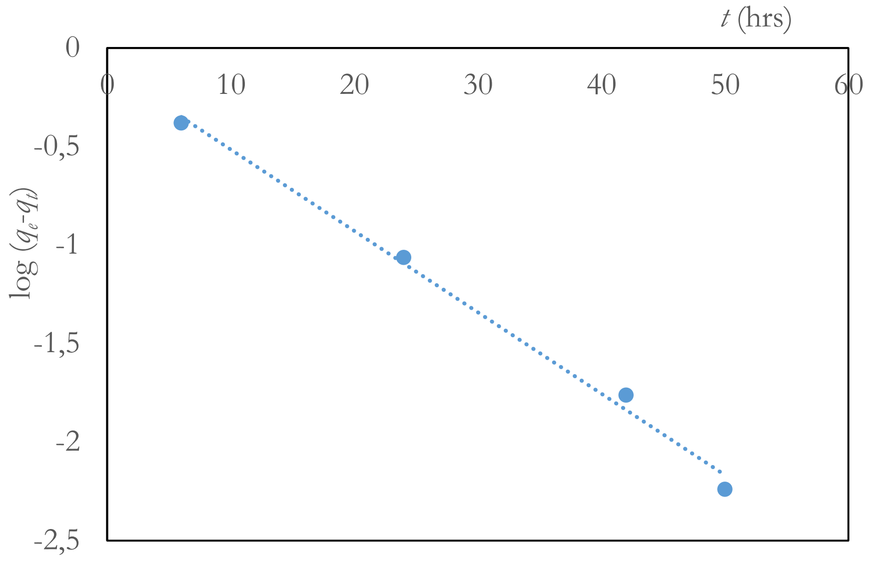

Figure 4-42 Pseudo-first order kinetic model for Sr removal by antimony pentoxide

Table 4-16 Calculated values of the pseudo-first order kinetic model constants fir Sr removal by antimony pentoxide

Sr ions solution concentration (mg/L)	10
k_1 (hr^{-1})	0.09
q_e (mg/g) (calculated)	0.79
r^2	0.993
q_e (mg/g) (experimental)	0.92

The time dependent data was also fitted to the pseudo-second order kinetic model. The resultant linear plot is presented in Figure 4-43. The kinetic parameters derived from the kinetic model are presented in Table 4-17. The good correlation coefficient obtained from the fitting and the good agreement between the calculated and experimental q_e values suggests that Sr sorption on antimony pentoxide can be explained by the pseudo-second order kinetic model.

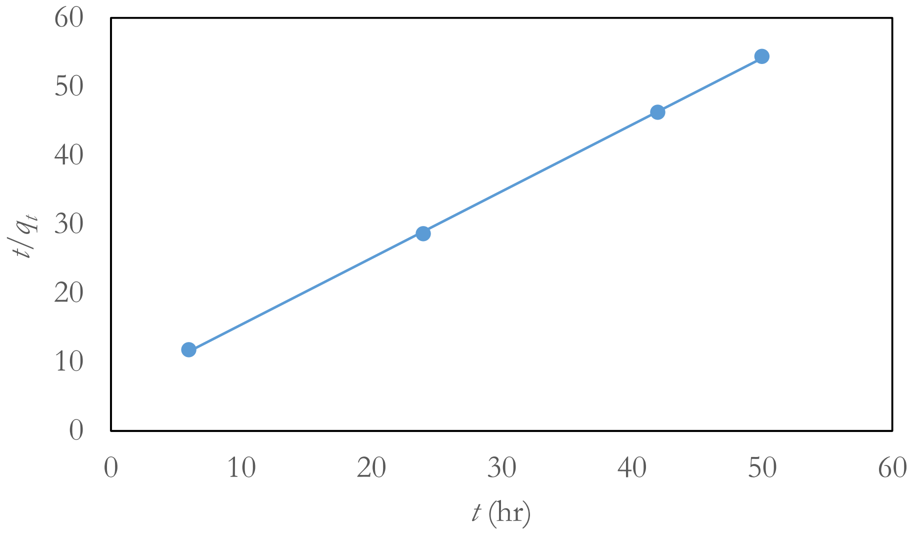

Figure 4-43 Pseudo-second order kinetic model for Sr removal by antimony pentoxide

Table 4-17 Calculated values of the pseudo-second order kinetic model constants for Sr removal by antimony pentoxide

Sr ions solution concentration (mg/L)	10
k_2 (g/(mg hr))	0.03
q_e (mg/g) (calculated)	1.03
r^2	0.999
q_e (mg/g) (experimental)	0.92

Overall the sorption kinetics of Sr on antimony pentoxide are considerably slow. Therefore, this sorbent material is not a good candidate for this research. However in a different application it can be a good material to target Sr from aqueous solutions because of its high sorption capacity of 0.92 mg/g.

Additional experimental work could not be conducted on this material due to material shortage. When a material supplied by a different commercial supplier (Alfa Aesar) was used, it gave contradicting results (given in Table 4-18) to the results obtained from the Sigma Aldrich product. The discrepancy in the results may be due to that the two products may have different sorption characteristics due to their different properties attributed to their preparation methods which may be different in the two commercial suppliers.

Table 4-18 Sorption results for Sr removal by antimony pentoxide supplied by (Alpha Aesar)

Time (hr)	% Sorption
14	1.290

4.9 Sr removal by SrTreat®

The SrTreat® exchanger is a highly selective inorganic material originally developed by a research group at the Helsinki University. Its structure is based on sodium titanate. The exchanger is highly effective in the removal of radiostrontium (Lehto *et al*, 1999). This material was used in this study for Sr removal from aqueous acidic solutions.

4.9.1 Effect of solution pH on Sr removal by SrTreat®

The effect of pH on the sorption capacity of SrTreat® was studied using the batch method described in 3.3.2 within a narrow pH range of 1.05-2.68. The Sr containing solutions were kept in contact with SrTreat® for 10 minutes.

The results obtained are presented in Figure 4-44, which reveal that a solution pH of ≈2 and greater is required for optimum Sr sorption on SrTreat®. It is surprising that the exchanger material possesses such efficacy in the ultra acidic pH range, given that Tusa *et al* (2007) reported that the best results are obtained at pH 9 and higher. The results obtained in this study prove that the SrTreat® exchanger is capable of effectively removing Sr from acidic aqueous solutions.

