Chapter 2

LITERATURE REVIEW
The presence of high levels of hexavalent chromium in surface water, groundwater, and soil has become a major concern. Health hazards due to hexavalent chromium have been widely reported around the globe. Yet, hexavalent chromium toxicity has no known effective treatment. Therefore, the most important measure needed is to prevent further environmental pollution of chromium and develop treatment processes for contaminated water and soils.

In view of the above circumstances, the development of suitable treatment systems for hexavalent chromium removal from industrial wastewater appears to be the most promising option. The treatment options should be effective, reliable and affordable for chromium removal from the wastewaters.

The common methods of treatment include

**2.1 REDUCTION OF Cr(VI) TO Cr(III)**

**2.1.1 General**

Cr (VI) is a strong oxidant and therefore can be reduced in the presence of electron donors. The most common forms of chromium dissolved in natural waters, within the environmentally normal range of pH, are \( \mathrm{CrO}_4^{2-} \), \( \mathrm{HCrO}_4^- \) and \( \mathrm{Cr}_2\mathrm{O}_7^{2-} \) ions\(^1\), which form many of the Cr(VI) compounds that can be quite readily reduced to Cr(III) forms in the presence of electron donors like organic matter and inorganic compounds in their reduced state, many of which are quite common in soil, water and the atmosphere. The reduction of Cr (VI) by soil humic and fulvic acids has been demonstrated by several researchers. Cr (VI) can be reduced by biological and chemical (abiotic) processes. It is difficult to determine that which processes are responsible for the reduction of metal contaminants. By comparing the reduction rates involving Fe (II) and sulfides with those reported for direct microbial reduction, the chemical reduction of chromate by Fe (II) is more than 100 times faster than the observed biological reduction rate.

**2.1.2 Chemical Precipitation**

Chemical precipitation is an effective and the most widely used process in industry because it is relatively simple and inexpensive to operate. The removal of Cr (VI) by chemical reduction from industrial waste water involves a two-step process:
reduction of Cr (VI) under acidic conditions (usually pH 2 to 3) and the precipitation of trivalent Chromium as hydroxyl species. The most commonly used reducing agents are gaseous sulphur dioxide, sodium sulfite, sodium meta bisulphite, ferrous sulphate, barium sulphite [2,3].

2.1.2.1 Hydroxide Precipitation

Lime and Limestone are the commonly employed precipitating agents due to their availability and low-cost in most of the countries [4]. Lime precipitation can be employed to effectively treat the inorganic effluent with a metal concentration of higher than 1000 mg/l.

\[ M^{2+} + 2(OH)^{-} \rightarrow M(OH)_2 \]

Maximum precipitation of Cr (III) was occurred at pH 8.7 with the addition of Ca(OH)\(_2\) from the maximum concentration of Chromate of 30 mg/l. To enhance lime precipitation, fly ash was used as a seed material [5]. The fly ash-lime-carbonation treatment increases the particle size of the precipitate and significantly improved the efficiency of heavy metal removal. Although widely used, hydroxide precipitation also has some limitations. Those are (i) Hydroxide precipitation generates large volumes of relatively low density sludge, which can prevent dewatering and disposal problems [6]. (ii) Some metal hydroxides are amphoteric and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into the solution (iii) When complexing agents are in the waste water, they will inhibit metal hydroxide precipitation.

2.1.2.2 Sulphide Precipitation

The sulphide precipitation is also an effective process and is more advantageous over hydroxide precipitation. The solubility of metal sulphide precipitates is dramatically lower than hydroxide precipitates and sulphide precipitates are not amphoteric. The other advantage of sulphide precipitation is, that it can reduce hexavalent chromium to the trivalent state under the same process conditions required for the metal precipitation, it allows for the precipitation of metals when chelating agents are present and most metals can be removed to extremely low concentrations at a single pH. Limitations of the process involve the potential hydrogen sulphide gas evolution and the concern for
sulphide toxicity. However eliminating sulfide reagent overdose prevents the formation of the odor causing hydrogen sulfide. Nowadays, a combination of hydroxide and sulfide precipitation for optimal metals removal is being well considered. A common configuration is a two-stage process in which hydroxide precipitation is followed by sulfide precipitation with each stage followed by a separate solids removal step. This will produce the high quality effluent of the sulfide precipitation process while significantly reducing the volume of the sludge generated and the consumption of the sulfide reagent.

