CHAPTER-1

INTRODUCTION

1.1 BACKGROUND

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out. If an ion exchanger $M^- A^+$, carrying cations $A^+$ as the exchanger ions, is placed in an aqueous solution phase containing $B^+$ cations, an ion exchange reaction takes place which may be represented by the following equation:

\[
M^- A^+ + B^+ \rightleftharpoons M^- B^+ + A^+
\]  
(1.1)

For reasons which will be considered later, the anion in solution does not necessarily take part in the exchange to any appreciable extent. The equilibrium represented by the above equation is an example of cation exchange, where $M^-$ is the insoluble fixed anionic complement of the ion exchanger $M^- A^+$, often called simply the fixed anion. The cations $A^+$ and $B^+$ are referred to as counter-ions, whilst ions in the solution which bear the same charge as the fixed anion of the exchanger are called co-ions. In much the same way, anions can be exchanged provided that an anion-receptive
medium is employed. An analogous representation of an anion exchange reaction may be written:

\[ M^+ A^- + B^- \xrightarrow{\text{Solid \ to \ Solution}} M^+ B^- + A^- \] (1.2)

Further development of a physical model for the exchanger phase is best left until Chapter 2 when synthetic ion exchangers will be considered in more detail, but the previous equations illustrate the essential difference between ion exchange and other sorption phenomena. The main fact is that electroneutrality is preserved at all times in both the exchanger and solution phases, and this in turn required that counter–ions are exchanged in equivalent amounts. The most important features characterizing an ideal exchanger are:

1. A hydrophilic structure of regular and reproducible form.
2. Controlled and effective ion exchange capacity.
5. Physical stability in terms of mechanical strength and resistance to attrition.
6. Consistent particle size and effective surface area compatible with the hydraulic design requirements for large scale plant.
Manufacturers of modern ion exchange materials have progressed a long way towards meeting all these requirements when compared with the prototype materials described below. The cost to industry of modern ion exchange resins in high, varying typically from £1000 to £4000 per m³. Therefore exchanger properties which minimize the volumes required (e.g. high exchange capacity), or which prolong resin life (e.g. physical and chemical stability), are important considerations. It therefore follows that continued efforts to improve the exchanger characteristics listed above play an important part in the activities of resin manufacturing companies.

**INORGANIC MATERIALS:**

The ion exchange phenomenon was found by the English agriculturist, H.S. Thompson\textsuperscript{[1]} and the chemist J.T. Way\textsuperscript{[2]} in 1850, who noted the adsorption of ammonium sulphate on soil as follows.

\[
\text{Ca-Soil} + (\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_4\text{-Soil} + \text{CaSO}_4, \quad \ldots \ldots \quad (1)
\]

M.R.J. Wyllie\textsuperscript{[3]}, W.Juda and M.R.C. Mc. Rao\textsuperscript{[4]} reported the synthesis of cation and anion exchange membranes around 1950. The former membrane is prepared by using a powdery ion exchange resin and binding polymer and the latter is composed of ionic condensation type polymers. After these works, studies on the ion exchange membranes, synthetic methods, theoretical explanation of membrane phenomena and trials for
industrial applications became very active. The ion exchange membrane, non-porous membranes polymers having the characteristics, of membrane are:

(i) Ion conductivity

(ii) Hydrophilicity

(iii) The existence of fixed carrier ion exchange group.

**Table 1.1: Characteristics and Applications of Ion Exchange Membrane**

<table>
<thead>
<tr>
<th>CHARACTERISTICS</th>
<th>APPLICATION</th>
<th>EXAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Conductivity</td>
<td>Electro dialysis</td>
<td>Concentration or desalination of electrolytes, separation between electrolyte and non-electrolyte, bipolar ion exchange membrane process to produce acid and alkali, ion-exchange reaction acid and alkali, ion exchange reaction across the membrane, electro-deionization (EDI,CDI) etc.</td>
</tr>
<tr>
<td>Separator for Electrolysis</td>
<td>Chlor-alkali production, organic synthesis by electrolysis etc. synthesis of $O_3$, $H_2O_2$ etc.</td>
<td></td>
</tr>
<tr>
<td>Diffusion Dialysis</td>
<td>Acid or alkali recovery from waste</td>
<td></td>
</tr>
<tr>
<td>Neutralization dialysis</td>
<td>Separation of electrolyte and non-electrolyte, Desalination of water etc.</td>
<td></td>
</tr>
</tbody>
</table>
1. Exchange involved equivalent quantities of ions.