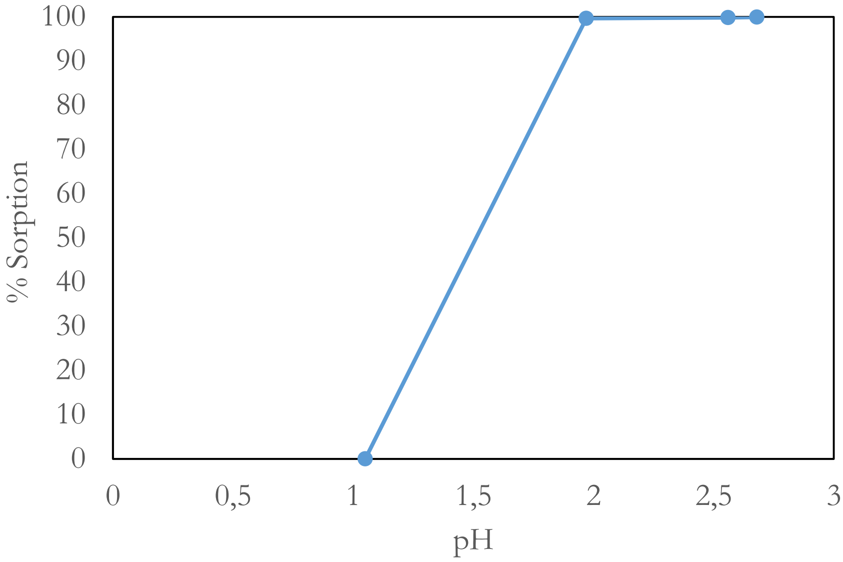

Figure 4-44 The sorption extent of SrTreat® for Sr in varying nitric acid pH

4.9.2 Sorption kinetic modelling of Sr removal by SrTreat®

The kinetics study on the amount of Sr sorbed on SrTreat® at different initial Sr concentrations was conducted using the method described in 3.3.2. The results obtained are given in Figure 4-45. From the results, it can be observed that the SrTreat® exchanger is highly effective in removing Sr from acidic aqueous solutions. For the initial Sr concentrations 5, 10 and 20 ppm, complete Sr removal is attained after 5 minutes contact time. The sorption capacity (*q*) increases with increasing initial concentration of Sr ions. This is expected because there are more free Sr ions available to be sorbed at high concentrations. There data obtained in 40 ppm Sr involves a sharp increase (in sorption capacity) from 0-10 minutes contact time, followed by reaction completion after 15 minutes contact time.

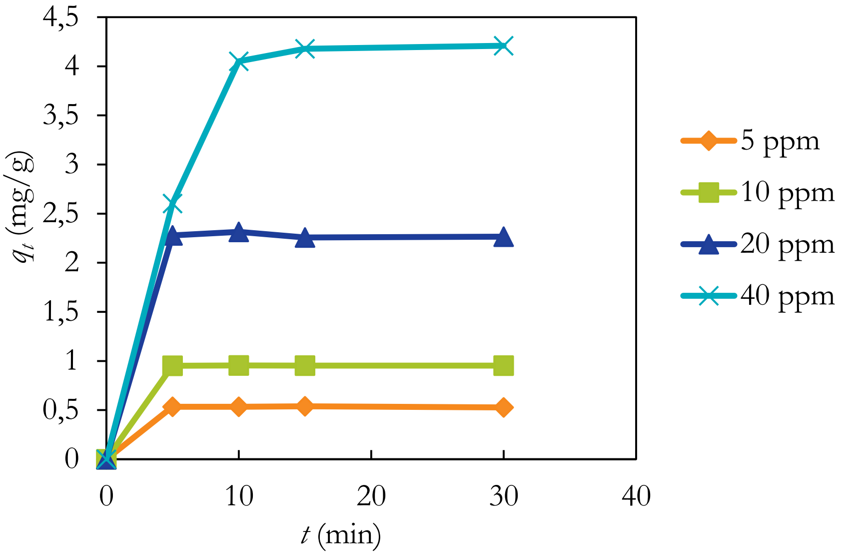

Figure 4-45 Time variation of the amount of Sr retained on SrTreat® at various concentations of Sr

The time dependent data obtained in 5, 10 and 20 ppm initial Sr concentration could not be fitted to the theoretical kinetic models because it was impossible to obtain more data before the reactions reaches completion which occurs after 5 minutes contact time. The time dependent data obtained in 40 ppm Sr was fitted to the pseudo-first kinetic model. The resultant linear plot is presented in Figure 4-46. The kinetic parameters derived from the kinetic model are presented in Table 4-19. The discrepancy between the calculated and experiment q_e values suggests that the pseudo-first order kinetic model cannot be used to explain Sr sorption on SrTreat®.

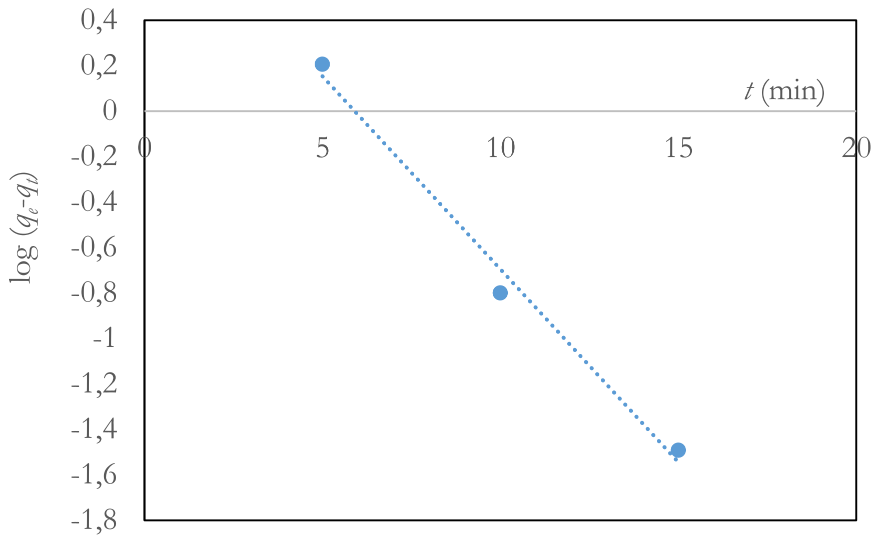

Figure 4-46 Pseudo-first order kinetic model for Sr removal by SrTreat® ([Sr] = 40 ppm, pH 2.7)

Table 4-19 Calculated values of the pseudo-first order kinetic model constants for Sr sorption on SrTreat®

Sr ions solution concentration (mg/L)	40
k_1 (min^{-1})	0.39
q_e (mg/g) (calculated)	10.05
r^2	0.989
q_e (mg/g) (experimental)	4.21

The time dependent data obtained in 40 ppm Sr was also fitted to the pseudo-second order kinetic model, giving a good linear plot presented in Figure 4-47. The kinetic parameters derived from the kinetic model are presented in Table 4-20. The good correlation coefficient obtained and the agreement between the calculated and experimental q_e values supports that the pseudo-second kinetic model can be used to explain Sr sorption on SrTreat®.