2.1.3 Ion exchange

Among the physicochemical methods developed for the chromium removal from waste water, ion exchange processes have been widely used to remove heavy metals due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [7]. This is a promising technique based on the adsorption/exchange of cations or anions on synthetic resins with essential characteristics of its regeneration after elution/release of ions. The most common cation exchangers are strongly acidic resins with sulphonic groups (-SO_3H) and weakly acid resins with carboxylic acid groups (-COOH). Hydrogen ions in the sulphonic group or carboxylic group of the resin can serve as the solution containing heavy metal, passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process.

\[
\text{nR-SO}_3\text{H} + \text{M}^{n+}-(\text{R-SO}_3\text{)-}_n\text{M}^{n+} + \text{nH}^+
\]

\[
\text{nR-COOH} +\text{M}^{n+}-(\text{R-COO-})_n\text{M}^{n+} + \text{nH}^+
\]

Among the materials used in ion-exchange processes, synthetic resins are commonly preferred, as they are effective to remove the heavy metals from the solution. The commercial cation exchange resins are based on the carboxylic acid functionality with acrylic matrix (Purolite C105 and C106) and sulphonic acid functionality with styrene matrix (Amberlite IR120, Amberlite 252). The resin used is a strongly basic type I quaternary ammonium anion exchange resin with a styrene-divinyl benzene copolymer gel matrix.
Table 2.1 Comparative performance of various ion exchangers in the remediation of chromium

<table>
<thead>
<tr>
<th>Ion-exchangers</th>
<th>Chromium concentration</th>
<th>Experimental conditions</th>
<th>Removal efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IR 120</td>
<td>20 mg/l</td>
<td>pH 5.5</td>
<td>68.2%</td>
<td>Kacaoba (2005)</td>
</tr>
<tr>
<td>Purolite C106</td>
<td>-</td>
<td>Acidic, Saline</td>
<td>-</td>
<td>Petruzelli (1997)</td>
</tr>
<tr>
<td>Chelax-100</td>
<td>2mM</td>
<td>Basic, saline</td>
<td>100%</td>
<td>Chanda (1997)</td>
</tr>
<tr>
<td>Natural exchangers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinoptilolite(C)</td>
<td>100 mg/l</td>
<td>Surface area 20-2 gm²/g</td>
<td>100% 90%</td>
<td>Alveraz (2003)</td>
</tr>
<tr>
<td>Synthetic Zeolite</td>
<td>2.5 g/l</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dowex 2-X4</td>
<td>9.8 mg/l</td>
<td>Strongly basic</td>
<td>100%</td>
<td>Sapari (1996)</td>
</tr>
<tr>
<td>Indion-790</td>
<td>500 mg/l</td>
<td>pH 0.5-3.5</td>
<td>100%</td>
<td>S.K.Sahu (2009)</td>
</tr>
<tr>
<td>Ambersep 132</td>
<td>750 mg/l</td>
<td>strongly basic</td>
<td>-</td>
<td>Lin (2003)</td>
</tr>
</tbody>
</table>

2.1.4 Membrane Separation

A membrane is a semi permeable barrier between two phases, which restricts the movement of ions/molecules in a very specific manner. These movements are based on the size exclusion, differences in diffusion coefficients, electrical charge and solubility. Membrane processes are often governed by the driving forces to effect separation like micro, ultra, and nano-filtrations and reverse osmosis by hydrostatic pressure, dialysis by concentration gradient, electro dialysis by electric potential and gas permeation by pressure and concentration gradients.
Ultra filtration (UF) utilizes permeable membrane to separate heavy metals, macro molecules and suspended solids from inorganic solution on the basis of pore size and molecular weight of the separating compounds. These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macro molecules, which have a size larger than the pore size of the membrane [8]. Liquid membranes have been proved to be an effective and inexpensive method with the potential application for the removal of heavy metals. There are two basic types of liquid membranes, Emulsion Liquid Membrane (ELM) and Immobilized Liquid Membrane (ILM), also called as a Supported Liquid Membrane (SLM).

2.1.5 Electrochemical treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical waste water technologies involve relatively large capital investment and the expensive electricity supply, so, they haven’t been widely applied. Electro coagulation (EC) involves the generation of coagulants in situ by dissolving electrically either aluminium or iron ions from aluminium or iron electrodes [9]. The metal ion generation takes place at the anode and hydrogen gas is released from the cathode. The hydrogen gas can help to float the flocculated particles out of the water. Some studies using electrochemical precipitations (ECP) was carried out for the removal of Cr (VI) from the real electroplating waste water. Kongsricharoern and Polprasert [10] investigated the Cr (VI) removal from the electroplating waste water using the ECP process. In this process the Cr (VI) concentration remaining in the effluent was less than 0.2 mg/l. Electro dialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and the cation-exchange membranes.
2.1.6 Photocatalysis

In the recent years, photocatalytic process in aqueous suspension of semiconductor has received a considerable attention in view of solar energy conversion. This photocatalysis was achieved for rapid and efficient destruction of environmental pollutants. Upon illumination of semiconductor-electrolyte interface with light energy greater than the semiconductor band gap, electron-hole pairs (e-/h+) are formed in the conduction and the valence band of the semiconductor, respectively [11]. These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in the solution having suitable redox potential.