2. Certain ions were more easily exchanged than others.

3. The temperature coefficient for the rate of exchange was small.

4. The aluminosilicate fractions of soils were responsible in the main for the exchange although these components rarely took part in the exchange itself.*

5. Materials possessing exchange properties could be synthesized from soluble silicates and aluminium sulfate.

The equivalence law governing the phenomenon was established in the early scientific history of the subject, as also was the fact that some ions were more easily exchanged than others; in other words ion exchangers showed greater selectivity or affinity for different ions. That an exchanger could be chemically synthesized proved to be of the utmost importance; it is for this reason that ion exchange studies and applications have reached such an advanced state today.

The ion exchange capacity of an exchanger is a measure of its total content of exchangeable ions, and is conventionally expressed in terms of the total number of equivalents of ion per kilogram (mili-equivalents per gram) of the exchanger in its dry state and in a given univalent ionic form. It will become evident when describing practical applications, the operating
<table>
<thead>
<tr>
<th>Process</th>
<th>Application</th>
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<tbody>
<tr>
<td>Donnan dialysis</td>
<td>Recovery of precious metals, softening of hard water, preconcentration of a trace amount of metal ion for analysis etc.</td>
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<tr>
<td>Up-hill transport</td>
<td>Separation and recovery of ions.</td>
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<tr>
<td>Piezeodialysis</td>
<td>Desalination or concentration etc.</td>
</tr>
<tr>
<td>Thermo-dialysis</td>
<td>Desalination or concentration etc.</td>
</tr>
<tr>
<td>Battery</td>
<td>Alkali battery, redox-flow battery, concentration cell etc</td>
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<tr>
<td>Fuel cell</td>
<td>Hydrogen-oxygen, methanol-oxygen</td>
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<td>Actuator</td>
<td>Catheter for medical use.</td>
</tr>
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<td>Hydrophilicity</td>
<td>Evaporation</td>
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<td></td>
<td>Dehydration of water miscible organic solvent</td>
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<td></td>
<td>Dehumidification</td>
</tr>
<tr>
<td></td>
<td>Dehumidification of air and gases.</td>
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<td>Sensor</td>
<td>Gas Sensor (humidity, CO, NO, O₂ etc.), medical (enzyme Immobilization, etc.)</td>
</tr>
<tr>
<td>Fixed carrier (Ion)</td>
<td>Facilitate transport (gas separation)</td>
</tr>
<tr>
<td></td>
<td>Removal of acidic gas, separation of olefins</td>
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<tr>
<td>Exchange groups</td>
<td>Modified electrodes</td>
</tr>
<tr>
<td></td>
<td>Alkanes, separation of sugars etc.</td>
</tr>
</tbody>
</table>

Further studies furnished many sound conclusions as to the nature of ion exchange reactions, some of the more important ones being:
exchange capacity of an exchanger is invariably less than its total capacity. Also because of the presence of 'colloidal humus' in natural soils, exchange capacity data was difficult to systematize and to reproduce in relation to the inorganic minerals which were present. Consequently further studies were carried out utilizing the separated microcrystalline aluminosilicates, or 'clay fractions' of the soil which were obtainable in quite a pure form. These experiments proved that the main exchange agents were indeed contained in the finest or clay like fractions of soils. Our knowledge of the structure and classification of such materials has shown that some of the inherently finely divided clay materials are directly responsible for the exchange characteristics observed; however, the phenomenon is not purely a property of particle size.

Why the clay minerals should possess an appreciable exchange capacity became more fully understood with the establishment of the crystal structures of the various types, for which most of the early credit is due to W.L. Bragg, L. Pauling, and others. Therefore before the ion exchange relationships of such materials can be fully understood a general appreciation of their structures is essential.

Geologically and genetically, clay minerals are difficult to define simply and adequately, but broadly they are layer lattice silicates of
secondary origin. In the same classification are the micas, tale, chlorites, and serpентines which are not strictly clay minerals. In this context, secondary origin means that mineral formation has arisen from the weathering of primary or igneous rock, e.g. granites and basalts.