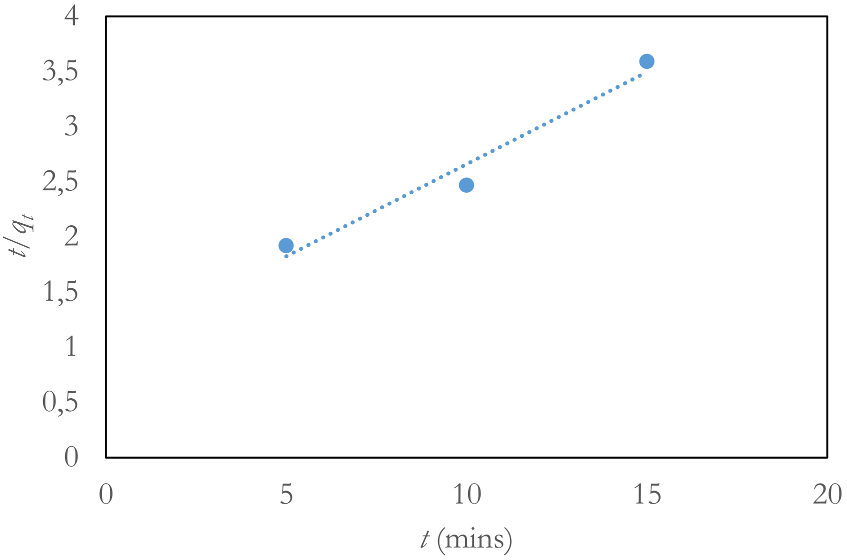

Figure 4-47 Pseudo-second order kinetic model for Sr removal by SrTreat® ([Sr] = 40 ppm, pH 2.7)

Table 4-20 Calculated values of the pseudo-second order kinetic model constants for Sr removal by SrTreat®

Sr ions solution concentration (mg/L)	40
k_2 (g/mg min)	0.03
q_e (mg/g) (calculated)	5.99
r^2	0.962
q_e (mg/g) (experimental)	4.21

Overall, the sorption kinetics are relatively fast, showing that SrTreat® is an exceptional sorbent material for Sr removal from aqueous acidic solutions.

4.9.3 Selectivity of SrTreat®

The selectivity experiment of the SrTreat® exchanger was conducted based on the method described in 3.3.6. The sorbate solution contained 2 ppm of Ce, Co, Ru, Sb and Sr. The results obtained are presented in Figure 4-48. The results show that the SrTreat® exchanger material does not specifically target Sr when exposed to a pool of adsorbate ions, but effectively removes Ce, Co and Ru as well. Given that the contact time selected was 5 minutes, it cannot be concluded that

SrTreat® has a low affinity for Sb ions in comparison to the other sorbate ions. The sorption kinetics of Sb on SrTreat® may be slower than that of the other sorbate ions. Slow kinetics does not automatically results to low sorption capacity. Given enough time, the sorption capacity might rise.

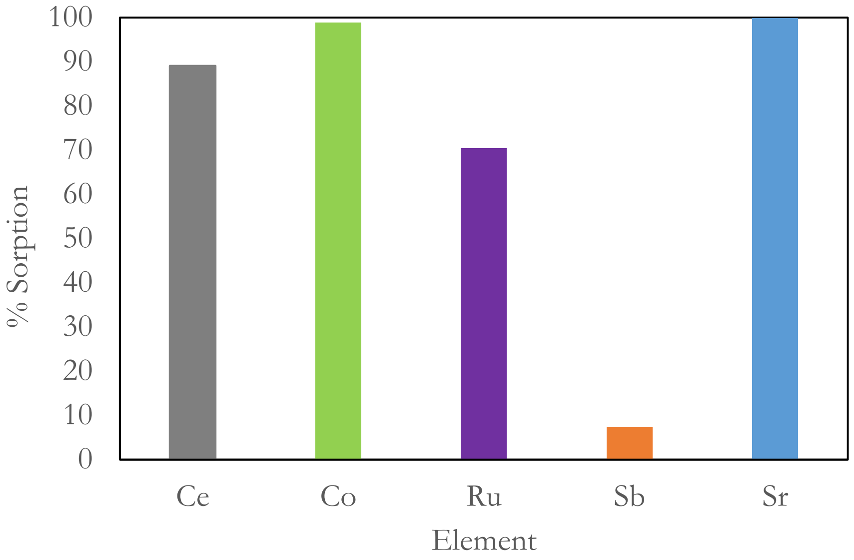

Figure 4-48 The sorption extent of Ce, Co, Ru, Sb and Sr on SrTreat® (5 minutes contact time, 2 ppm element concentration, pH 2.7)

Based on this project's purpose, these selectivity results are good in a way that a there is a possibility that one material can be used to remove multiple contaminants.

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Chapter 5: Dynamic sorption studies

Batch sorption studies provide useful information on the application of adsorption and ion exchange to the removal of specific waste contaminants. Chapter 4 presented extensive batch results and discussions on the efficacy of the sorbent material candidates in removing the studied contaminants. It is important to study the behaviour of the sorbent materials in a column as well because column experiments provide a more practical application of sorption as a nuclear waste processing technique. This experiments investigated the behaviour of the best performing sorbent materials in a column setting. The chosen sorbent material are CoTreat®, Manox A, titania and SrTreat® which were chosen to selectively target Co, Ru, Sb and Sr respectively. Unfortunately, the particle size distribution and specific surface area of these sorbent materials were not measured.

One of the main objectives of this study is to design an ion exchange purification scheme for post radiation U. It is therefore crucial to study the efficacy of sorbent materials to remove their target contaminants in the presence of U. Column experiments in the presence of U were conducted in this study to investigate the degree of the separation of the contaminants from U to judge the efficacy of the sorbent materials as potential candidates in the purification of post radiation U.

5.1 Co removal by CoTreat®

The behaviour of CoTreat® in removing Co from aqueous solution was studied using the method described in 3.3.8. The results obtained are presented in Figure 5-1, which reveal that Co is completely retained on the CoTreat® column. These results are good, showing that the behaviour of the CoTreat® exchanger in a column is as exceptional as was displayed in a batch setting.