![Fig 2.1 The conceptual reaction path of photocatalysis over TiO2](image)

Photocatalytic reduction of Cr (VI) over TiO2 catalysts was investigated in both the absence and presence of organic compounds [12]. The results demonstrated that the photocatalytic reduction of Cr (VI) alone was dependent on both the specific surface area and crystalline structure of the photo catalyst in the absence of any organic compounds, but was dominated by the specific surface area of the photo catalyst in the presence of organic compounds because of the synergistic effect between the photo catalytic reduction of Cr(VI) and the photo catalytic oxidation of organic compounds.
Table 2.2 Photoreduction process in remediation of chromium

<table>
<thead>
<tr>
<th>Photoreduction removal efficiency</th>
<th>Chromium concentration</th>
<th>Experimental conditions</th>
<th>Removal efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-Polyoxometallates</td>
<td>5-100 ppm</td>
<td>-</td>
<td>98%</td>
<td>Gkika et al (2006)</td>
</tr>
<tr>
<td>OS-Salicylic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immobilised and anodized TiO₂</td>
<td>2 ppm</td>
<td>pH&lt;2</td>
<td>98%</td>
<td>Yoona et al (2008)</td>
</tr>
<tr>
<td>electrodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1.7 Adsorption

Adsorption offers significant advantages like low cost, availability, profitability, ease of operation and efficiency, in comparison with the conventional methods (such as membrane filtration and ion exchange) especially from economical and environmental points of view.

2.1.7.1 Adsorption on natural materials

Natural Zeolites gained a significant interest, mainly due to their valuable properties as anion exchange capability. NaA zeolite is used for Cr(III) at neutral pH [13] whereas Barakat et al used 4A zeolite which was synthesized by dehydroxylation of low grade Kaolin. Barakat reported that Cr (VI) was adsorbed at acidic pH. The affinity of soils and sediments for the adsorption of Cr (VI) varies widely depending on the composition. The natural clay minerals can be modified with a polymeric material in a manner that this significantly improves their capability to remove heavy metals from aqueous solutions. Adsorption of Cr (VI) onto aquifer sediment whose grain surfaces were coated with Fe and Al containing hydrous oxides was significantly extensive than expected from adsorption onto pure hydrous oxides of Fe or Al [14].

2.1.7.2 Activated carbon adsorbents

Activated carbon adsorbents are used widely in the removal of heavy metal contaminants in product purification and pollution control. The two types of activation, thermal/physical or chemical activation, impart a porous structure within a starting material of relatively low surface area. Cr(VI) was more effectively adsorbed by acid
treated activated carbons. However, base treated activated carbons were not effective Cr(VI) adsorbents, probably due to the decrease of specific surface area. Selomulya et al [15] used different types of activated carbons, produced from coconut shells, wood and dust coal to remove Cr(VI) from synthetic waste water. Several activated carbons were prepared from *Terminalia arjuna* nuts, an agricultural waste, by chemical activation with Zinc Chloride and then tested for aqueous Cr(VI) removal. Bishnoi et al [16] conducted a study on Cr(VI) removal by rice-husk activated carbon from an aqueous solution. They found the maximum metal removal by rice husk took place at pH 2.0. Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for Cr(VI) removal from simulated solution[17]. To enhance its metal removal, the adsorbent was modified with ethylene diamine. The maximum Cr(VI) adsorption of 23.4 mg/g was reported to take place at pH 2.

### 2.1.7.3 Chitosan

Chitosan is also known as the excellent adsorbent and its applicability for heavy metal removal is attributed to high hydrophilicity of chitosan due to a large number of hydroxyl groups, a large number of primary amino groups with high activity and flexible structure of polymer chain of chitosan making a suitable configuration for adsorption of metal ions.