The basic structural unit making up the layer lattice silicates is the silica tetrahedron, $(\text{SiO}_4)^4^-$. When three oxygen atoms of every tetrahedron are linked to similar units a continuous sheet structure is formed which is capable of indefinite extension in two directions at right angles; as a consequence the important physical property of minerals within this group is their plate-like character. One oxygen atom of each tetrahedral unit is not satisfied electrically and requires to be linked to external cations in order to establish electrical neutrality within the lattice. In most structures of this type the silica units are arranged in the form of hexagonal rings, each of which is surrounded by six similar ones, so that bonding takes place by the silica tetrahedral sharing three corners, as shown in

Each silica unit in the hexagonal sheet is linked to others through an oxygen atom. The Si–O–Si bond angle can vary, thus giving rise to different conformations of the ring structure, but the majority are based on a bond angle of about 141°34. As result, the single oxygen atoms of each silica
tetrahedron which are unsatisfied electrically are oriented in the same spatial direction.

The phenomenon of the Base Exchange was systematically studied to be reversible and to involve equivalent quantities of the base taken up and of that released, nevertheless, it was recognized as the important phenomenon in soil fertility. It was established by Eichorn[9] that Zeolites were responsible for this exchange in soil. According to Lemberg[10,11] and Weigner[12], the material responsible for this phenomenon were mainly zeolites clays, gluconites and humic acid. An investigation for stable ion exchangers may be cationic, anionic or amphoteric. Organic ion exchangers are generally referred as "resin" that have been used in laboratories and industries for separation, metal recovery and water purification. Organic ion exchanger may be cationic, anionic or amphoteric. These resins have higher ion exchange capacity, chemical stability, and uniformity and provide reproducible responses. These resins consist of three dimensional networks of polymeric chains. Cross linked with short chains containing ionizable functional groups.

Organic ion exchangers also suffer from certain limitations. They are unstable in aqueous system at high temperature and in presence of ionizing relations
The selectivity of an ion exchanger is affected by the nature of its functional
group and by the degree of its cross linking. If the degree of cross linking
increases, this enhances its selectivity behavior towards ions of different
sizes. On decreasing in cross linking swelling property of materials will be
increased.

The fundamental principles underlying all ion exchange applications
are based on following facts involving the exchange relations.

(i) Equivalence of exchange

(ii) Ionic mobility restricted to the exchangeable ions and counter ions
     only.

(iii) Screening effect of exchanger.

(iv) Differences in migration rates of absorbed substances down a column
     primarily a reflection of differences in affinity.

(v) Donnan exclusion-the ability, under most conditions of the resin to
    exclude ions but not undissociate substances.

(vi) Swelling surface area and other mechanical properties.

With the advent of the 20th Century, scientific understanding of the
physical chemical mechanisms mediating ion exchange reactions grew in
sophistication of theory and application. Kinetics of exchange reactions in
soils were studied separately by K.K. Gedroiz and D.J. Hissink.
Prominent among the progress made in describing ion exchange reactions were attempts to interpret exchange equilibrium quantitatively by empirical analysis. Alberti \(^9\) developed his ion exchange equation based on H. Kerr's earlier equation (1920), incorporating principles of mass action to describe exchange.

The advent of nuclear technology initiated a search for ion exchange material that would remain stable at high temperature and in high radiation fields. Inorganic ion exchangers of some selected type possess these properties and hence have good application in the treatment of industrial and radioactive waste and processing of radioisotope in nuclear technology. Most of these inorganic ion exchangers have the following qualities to be practically useful:

A. They have good ion exchange capacity.

B. They have high selectivity for certain metal ions.

C. They show rapid sorption and elution behavior.

D. They are virtually insoluble with a reasonable wide pH range.

Systematic and fundamental studies on inorganic ion exchange studies on reignited in 1943. With the discovery of insoluble compound Zirconium phosphate and its application to the separation of uranium plutonium from fission products \(^{10}\) Zirconium phosphate has also been reported to be useful
as adsorbent in the portable artificial kidney device. The most intensively studied group of synthetic inorganic ion exchangers are acidic salt of multiple metals prepared in combination with the anion of arsenate, phosphate etc., as well as two component ion exchangers. The main emphasis has been given to the development of new materials possessing chemical stability.

Reprducibility in ion exchange behavior and selectivity for certain metal ions important from analytical and environmental point of view.

The various monographs and reviews published in this field have been summarized. Most important of which are Fuller, Amphlett, Qureshi, Morinsky, Varshney, Clearfield, Alberti, Ivanov, Terres-Rajas, Szirics, Rawat, Jenny and Parikh and Singh. Recently developments of ion exchange resins with their applications have been reviewed by several researchers. A historical prospective of ion exchange technology has been given by Kunin. The inorganic ion exchangers developed till 1972 are reviewed by Vesely and Pekarek.