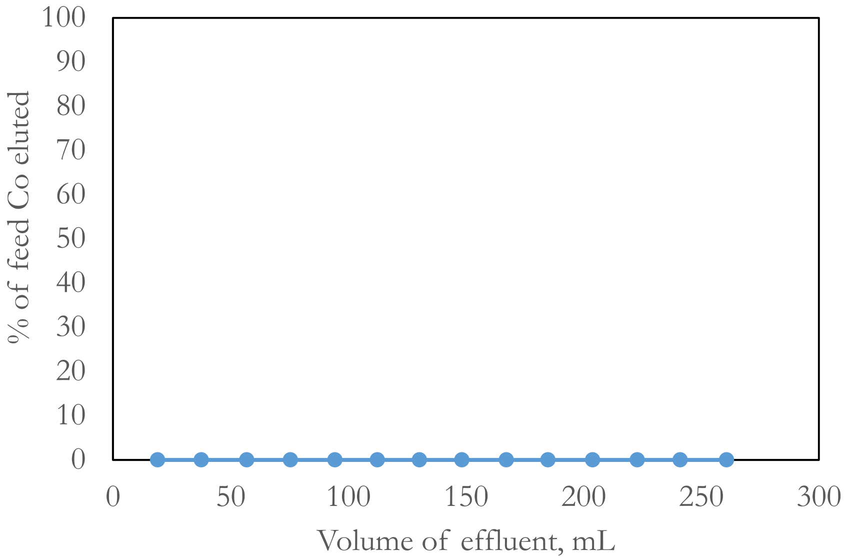

Figure 5-1 Breakthrough curve for Co run on 5 mL CoTreat® (feed Co concentration = 10 ppm, pH 2.53)

The effect of U on the efficacy of CoTreat® to remove Co was studied using the method described in 3.3.8. The results obtained are presented in Figure 5-2. The results show that 41.4 % of Co was eluted in the presence of U, while 95.4 % U was recovered. The amount of U not recovered is deemed insignificant, however the amount of Co eluted is significant. Therefore it can concluded that the presence of U negatively influences the sorption efficacy of CoTreat® for Co.

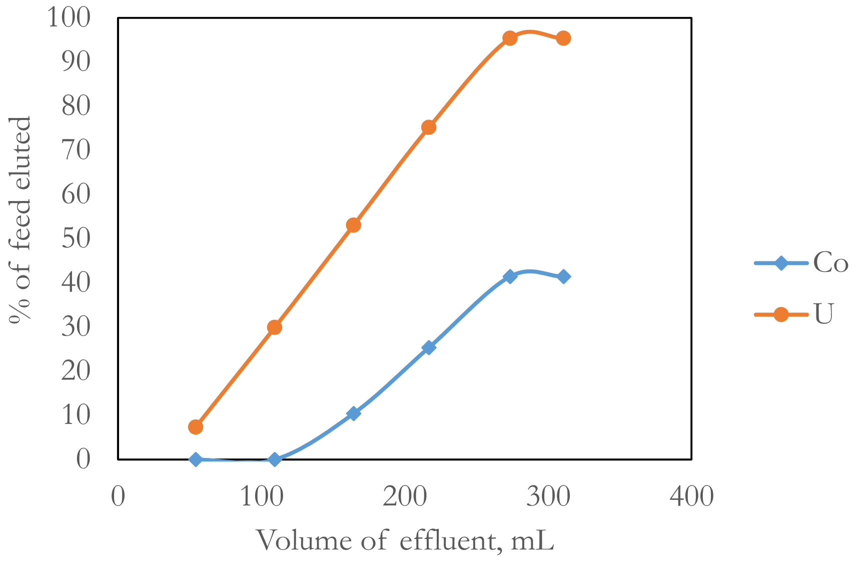

Figure 5-2 Breakthrough curve for U and Co run on 5 mL CoTreat® (feed Co concentration = 4 ppm, feed U concentration = 5360 ppm, pH 2.53)

5.2 Ru removal by Manox A

The manganese oxide material used for the batch studies was too fine to be used in the column experiments. Manox A (a hydrous metal oxide $MnO_2 \cdot nH_2O$) was used as an alternative. The behaviour of manganese oxide in a column setting was studied in the presence of both U and Ru using the method described in 3.3.9. The results obtained are given in Figure 5-3. The results reveal that 95 % U is recovered while 59.8 % Ru is eluted. Based on these results, the presence of U negatively influence the efficacy of manganese oxide to remove Ru from aqueous solution.

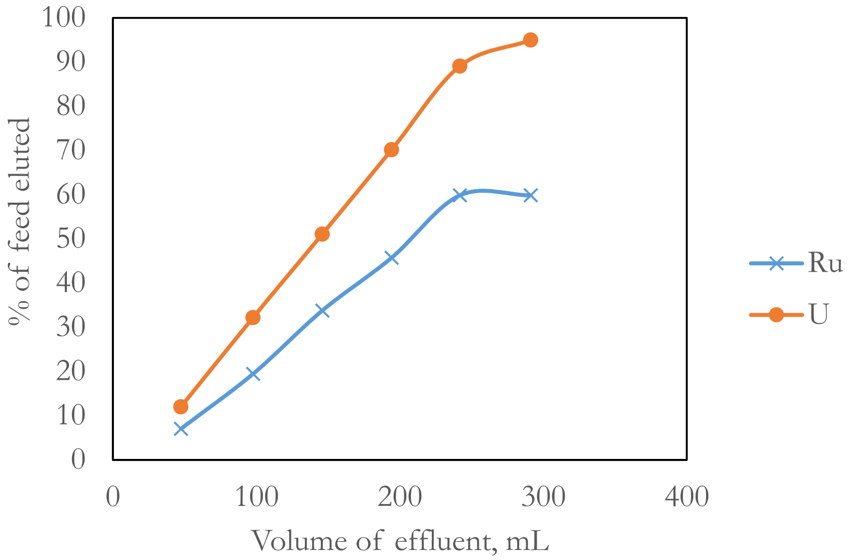

Figure 5-3 Breakthrough curve for U and Ru run on 5 mL Manox A (feed U concentration = 6234 ppm, feed Ru concentration = 8 ppm, pH 2.49)

5.3 Sb removal by titania

The behaviour of the titania in a column was studied using the method described in 3.3.10. The results obtained for a feed solution containing only Sb ions are presented in Figure 5-4, which reveal that Sb is completely retained a titania column. The results obtained for a feed solution containing U only are presented in Figure 5-5, which show that 97.9 % U is recovered. The results obtained for a feed solution containing both U and Sb are presented in Figure 5-6. The results show that 97.8 % is recovered, while 62.6 % Sb is eluted. Based on these results, titania is not a good sorbent material for the removal of Sb ions from aqueous solutions containing uranium.