### 2.1.8 Bioremediation

#### 2.1.8.1 Bioreduction

The processes that control the environmental chemistry and fate of Cr include adsorption, redox transformations and precipitation reactions. Biological approaches utilizing microorganisms offer the potential for a highly selective removal of toxic metals coupled with considerable operational flexibility, hence they can be both *insitu* or *ex situ* in a range of bioreactor configurations. Microbes, especially bacteria capable of Chromium (VI) reduction exhibits plasmid-mediated chromate resistance and the reduction is enzymatically mediated [18]. Biological activity of some of the bacteria and fungi can adsorb an effective means of detoxification of effluents. Bacterial chromate reductases can convert soluble and toxic chromate to the insoluble and less toxic Cr(III). Bioremediation can therefore be effective in removing chromium from the environment,
especially if the bacterial propensity for such removal is enhanced by biochemical engineering.

Under aerobic, field-moist conditions, soil rich in organic matter could reduce 96% of Cr (VI), demonstrating the importance of the presence of soil microorganisms in conjunction with a readily available carbon source. Because the insolubility of Cr (III) facilitates its precipitation and removal, the biotransformation of Cr(VI) to Cr(III) has been considered as an alternative process for treating Cr(VI) contaminating wastes. A number of bacteria in other genera, viz. Bacillus spp., E.Coli ATCC 33456, Shewanella alga BrY-MT and a few unidentified strains have also been shown to reduce Cr(VI). Ackerley et al [19] described ChrR as a dimeric flavoprotein catalyzing the reduction of Cr(VI) optimally at 70°C. In the presence of oxygen, bacterial Cr(VI) reduction commonly occurs due to the presence of NADH, NADPH and electron from the endogenous reserve which are implicated as electron donors in the Cr(VI) reduction process [20].

Earlier investigations on the biotransformation of Cr(VI) focused on the facultative anaerobes such as Ps.dechromaticans, Ps.chromatophila and Aeromonas dechromatica. A number of chromium resistant micro-organisms were subsequently isolated, such as B.Cereus, B.subtilis, Ps.aeruginosa, Ps.ambigua, Ps.flourosrens, E.coli, Achromobacter Eurydice, micrococcus roseus, enterobacter cloacae, desulphovibrio desulfuricans and D.vulgaris. The radiation-resistant Dienococcus radiodurans R1[21], a close relative of Thermoanaerobacter ethanolicus isolated from deep subsurface sediments and pyrobaculum islandicum [22] have been found to reduce Cr(VI) at high temperature.

2.1.8.2 Phytoremediation

Phytoremediation is an ecofriendly approach for the remediation of contaminated soil and water using plants comprised of two components, one by the root colonizing microbes and the other by plant themselves, which accumulates the toxic compounds to further non-toxic metabolites. Phytoremediation is the emerging technology for cleaning up the contaminated sites, which combines the disciplines of plant physiology, soil chemistry and soil microbiology. It is cost effective and has aesthetic advantages and
long term applicability. It is best applied at sites with shallow contamination of organic, nutrient or metal pollutants that are amenable to one of the five applications: phytotransformation, rhizosphere bioremediation, phytostabilization, phytoextraction and rhizofiltration. After sufficient plant growth and metal accumulation, the above ground portion of the plant are harvested and removed, resulting in the permanent removal of metals from the site [23].

Certain species of higher plants can accumulate very high concentrations of metals in their tissues without showing toxicity. Such plants can be used successfully to clean up heavy metal polluted soils if their biomass and metal content are large enough to complete remediation within a reasonable period. For this cleanup method to be feasible, the plants must (i) extract large concentrations of heavy metals into their roots, (ii) translocate the heavy metal into the surface biomass and (iii) produce a large quantity of plant biomass. Over 400 hyper accumulator plants have been reported and include members of *Brassicaceae, Fabaceae, Euphorbiaceae, Asteraceae, caryophylllaceae, Lamiaeceae and Scrophulariaceae*. Dushenkov et al [24] observed that the roots of many hydroponically grown terrestrial plants such as Indian mustard (*B.juncea (L)czem*) and sunflower (*H.annus L*) effectively removed chromium from aqueous solutions. Some plant species such as *Sutera fodina, Dicomaniccolifera* and *Leptospermum scoparium*, have been reported to accumulate Cr to high concentrations in their tissues.