During last three decades a large number of inorganic ion exchangers have been synthesized and studied for their analytical applications. Now a days, There is great interest in engineering mixed materials (organic
inorganic) in which features of the organic and inorganic components complement each other, leading to the formation of new solid-state structures and materials with new composite properties\textsuperscript{71}. Zirconium (IV) Phosphate has been widely used as cation exchanger. In the tetrahedral moiety of phosphoric acid, $\text{H}^+$ or $\text{OH}^-$ is replaced by $R$ (where $R=\text{alkyl or aryl}$), phosphoric acids are obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce etc. give rise to metal phosphonates\textsuperscript{72-77}.

1.2 **INTERCALATION BEHAVIOUR**

Intercalated compounds have played an important role in the field of ion exchange phenomenon. These can be synthesized by introducing some amino group or organic molecule in the matrix of inorganic ion exchangers. Intercalation is concerned with the layered crystalline structure of some synthetic inorganic ion exchangers such as the insoluble salts of tetravalent metals.

The intercalating properties were discovered by Michel and Weiss\textsuperscript{78-80}. Zirconium phosphate has a number of superior properties as compared to other intercalating compound. The layered structure of $\text{Zr(HPO}_4)_2 \cdot \text{H}_2\text{O}$ was given by Clearfield and Stynes\textsuperscript{81}. Amine intercalated compound has also drawn much interest due to its ambiguous use, intercalated compound of $\alpha$-Zirconium phosphate with hexa-methylene-tetramine was prepared and
characterized\(^{[83]}\). Intercalation behavior of Titanium Phosphate \(^{[83]}\) and Titanium 2-Carboxyethyl Phosphonate\(^{[64]}\) was studied.

1.3 **INORGANIC ION EXCHANGERS & THEIR DEVELOPMENT**

Inorganic ion exchange materials may be classified as:

1. **Hydrous oxides of polyvalent metals,**
2. **Acidic Salts of polyvalent metals,**
3. **Insoluble Ferrocyanides,**
4. **Alumino Silicates,**
5. **Salts of heteropolyacids.**

Hydrous oxides are of particular interest because most of them can function as both cations and anion exchangers and under certain conditions both cation and anion exchange occur simultaneously. These materials are mostly amphoteric in nature. Acidic salts of multivalent metals are formed by mixing the solution of salts of III and IV group elements of periodic table with the more acidic salts. These salts act generally as cation exchangers. These are gel like or micro crystalline materials and possess mostly a high chemical, thermal and radiation stability.

Insoluble Ferro cyanides can be precipitated by the metal salt solutions with \(H_4[Fe(CN)_6]\), \(Na_4[Fe(CN)_6]\) or \(K_4[Fe(CN)_6]\) solution. They
have good ion exchange capacity, chemical stability and mechanical stability. Alumino Silicates are of three types.

1. Amorphous,

2. Two Dimensional Layered and

3. Three Dimensional Layered.

Heteropolyacid salts are much more important inorganic ion exchanger. Ammonium Molybdophosphate, complex cyanides of various acids Zirconium salts such as phosphates, molybdates and vanadates, hydrous oxides of Zirconium (IV), Antimony (IV), Silicon and Stannic (IV) and a number of basic salts of metals in high oxidation state particularly Zirconium and Titanium [85-88] for a complete description of a material as an ion exchanger. Its physical characterization should be made on the basis of following essentially required properties.

1. Ion exchange capacity,

2. Chemical Composition,

3. Potentiometer studies,

4. Resistance towards acids and bases.

The use of ion exchange materials can be developed by studying kinetics thermodynamics, Distribution of counter ions and analytical applications.
The distribution of an ion between exchanger phase and solution phase can give direct measure of their relative selectivity's. Often the ion exchanger takes up certain ions in preference to other counter ions present in the solution. The selectivity is an important factor for the study of the separations and it may depend mainly on:

1. **Donnan potential,**

2. **Sieve action,**

3. **Complex formation.**

The distribution coefficient is a practical guide to the separation procedure. The rate at which ions move in an exchanger column depends on their distribution coefficient values. Theoretical behavior of ion exchange equilibrium can be described by using thermodynamics. Rigorous thermodynamics is an important method to find out equilibrium between ion exchanger and solution. This requires no models and assumptions about the mechanism of ion exchange phenomena. The properties of any particular model are reflected in forms of the equations obtained and usually also in the physical interpretation in which these equation lead. Hence there is a number of different theoretical approaches.