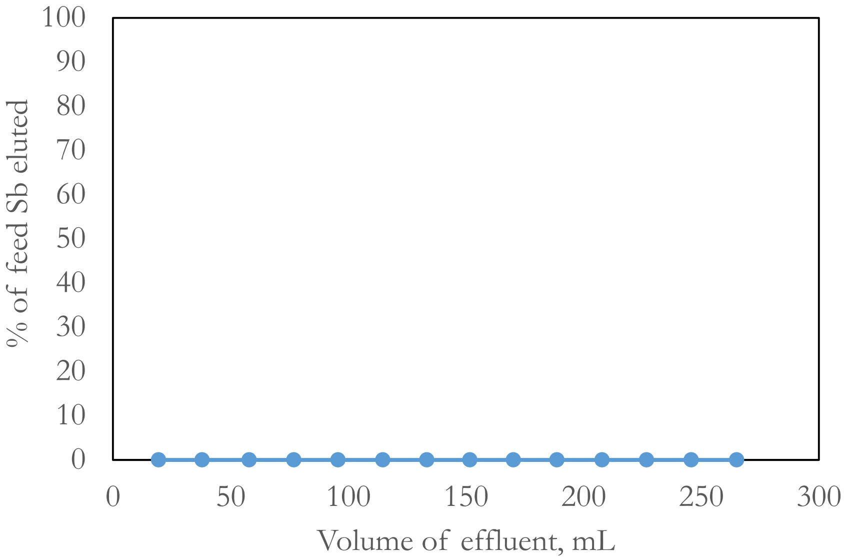

Figure 5-4 Breakthrough curve for Sb run on 5 mL titania (feed Sb concentration = 10 ppm, 0.1 M HNO_3)

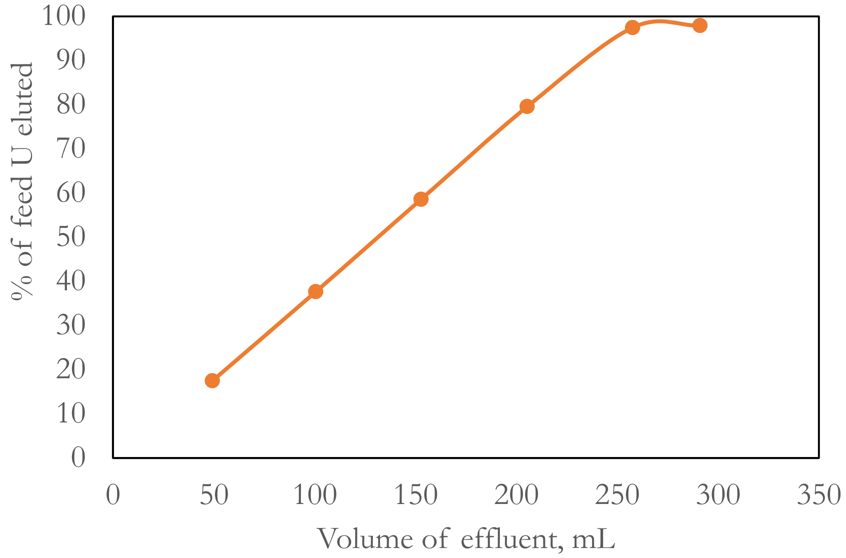

Figure 5-5 Breakthrough curve for U run on 5 mL titania (feed U concentration = 6754 ppm, pH 0.97)

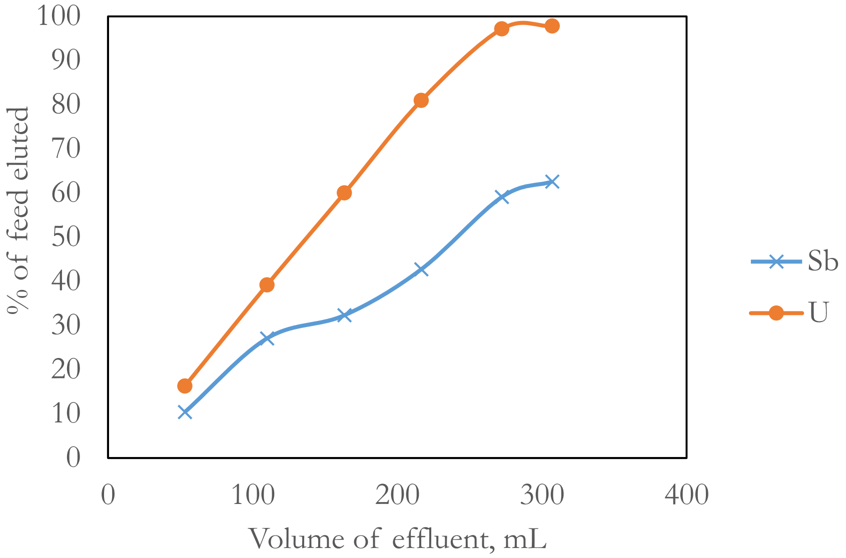

Figure 5-6 Breakthrough curve for U and Sb run on 5 mL titania (feed U concentration = 5900 ppm, feed Sb concentration = 4 ppm, pH 0.96)

5.4 Sr removal by SrTreat®

The behaviour of SrTreat® in a column was studied using the method described in 3.3.11. The results obtained are given in Figure 5-7, showing that complete Sr retention is obtained. The results obtained for the study of the effect of U presence on the efficacy of SrTreat® are presented in Figure 5-8. The results show that 75.6 % U is recovered while 63.8 % of Sr was eluted. Based on the results, the SrTreat® is not a good sorbent material for Sr removal from aqueous solutions containing uranium. A significant amount of U (24.4 %) was retained on the SrTreat® column.