Rhizosphere, as an important interface of soil and plant, plays a significant role in the phytoremediation of contaminated soil by heavy metals, in which, microbial population are known to affect heavy metal mobility and availability to the plant through release of chelating agents, acidification, phosphate solubilization and redox changes and therefore, have the potential to enhance phytoremediation processes. Some rhizobacteria can release a class of rhizobacteria secretion, such as antibiotics, phosphate solubilization, hydrocyanic acid, indole acetic acid (IAA), siderophores, 1-aminocyclopropane-1-carboxylic acid(ACC) deaminase which increase bioavailability and facilitate root absorption of heavy metals. The highest incidence of the biochemical activity of isolates and metal resistance was recorded for: phosphate solubilizers with 92.5% of Cr, siderophore producers with 78.5% of Cr and finally for acid producers with 63.5% of Cr.
However, most of the above mentioned treatment technologies have limitations which include one or more of the following [25]:

Generation of toxic sludge,

Increased overall cost of the process due to treatment, handling and disposal of sludge,

High operational and maintenance expenditure,

High energy requirements,

Requirement of new infrastructure,

Too long treatment time,

Poor removal efficiency,

Negative impact on water quality parameters,

Requirement of additional chemical
Table 2.3 Comparative performance characteristics, advantages & disadvantages of various methods in remediation of chromium

<table>
<thead>
<tr>
<th>Method</th>
<th>pH range</th>
<th>Metal selectivity</th>
<th>Working level (ppm)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxide precipitation</td>
<td>Tolerant</td>
<td>non-Selective</td>
<td>&gt;10 00</td>
<td>low capital cost, simple operation.</td>
<td>sludge generation, extra operational cost</td>
</tr>
<tr>
<td>Sulphide precipitation</td>
<td>Limited</td>
<td>Tolerant</td>
<td>&gt;10</td>
<td>no secondary waste generation.</td>
<td>Toxic gas intermediate, gas delivery to aquifier is difficult.</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Limited</td>
<td>Tolerant</td>
<td>&lt;10</td>
<td>wide variety of target pollutants, low cost</td>
<td>performance depends on type of adsorbent,</td>
</tr>
<tr>
<td>Electrochemical Treatment</td>
<td>Tolerant</td>
<td>moderate</td>
<td>&gt;10</td>
<td>No additional chemical reagents required</td>
<td>Spongy deposit production of sludge</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>Limited</td>
<td>selective</td>
<td>&gt;100</td>
<td>Removal of metals, organic pollutants simultaneously</td>
<td>Long duration time, limited applications.</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>Limited</td>
<td>Non-selective</td>
<td>&gt;10</td>
<td>Low solid waste generation, low chemical consumption</td>
<td>High initial cost, high maintenance cost, limited flow rates.</td>
</tr>
<tr>
<td>Bioremediation</td>
<td>Limited</td>
<td>Non-selective</td>
<td></td>
<td>Cost effective, low price, minimization of chemical and possibility of metal recovery</td>
<td>Not applicable to synthetic waste, no recycling</td>
</tr>
<tr>
<td>Phytoremediation</td>
<td>Tolerant</td>
<td>Non-selective</td>
<td>&gt;100</td>
<td>Eco-friendly, high accumulation rate</td>
<td>Long duration time, phytotoxic at high concentrations.</td>
</tr>
</tbody>
</table>

2.2 NANO-SCALED ZEROVALENT IRON

Iron is a transition metal with atomic number 26. It is placed in group 8 and period 4 of the periodic table. It possesses several isotopes but the most important ones are: radioactive $^{54}\text{Fe}$ with half-life $>3.1 \times 10^{22}$ years (5.8%), stable $^{56}\text{Fe}$ (91.72%), stable $^{57}\text{Fe}$ (2.2%), and stable $^{58}\text{Fe}$ (0.28%). The oxidation states and reduction potentials of iron are shown in Figure 2.2.
Iron is the sixth-most abundant element in the world. It is a very reactive element and is oxidized very rapidly and as a result it usually exists in nature in the form of magnetite (Fe$_3$O$_4$) and hematite (Fe$_2$O$_3$). Iron is an essential element for living organisms through facilitating oxygen transport on the haemoglobin and myoglobin proteins as it can bind oxygen easily via redox reaction. Low iron limits in blood can cause anemia. Excess amount of iron can, however, be toxic because free ferrous iron reacts with peroxides to produce free radicals that can damage DNA. Iron Tolerable Upper Intake Level (UL) for adults is 45 mg/day, for children under fourteen, UL is 40 mg/day.