In the first approach more and more elaborate models are designed for deriving equations which reflect the action of various physical forces. These
models have particular properties resembling those of ion exchangers. These approaches give a semi quantitative picture to understand the physical course of this phenomenon.

In second approach various attempt have been correlate the activities with some measurable quantities with a thermodynamic equations. The earliest approaches were based on semi-empirical or empirical equations. Gans[89] was the first man who made the first quantities formulation of ion exchange equilibrium this concept extended by Kiell, Gains and Thomas[90] have a general treatment using an expression for the calculation of thermodynamic equilibrium constant which is a suitable choice for this purpose.

The kinetic studies of ion exchange were first attempted seriously by Nachood and Wood[91]. They studied the rate of reaction with which ions from solution are removed by a solid ion exchanger.

Some important applications of inorganic ion exchangers are given below:

1. Softening of Water
2. Recovery of Precious Metal
3. Separation of Metal ions
4. Gas Chromatography
5. To preserve dead bodies
6. Specific spot test
7. Location of end point
8. In Catalysis
9. Formation of deionized water
10. Water Pollution
11. Water purification
12. Removal of interfering ions
13. Separations of organic and biologically important substances
14. Preparation of ion selective electrodes and ion exchanger fuel cell.

1.4 CHELATE EXCHANGERS

One of the most important uses of the study of metal chelate formation is the detection and the determination of inorganic ions using chelating agents. The metal chelates formed may be soluble or insoluble, colored or colorless. The chelates, if colored enable the detection by spot test methods. If the colored species is soluble, the reaction can be used profitably for the colorimetric determination[^2] of the inorganic ions. Solubility in water provides an added advantage that solvent extraction is not necessary.

Innumerable colorimetric reagents for inorganic ions have been described in literature, but most of them have been derived by trial and error
methods. Attempts, however, have also been made to correlate their chelating tendencies to yield colored chelates on the basis of the functional groups present.

In colorimetric reactions more compasses have been held on details of the methods of determination, rather than on the nature and the characteristics of the chelates (or complexes) formed in such systems. In these laboratories a comprehensive programme of work by Mush, Ran and Coworkers [93] has been undertaken on the investigation of these color forming reactions especially from the viewpoint of the metal chelates formed in the systems.

On the basis of the nature of charge carried by the chelates it has been possible to suggest the position of the chelates ring in the complexes studied, the following tentative structure for the complexes, which have been found to be anionic in nature have been suggested.

The colored chelates of Uranium (VI) and Vanadium (IV) with pyrogallol red have been reported and studied in detail for the first time in the present thesis. Pan and co-workers and Staroscik and Landgorski have mentioned the use of this reagent for the colorimetric estimation of zirconium, hafnium and indium.
1.5 ELECTRON AND REDOX EXCHANGERS

In addition to the materials mentioned so far, a number of other types of exchangers have been developed for example electron exchanger and redox exchanger. The electron exchanger may be considered as solid oxidation and reducing agents. They are resins with a cross linked hydrocarbon forming a redox couple which can be reversible oxidized or reduced. The electron exchange can be regenerated by a suitable reducing (or oxidizing) agent after having been oxidized (or reduced) by a substrate.

Redox ion exchangers are conventional ion exchange resin containing reversible oxidation-reduction couples such as Fe$^{3+}$/Fe$^{2+}$, Cu$^{2+}$/Cu$^{+}$ and methylene blue etc.$^{[94-102]}$. These redox couples are held by the ion exchange resin. The redox ion exchangers are easily prepared from conventional cation or anion exchangers. Duolite S-10 is the commercial redox exchanger.

The behavior of redox ion exchangers and electron ion exchanger is similar to that of the soluble oxidation reduction couples.

The redox potential of a couple is little affected by incorporation of the couple into a resin.$^{[103-106]}$ They possess some advantage over dissolved oxidizing or reducing agents. The most important advantage is their insolubility and hence they can be easily separated from the solution containing a substrate being oxidized or reduced. No contamination of the
solution by these exchangers occur as only electrons and protons are transferred between the exchanger and solution phases, except for the redox reaction of the substrate is a change in pH. Another advantage is that they can be readily regenerated after use by a suitable reducing or oxidizing agent.