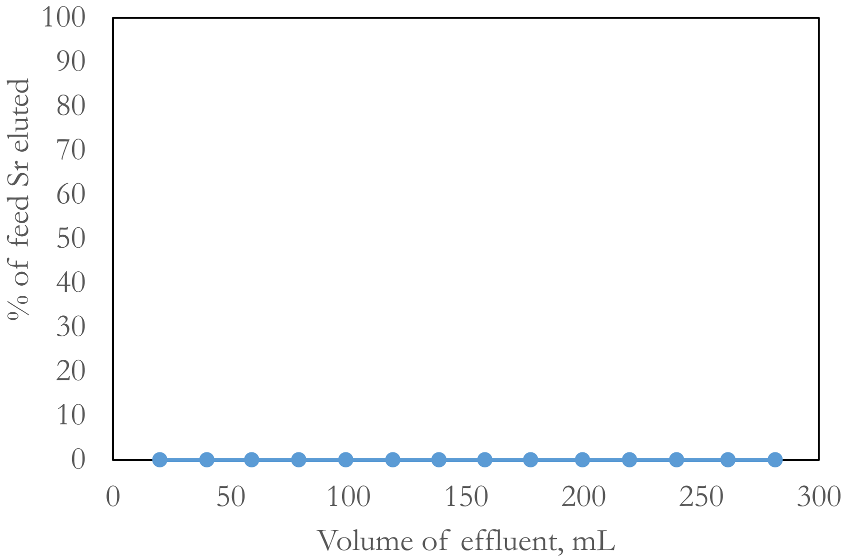

Figure 5-7 Breakthrough curve for Sr run on 5 ml SrTreat® (feed Sr concentration = 10 ppm, pH 2.44)

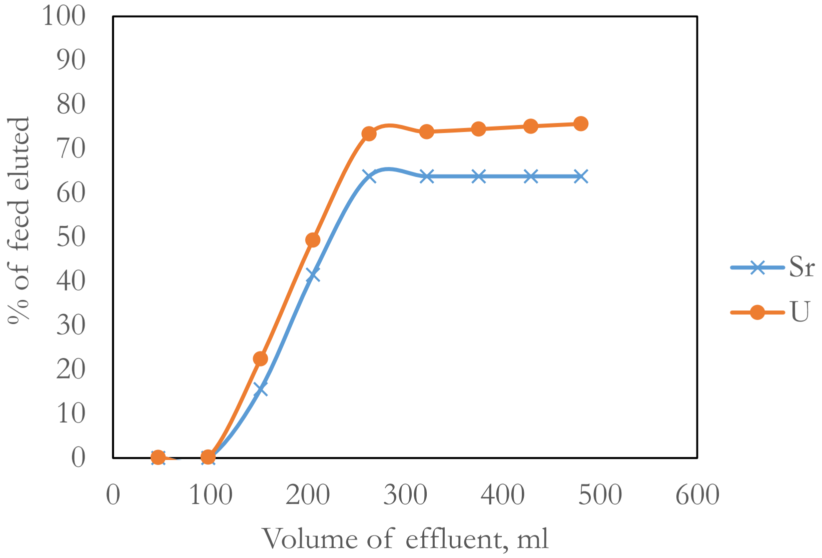

Figure 5-8 Breakthrough curve for U and Sr run on 5 ml SrTreat® (feed Sr concentration = 4 ppm, feed U concentration = 5910 ppm, pH 2.39)

In summary, these results show that the studied inorganic materials cannot be used to purify post reactor U under the studied conditions, but are potential candidates to substitute the organic ion exchangers used to purify coolant water of research reactors.

Chapter 6: Conclusions and recommendations

A group of 10 inorganic sorbent materials (activated charcoal, activated carbon, alumina, antimony pentoxide, CoTreat®, IONSIV R9120-B, manganese oxide, Manox A, SrTreat® and titania) was studied for their capability to remove 5 known problematic nuclides namely Ce, Co, Ru, Sb and Sr from acidic solutions. It was determined that the parameters: contact time, element concentration, solution pH, temperature and the presence of U ions played a significant role in the outcomes of the sorption processes.

The batch studies revealed that antimony pentoxide is not an efficient sorbent material for Ce and Sr removal from acidic aqueous solutions because of its slow kinetics. It was revealed that Co removal by CoTreat® sorption process conforms to ion exchange, is an endothermic process, favourable and spontaneous. The kinetic data revealed that ion exchange process can be explained by the pseudo-first order kinetic model at high concentrations of Co ions and can be explained by the pseudo-second order kinetic model at lower concentrations of Co ions. The equilibrium data best fitted the Langmuir isotherm, supporting that the CoTreat® ion exchange sites are identical and equivalent resulting to a monolayer formation. Relative to CoTreat®, the selective media (IONSIV R9120B) showed to have poor sorption capacity for Co ions.

The sorption capacity of activated carbon and charcoal for Ru ions was poor as well. Given that the sorption mechanism of activated carbons is well documented to be an exothermic process, conducting experimental work at lower temperatures is expected to yield better results. Manganese oxide was the best candidate studied for the removal of Ru ions. The sorption of Ru ions on manganese oxide was revealed to be an endothermic, favourable and spontaneous ion exchange process and conforms to the pseudo-second order kinetic model at the studied experimental conditions. The equilibrium data best fitted the Freundlich isotherm, supporting the heterogeneity of the manganese oxide sorption surface sites. Sb ions removal was extensively studied as well. The sorption of Sb ions on alumina was determined to be explainable by the pseudo-second order kinetic model. The equilibrium data fitted the Freundlich isotherm model best, indicating that the sorption of Sb ions on alumina is non-uniform.

Optimal sorption of Sb ions on titania was achieved in 0.1 M HNO_3. The sorption process could be explained by the pseudo-second order kinetic model. The equilibrium data revealed that Sb sorption on titania is an endothermic, favourable and spontaneous ion exchange process. Both the Langmuir and Freundlich isotherm models gave good linear fits. The SrTreat® material was discovered to be an exceptional material for the removal of Sr ions from acidic media, given the fast sorption kinetics and high sorption capacity obtained.

The column experimental work revealed that the sorption capability of CoTreat®, manganese oxide, titania and SrTreat® declines in the presence of U ions.

Various tests and experiments were left to subsequent researchers due to lack of time and material. The following ideas would be beneficial to investigate in the future:

- Further sorption studies can be conducted (e.g. determination of activation energies of sorption) to obtain the optimal conditions that give a better separation between U species and the problematic nuclides.
- Speciation studies to determine the species in solution to optimize U recovery.
- Studies using simulated contaminated cooling water to evaluate the practical applicability of the sorption process.

6.1 Final Conclusion

The primary aim of this study was not achieved. Therefore, the sorption process cannot be used for U recovery from ^{99}Mo waste. Nonetheless, the secondary aim was achieved. This study revealed that the studied inorganic sorbent materials could be used to replace current ion exchangers used in the purification of reactor cooling waters.

Appendix A

The list of batch and column experiments conducted are presented in Table A 1 and Table A 2. The batch experiments omitted for each sorbent-element pair are given in Table A 3 to Table A 6 along with appropriate reasoning for the omission. The XRF and XRD results of CoTreat® are given in Table A 7 and Figure A 1 respectively.