![Standard reduction potentials of iron species](image)

**Fig 2.2 Standard reduction potentials of iron species**

There are reports that zero valent iron has great activity towards contaminants by its high reducing character. When zero valent iron is synthesized in nano scale its surface area and reactivity increases largely. This increase in reactivity can amount to 30 times that of iron powder [26]. The surface area-size relationship is demonstrated in Figure 2.3.
Synthesis of nanoscale zero-valent iron methods can be achieved by a variety of physical and chemical synthetic techniques. A summary of these techniques was recently outlined in a review paper on the topic by Li and coworkers [27]. Liquid phase reduction method is among the most common method. In this method Fe$^{2+}$ and Fe$^{3+}$ ions are reduced to zero-valent iron with sodium borohydride, a strong reducing agent. Because of this, liquid phase reduction method is also called as borohydride reduction. This method is very simple because it needs only two common reactants without a need to any special equipment [28]. The reduction process is thought to occur through the reaction:

\[
\text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{Fe}^0 + 2\text{B(OH)}_3^- + 7\text{H}_2\uparrow
\]

The synthesized nano zero valent iron (ZVNI) particles are usually in spherical shape and have a core-shell structure. The ZVNI particles are unstable in atmospheric conditions and it tends to form oxides/hydroxides in the forms Fe$_2$O$_3$, Fe$_3$O$_4$ and FeOOH. The shell consists of oxides and hydroxides and the core consists of Fe$^0$ [29].

This structure is conceptualized in the model given in Fig. 1.6. The oxide shell has a thickness of about 5 nm and consists of iron oxide [30]. Alternatively, Wang, et al. stated that the surface of ZVNI is mainly an iron-boron noncrystalline alloy and that the slow oxidation of the nanoparticles can be ascribed to this [31]. The core of the nanoparticle forms the source of electrons in the redox reaction. The shell also plays an important role in the fixation of ions by the external surface of the nanoparticles. The overall process can be thought to consist of three mechanisms [32]. These mechanisms
are: (i) physical sorption that takes place for cations having standard reduction potential, \(E_0\), that is more negative than or close to that of Fe, (ii) both sorption and chemical reduction arises for cations having \(E_0\) slightly more positive than that of Fe and (iii) only chemical reduction occurs for cations with \(E_0\) higher than that of Fe.

Fig 2.4 A model for core-shell structure of ZVNI and uptake mechanisms of metals

So far, ZVNI has been tested under laboratory conditions for the destruction, stabilization, and/or removal of a variety of chemicals. These include various organic compounds and inorganic cations/anions. Among the organic compounds, chlorinated hydrocarbons [33], polychlorinated biphenyls, chlorinated ethenes, heavy metals such as Pb\(^{2+}\), Cr\(^{6+}\), Ni\(^{2+}\), As\(^{3+}\), As\(^{5+}\), Cd\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\) and Ba\(^{2+}\) and inorganic anions, nitrate, sulphate, phosphate [34]. The high remediation efficiency of ZVNI is mainly attributed to its high surface area to volume ratio, high levels of surface defects, high density of reactive surface sites and greater intrinsic reactivity of surface sites, which make the nanoparticles very reactive in the degradation of the contaminants.

2.3 NANOPARTICLE SYNTHESIS

The nano-scale represents an incredibly small particle size and while these aggregate sizes can be achieved through conventional mechanical grinding, nano-scale size synthesis is extremely energy intensive and difficult to produce consistent results. In order to achieve a particle diameter within the nano-scale without resorting to mechanical means, one must adopt a chemical approach, of which there are three primary methods
commonly used. Each requires the ZVNI to be reduced and precipitated out from aqueous iron salts through the utilization of sodium borohydride [35].

### 2.3.1 Vapour Phase Nanoparticle Synthesis

Vapour-phase synthesis of nanoparticles is an example of a synthetic technique that induces particles to form a vapour-phase mixture that must be thermodynamically unstable in favour of the solid phase. What often results when such conditions are present is the formation of a supersaturated vapour that can then be induced to precipitate or nucleate, nanoparticles. For nucleation to occur homogeneously the supersaturated vapour must be of a high degree of saturation and the condensation reaction kinetics must be favourable [36]. In order to manage the growth of newly forming nanoparticles there must be a high degree of control over the reaction kinetics.

#### 2.3.1.1 Flame Synthesis

The production of nanoparticles by flame synthesis is reportedly the most prolific method in use today with approximately 100 metric tons being produced daily throughout the global industry [37]. As the name suggests that the synthesis of nanoparticles is conducted within the flame and as such the coupling of particle production to flame chemistry makes for a very complex process [38]. While the process is very complex and requires a fine degree of control, the apparatus is relatively simple and lends itself to a wide range of nanoparticle types that can be produced by this method. Though it does not appear that ZVNI is manufactured by this method at this time, iron oxide nanoparticles have been produced by the flame synthesis technique.

#### 2.3.1.2 Chemical Vapour Synthesis

For chemical vapour synthesis of nanoparticles, vapour-phase base materials or precursors are added to a hot-walled reaction vessel under conditions that favour nucleation instead of precipitating a thin film layer on the reactor wall [39]. With so many potential precursor additives there exists a wide range of possible nanoparticles that can be synthesized by this method.
2.3.1.3 Physical Vapour Synthesis

The category of physical vapour synthesis techniques encompasses those methods by which nanoparticles are produced from a vapour phase by physical means, as opposed to the thermodynamically induced nucleation reactions of the chemical vapour synthesis methodologies.