Redox ion exchanger and electron exchangers are characterized by their redox capacity, redox potential and rate of reaction. The redox capacity is the amount of a substrates being oxidized in terms of the mili equivalents per gram of dry resin. The reaction rate determines the time required for the redox process. The redox potential of a couple in solutions is defined as the electric potential difference between the solution of the redox couple and the standard hydrogen electrode. Direct measurement of the redox potential of redox exchanger is not possible. Some inorganic ion exchangers used as adsorbents are summarized in Table 1.2.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Material</th>
<th>Adsorption of</th>
<th>Other Studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Duolite ES-467</td>
<td>Sorption kinetics of Ga from Liquor</td>
<td>Langmuir Isotherm Calculation of $\Delta S^0$, $\Delta G^0$ and $\Delta H^0$</td>
</tr>
<tr>
<td>2</td>
<td>Duolite GT-73</td>
<td>Heavy Metals Toxic Metals such as</td>
<td>Break through curves</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd(^{2+}), Ni(^{2+}), Zn(^{2+}), Cu(^{2+})</td>
<td></td>
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<tr>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>Duolite ES-467, DV-101, C-264</td>
<td>U(^{6+}) &amp; Fe(^{3+})</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Amberlite-CG-50</td>
<td>Mn(^{2+}), Cu(^{2+}) &amp; Cd(^{2+})</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Amberlite IRA-68</td>
<td>Metal Chelates of EDTA</td>
<td></td>
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<tr>
<td>6</td>
<td>Amberlite XAD-7</td>
<td>Human Serum Fe(^{59}), Au(^{195})</td>
<td></td>
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<tr>
<td>7</td>
<td>Levestrel Resin N503</td>
<td>Fe</td>
<td>---</td>
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<tr>
<td>8</td>
<td>IR 200 EX</td>
<td>Base Metals and Precious Metals</td>
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<tr>
<td>9</td>
<td>Biorex-63</td>
<td>U(^{4+}), Th(^{4+}) &amp; Fe(^{2+})</td>
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<tr>
<td>10</td>
<td>Duolite A-113</td>
<td>Univalent ions</td>
<td>---</td>
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<td>11</td>
<td>Dowex 50W-X8</td>
<td>D(_2)O</td>
<td>Best Isotherm &amp; G evolution</td>
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<td>Mordentite</td>
<td>H(_2)O and C(_6)H(_6)</td>
<td>Langmuir and BET equation were studied.</td>
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<td>Silica</td>
<td>Methylene blue and Ethilium bromide</td>
<td>Freundlich Langmuir and Frumkin model.</td>
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<td>Silica gel</td>
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<td>Substance</td>
<td>Coefficients</td>
<td>Methodology</td>
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<td>$U^{5+}$ and $Th^{4+}$</td>
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<td>Adsorption thermodynamics, Freundlich Isotherm, K$\Delta$A$^0$, $\Delta$S$^0$, $\Delta$H$^0$</td>
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<td>Alkali earth metals</td>
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<td>Ferric antimonite</td>
<td>$H^+, Na^+, K^+$ and $Rb^+$</td>
<td>K$\Delta$A$^0$, $\Delta$H$^0$, $\Delta$S$^0$, $\Delta$G$^0$ were calculated</td>
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<td>Zirconium Phosphate</td>
<td>Cs$^{17+}$ and Sr$^{80+}$</td>
<td>$\Delta$S$^0$, $\Delta$H$^0$, and $\Delta$G$^0$ were calculated</td>
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<td>Titanium dioxide</td>
<td>Alkaline earth metals</td>
<td>Distribution studies</td>
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<td>$\alpha$-MnO$_2$</td>
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<td>Cl$^-$, ClO$_4^-$, SO$_4^{2-}$, H$_3$PO$_4^-$, NO$_3^-$</td>
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<td>Traces Ag$^+$ from acidic solution</td>
<td>Kinetics and Thermodynamics</td>
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<td></td>
<td>Amino ethylene Phosphoric acid resins</td>
<td>Dy (III)</td>
<td>$\Delta G, \Delta H, \Delta S$</td>
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<td>Freundlich Isotherm</td>
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<td>Chelating resin containing</td>
<td>U from Sea water</td>
<td>$\Delta G, \Delta S$, Freundlich Isotherm</td>
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</tbody>
</table>
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