Table A 1 Experimental matrix of batch experiments conducted in this study

Sorbent material	**Element**	**Element conc. (ppm)**	**Temp (°C)**	**Contact time**	**Medium**	**Purpose of experiment**
Antimony pentoxide (Sigma Aldrich)	Ce	5	30	1, 1.75, 2, 3.25 day	1 M HNO_3	Kinetics experiment
Antimony pentoxide (Alpha Aesar)	Ce	5	30	0.5, 4 hr	1 M HNO_3	Comparison of the Ce sorption capability to the Sigma Aldrich product
CoTreat	Co	5	30	3 hr	HNO_3 (pH 0.5-2.6)	Effect of solution pH on the sorption capacity
CoTreat®	Co	5, 10, 30, 40	30	5, 10, 30, 60, 120, 180, 240 min	HNO_3 (pH 2.6)	Sorption kinetics
CoTreat®	Co	10, 20, 30, 40	30	3 hr	HNO_3 (pH 2.6)	Sorption equilibrium data to construct sorption isotherms
CoTreat®	Co	10	30-60	3 hr	HNO_3 (pH 2.6)	Effect of solution temperature on the sorption equilibrium (thermodynamic parameters)
CoTreat®	Co	10	45, 60	5, 10, 20, 30 min	HNO_3 (pH 2.6)	Effect of solution temperature on the sorption kinetics
CoTreat®	Co, Ce, Ru, Sb, Sr	2	30	3 hr	HNO_3 (pH 2.6)	Selectivity of CoTreat for Co
IONSIV R9120B	Co	5	30	1, 2, 3, 4, 25, 66 hr	HNO_3 (pH 2.6)	Kinetics experiment

Sorbent material	Element	Element conc. (ppm)	Temp (°C)	Contact time	Medium	Purpose of experiment
Activated charcoal	Ru	10	30	3 hr	1-5 M HNO_3	Effect of solution pH on the sorption capacity
Activated charcoal	Ru	5	30	0.5, 1, 1.5, 2, 3, 4 hr	3 M HNO_3	Kinetics experiment
Activated carbon	Ru	5	30	1, 2, 4 hr	3 M HNO_3	Kinetics experiment
Manganese oxide	Ru	5	30	6 hr	0-4 M HNO_3	Effect of solution pH on the sorption capacity
Manganese oxide	Ru	2, 5, 10	30	0.5, 1, 2, 4, 5, 6 hr	ultrapure water	Sorption kinetics
Manganese oxide	Ru	2, 5, 15, 20	30	6 hr	ultrapure water	Sorption equilibrium data to construct sorption isotherms
Manganese oxide	Ru	5	30-60	6 hr	ultrapure water	Effect of solution temperature on the sorption equilibrium (thermodynamic parameters)
Manganese oxide	Ru, Ce, Co, Ru, Sb	2	30	5 hr	ultrapure water	Selectivity of manganese oxide for Ru
Alumina (UNILAB)	Sb	5	30	5 hr	0-3 M HNO_3	Effect of solution pH on the sorption capacity
Alumina (UNILAB)	Sb	5	30	0.25, 1, 2, 3, 5 hr	ultrapure water	Sorption kinetics
Alumina (UNILAB)	Sb	2, 5, 10, 15, 20	30	3 hr	ultrapure water	Sorption equilibrium data to construct sorption isotherms
Alumina (UNILAB)	Sb	5	30	15, 60, 120, 180, 300, 360 min	0.5 M HNO_3	Sorption kinetics at lower pH
Alumina (UNILAB)	Sb, Ce, Co, Ru, Sr	2	30	3 hr	ultrapure water	Selectivity of alumina for Sb
Alumina (Sigma Aldrich)	Sb	5	30	0.25, 3 day	ultrapure water	Compare the sorption capacity to

Sorbent material	**Element**	**Element conc. (ppm)**	**Temp (°C)**	**Contact time**	**Medium**	**Purpose of experiment**
						the UNILAB product
Titania	Sb	5	30	10 min	0-1 M HNO_3	Effect of solution pH on the sorption capacity
Titania	Sb	5, 10, 15	30	5, 10, 15, 20, 30, 60, 90 min	0.1 M HNO_3	Sorption kinetics
Titania	Sb	2, 5, 10, 15, 20	30	3 hr	0.1 M	Sorption equilibrium data to construct sorption isotherms
Titania	Sb	10	30-60	20 min	0.1 M HNO_3	Effect of solution temperature on the sorption equilibrium (thermodynamic parameters)
Titania	Sb	10	45	5, 10, 20, 30 min	0.1 M HNO_3	Effect of solution temperature on sorption kinetics
Titania	Sb, Ce, Co, Ru, Sr	5	30	10 min	0.1 M HNO_3	Selectivity of titania for Sb
Antimony pentoxide (Sigma Aldrich)	Sr	10	30	6, 24, 42, 50, 78 hr	1 M HNO_3	Sorption kinetics
Antimony pentoxide (Alpha Aesar)	Sr	10	30	14 hr	1 M HNO_3	Comparison to the Sigma Aldrich product
SrTreat®	Sr	5	30	10 min	HNO_3 (pH 1.05-2.68)	Effect of solution pH on the sorption capacity
SrTreat®	Sr	5, 10, 20, 40	30	5, 10, 15, 30 min	HNO_3 (pH 2.7)	Sorption kinetics
SrTreat®	Sr, Ce, Co, Ru, Sb	2	30	5 min	HNO_3 (pH 2.7)	Selectivity of SrTreat® for Sr

Table A 2 Experimental matrix of column experiments conducted in this study

Sorbent material (column volume)	**Element**	**Element conc. (ppm)**	**Medium**	**Purpose of experiment**
CoTreat® (5 mL)	Co	10	HNO_3 pH 2.53	To study the sorption behaviour of the CoTreat® material in a column setting
CoTreat® (5 mL)	U, Co	5360 ppm U, 4 ppm Co	HNO_3 pH 2.53	To study Co sorption in the presence of excessive U
Manox A (5 mL)	U, Ru	6234 ppm U, 8 ppm Ru	HNO_3 pH 2.49	To study the Ru sorption on manganese oxide in the presence of excessive U
Titania (5 mL)	Sb	10	0.1M HNO_3	To study the sorption behaviour of titania in a column setting
Titania (5 mL)	U	6754	HNO_3 pH 0.97	To investigate if the sorbent material has a significant sorption affinity for U
Titania (5 mL)	U, Sb	5900 ppm U, 4 ppm Sb	HNO_3 pH 0.96	To study Sb sorption on titania in the presence of excessive U
SrTreat® (5 mL)	Sr	10	HNO_3 pH 2.44	To study the sorption of behaviour of SrTreat® in a column setting
SrTreat® (5 mL)	U, Sb	5910 ppm U, 4 ppm Sr	HNO_3 pH 2.39	To study the Sr sorption on SrTreat® in the presence of excessive U

Table A 3 The list of sorbent-element pairs for which the pH effect was not determined

Sorbent: Element	**Reasons**
Antimony pentoxide: Ce, Sr	The material available was not adequate. The Sigma product was too expensive to purchase, given the slow kinetics showed by the initial tests.
IONSIV R9120B: Co	The material available was not adequate. The initial tests revealed slow kinetics and poor sorption capacity, therefore more product was not purchased.