2.3.1.4 Inert Gas Condensation

The process of producing nanoparticles by means of inert gas condensation operates by heating a solid to the point of evaporating it into a gas, at which point the vapour is mixed with a cold gas to reduce the temperature, thus producing the desired nanoparticles (Figure 2.5).

![Fig 2.5 Schematic of inert gas condensation method for synthesizing nanoparticles](image)

2.3.1.5 Pulsed Laser Ablation

When the desired solid source material is difficult to vaporize, one option would be, to adopt a pulsed laser ablation nanoparticle synthesis method. In this method the solid source is vaporized by subjecting it to a pulsed laser that produces a narrowly confined plume of vapour, though it is difficult to produce significant quantities of nanoparticles through these means.
2.3.1.6 Spark Discharge Generation

Spark discharge generation is not unlike the pulsed laser ablation method for producing nanoparticles as both look to vaporize the source metal, but in this case that source must first be made into electrodes that are placed against an inert background gas and have an electric arc formed between the electrodes. This arc vaporizes a small amount of the metal electrodes, producing a small quantity of nanoparticles that can be reliably reproduced (Fig 2.6).

Fig 2.6 Spark discharge schematic for nanoparticle synthesis

2.3.1.7 Sputtering Gas Aggregation

Baer et al [36] described the highly complex sputtering gas aggregation nanoparticle synthesis technique that they used for the production of nano scale iron for their research. The method uses a combination of magnetron-sputtering and gas aggregation techniques to produce nanoparticles of a smaller size than can generally be produced by other vapour deposition techniques. The apparatus they describe is largely composed of three parts, those being, (1) a cluster source, (2) an e-beam evaporation chamber and (3) a deposition chamber. Figure 2.7 shows a schematic of the apparatus.
2.3.2 Solution Phase Nanoparticle Synthesis

For solution-phase synthesis of nanoparticles a typical process involves the application of a metal salt solution to a solid support material. After a period of time the solution is removed and the metal ions are treated to produce the nanoparticles whether they are metal, metal oxides or metal sulphides [36]. It is solution phase synthesis, specifically the variation of Micellar techniques, wherein nano-scale zero valent iron is produced by borohydride reduction, which is the most prolific form of ZVNI production in the reviewed literature.

2.3.2.1 Micellar Techniques

Micellar techniques for synthesizing nanoparticles include “normal” oil in water method and “reverse” water in oil method, both of which operate by having a surfactant dissolved into a continuous phase while a second phase is mixed with the dissolved surfactant to create a thermodynamically stable, homogeneous solution [36]. While this solution appears clear and uniform it is actually composed of monodispersed droplets of the phase that was added to the continuous phase. It is a variation of this process that was pioneered by Lehigh University, using both their chloride and sulfate methods that have become among the most prolific techniques for producing specifically ZVNI.

Fig 2.7 Schematic of three chambered apparatus used for sputtering gas aggregation nanoparticle synthesis
2.3.2.1 a) The Chloride Method

This method for producing ZVNI was the first to be used when ZVNI experimental and field trials were being conducted at Lehigh University [35] and is also referred to as the Type I ZVNI method. The following description illustrates the procedure and outlines the reaction processes involved when producing ZVNI by means of the chloride method, as carried out by Elliott et al [35]. In their synthesis these researchers added 0.25 molar (M) sodium borohydride to 0.045 M ferric chloride hexahydrate in an aqueous solution and proceeded to mix the two vigorously, so that the volumes of both the borohydride and ferric salt solutions represented a 1:1 volumetric ratio. The mixing time for their procedure was approximately one hour. The reaction equation describing the chemical processes for this synthesis is shown as

\[4\text{Fe}^{3+}(\text{aq}) + 3\text{BH}_4^-(\text{aq}) + 9\text{H}_2\text{O}(l) \rightarrow 4\text{Fe}^0(\text{s}) + 3\text{H}_2\text{BO}_3^- (\text{aq}) + 12\text{H}^+(\text{aq}) + 6\text{H}_2(\text{g})\]