Table A 4 A list of sorbent-element pairs for which the equilibrium study was not conducted

Sorbent: Element	Reasons
antimony pentoxide: Ce, Sr	The same as given in Table A 3.
IONSIV R9120B: Co	The same as given in Table A 3.
(Activated carbon, activated charcoal): Ru	Initial studies showed low sorption capacity. Thus it was not worthwhile to investigate the sorbent materials further.
SrTreat®: Sr	The experiment was conducted successfully for this sorbent-element pair. However, the results obtained were not reported because the data could not be fitted to isotherm models (did not produce a linear plot) due to the minute difference between the residual concentration values at the studied Sr concentration range.

Table A 5 A list of sorbent-element pairs for which the temperature effect was not investigated

Sorbent: Element	**Reasons**
Antimony pentoxide: Ce, Sr	The same as given in Table A 3.
Alumina: Sb	In comparison to the titania's sorption capacity for Sb ions, alumina was determined to not be the best sorbent material for Sb ions removal. With the limited resources, it was not worthwhile to conduct this experiment.
IONSIV R9120B: Co	The same as given in Table A 3.
(Activated carbon, activated charcoal): Ru	The same as given in Table A 4.
SrTreat®: Sr	The data obtained did not produce a good linear plot worth reporting. With limited resources, the experiment could not repeated.

Table A 6 A list of sorbent-element pairs for which the competition experiment was not conducted

Sorbent: Element	**Reason**
Antimony pentoxide: Ce, Sr	The same as given in Table A 3.
IONSIV R9120B: Co	The same as given in Table A 3.
(Activated carbon, activated charcoal): Ru	The same as given in Table A 4.

Table A 7 Element concentration of CoTreat®

Element	**concentration %**
SiO_2	0,13
Al_2O_3	<0,01
MgO	0,22
Na_2O	8,96
P_2O_5	<0,01
Fe_2O_3	0,01
K_2O	0,09
CaO	0,54
TiO_2	89,61
V_2O_5	0,31
Cr_2O_3	<0,01
MnO	<0,01
NiO	<0,01
CuO	<0,01
ZrO_2	<0,01
S	0,05
Nb_2O_5	0,02
MoO_3	0,02

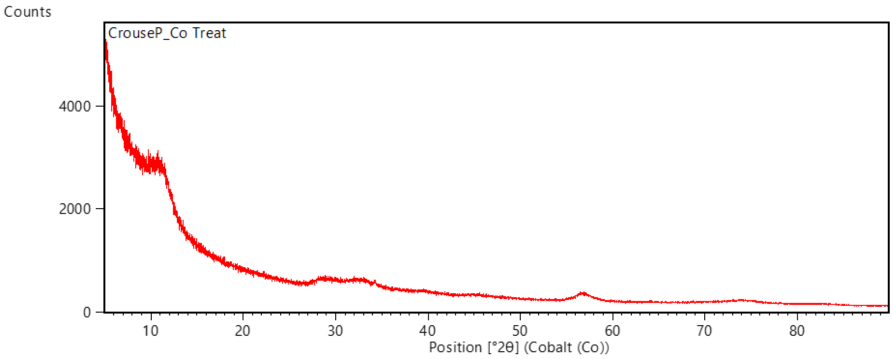

Figure A 1 XRD pattern of CoTreat®

Appendix B

Determination of U in solution with a UV/Vis method in CO_3^{2-}/H_2O_2 method

This method is based on the intensely coloured complex of uranium with peroxide in an alkaline carbonate medium. It is suitable for samples in the U concentration range 20–200 ppm. The step by step procedure is described below.

Prepare standards and samples:

1. Prepare four standard solutions using a 1000 ppm absolute U standard solution.

Into four 25 mL volumetric flasks, pipette respectively 1.25; 2.5; 3.75; and 5.0 mL of the standard solution. (When diluted to 25 mL, this will give standards with concentrations of 50, 100, 150 and 200 ppm).

2. Add 3 mL of 2 M Na_2CO_3 and 1 mL 30% H_2O_2 to each flask, dilute to 25 mL with demineralized water, and mix.

3. Prepare a reagent blank by diluting 3 mL of 2 M Na_2CO_3 and 1 mL of 30% H_2O_2 to 25 mL.

4. Use the approximate expected value of U concentration in a sample to be analysed, to calculate the amount of solution required to obtain a U concentration in a 25 mL volume, which would be within the range of the calibration curve. If the U concentration in the solution to be analysed is too high and the calculated aliquot is too small to be accurately pipetted, prepare a suitable dilution from the original uranium solution, from which an aliquot for analysis is then taken. Pipette this calculated volume into a 25 mL volumetric flask.

5. If the sample solution is acidic, calculate the volume of 2 M Na_2CO_3 required for neutralization of the sample aliquot, and add this volume.

6. Add 3 ml 2 M Na_2CO_3 and 1 mL 30% H_2O_2 to each flask, dilute to 25 mL with demineralized water, and mix.

Create calibration curve on UV/Vis instrument:

1. Change the wavelength on the UV/Vis instrument to 450 nm.

2. Pour blank solution into the two quartz cuvettes.

3. Place both quartz cuvettes in the instrument; one in the sample holder in the front beam line, and the other in the sample holder in the back beam line.

4. Change the absorbance value on the instrument to zero.

5. Remove the reagent blank from the sample holder in the front beam line, pour the blank solution out and add solution from the first 50 ppm standard. Rinse the cuvette with the new solution two times before adding the final amount to be measured.

6. Make a note of the absorbance value displayed.

7. Repeat step 5 and 6 for all the standards.

8. Draw up a calibration curve by plotting the absorbance values against the U concentration of the standards.

Run samples:

1. Measure absorbance for all the samples.

2. Calculate the U concentration in the samples from the calibration curve, and use this to calculate the U concentration in the original solution to be analysed.