In this method a large excess of borohydride, about 7.4 times that of the stoichiometric requirements for the reaction was utilized. They believed that it was this excess that was able to help ensure the rapid and uniform growth of ZVNI crystals. By following the mixing phase of the synthesis procedure the newly formed ZVNI particles were then washed with large quantities of distilled water, reportedly in excess of 100 mL/g. In order to recover the ZVNI the material was treated using vacuum filtration, followed by a wash with ethanol. The remaining residual water content of the nanoparticle mass was observed to be typically in the range of 40–60%. At this point the ZVNI would be considered fully synthesized, unless the remediation experiments utilizing the iron required bimetallic particles, as some researchers investigated [35]. For producing bimetallic particles, the researchers describe a procedure in which the ethanol-wet ZVNI was soaked in an ethanol solution containing approximately 1% palladium acetate. This is represented in the following equation.

\[\text{Pd}^{2+} + \text{Fe}^0 \rightarrow \text{Pd}^0 + \text{Fe}^{2+}\]

2.3.2.1 b) The Sulfate Methods

The sulfate method for producing ZVNI was also developed at Lehigh University as an answer to some of the problems associated with synthesizing nanoparticles by the
These problems were reported to be (1) the hazardous nature of handling the very acidic and hygroscopic ferric chloride salt and (2) the potentially negative effects of chloride present in the ZVNI matrix when attempting to use it for the remediation and dechlorination of hydrocarbons. It was also reported that in using Fe(II), instead of Fe(III) as in the chloride method, the sulfate method might favour a better reaction economy, though it is not known whether this aspect of the reaction mechanisms was actually investigated or not. This method of producing ZVNI was the second, to be developed at Lehigh University and is thus often referred to as the Type II ZVNI method. The following description illustrates the procedure and outlines the reaction processes involved when producing ZVNI by means of the sulfate method, as carried out at Lehigh University. In their synthesis Elliott and his colleagues prepared equal volumes of 0.50 M sodium borohydride, introduced at 0.15 L/min into 0.28 M ferrous sulfate and generated the reaction whose equation is presented below.

\[
2\text{Fe}^{2+}(\text{aq}) + \text{BH}_4^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Fe}^0(\text{s}) + \text{H}_2\text{BO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{H}_2(\text{g})
\]

The resulting borohydride excess, for the Type II synthesis method was reported to be only 3.6 times that of the stoichiometric requirements, as opposed to the 7.4 multiple from the chloride method production and so the processing duration was increased from 1 hour to 2 hours to better control of particle size. The procedure for the sulfate method was described to use much of the same equipment as with the chloride method. Once the mixing phase of the synthesis procedure was done, the ZVNI particles were left to settle out for an hour before being extracted, as was the case with the Type I ZVNI method, by vacuum filtration. As before, the newly extracted ZVNI particles were washed with in excess of 100 mL/g of distilled water and then again with ethanol. Next the particles were repeatedly purged with nitrogen and finally sealed in a polyethylene container under ethanol and refrigerated for the storage. The residual water content of ZVNI observed the following use of the sulfate method was of the order of 45–55%, while the chloride method left 40-60% residual water content within the ZVNI.

The Lehigh University research group also developed a third ZVNI product that utilized the sulfate method of synthesis that is known as the Type III ZVNI method. The procedures for Type II and Type III ZVNI synthesis are reportedly very similar with the
notable exception that the Type III ZVNI product has only 20-30% residual moisture content as compared with the Type I and II products that were reported to have typically 40-60% residual moisture contents.

2.3.3 Hydrothermal Synthesis

Hydrothermal synthesis of nanoparticles is another technique that utilizes metal salts. In this case the reaction occurs within the high temperature water contained within a pressure vessel to produce metal oxides by the hydrolysis of the metal ions [36]. Though applicable in batch reactions, Darab and Matson [40] described a technique whereby the hydrothermal synthesis of nanoparticles (zirconium, titanium and iron based oxide and oxyhydroxide particles) is achieved by a continuous process that has the salts and reactants pass through a heated reaction pipe and ejected through a nozzle at the end of the apparatus [40].

Stabilization of ZVNI

Perhaps the most significant challenge to applying ZVNI for remediation is their tendency to react rapidly with their surrounding media (e.g., dissolved oxygen or water) or agglomerate rapidly, resulting in the formation of much larger particles and rapid loss in the reactivity, rendering them undeliverable to the targeted contaminant locations. Agglomeration occurs due to attractive interparticle van der Waals and magnetic forces. The effect of agglomeration is two-folds, first, the available reactive surface area of the ZVNI particles is significantly reduced, negatively impacting reactivity and second the transport of the larger aggregates in porous media is severely restricted. Two approaches have been commonly used in the preparation of ZVNI: electrostatic repulsion and steric stabilization. Electrostatic repulsion is achieved by imparting or increasing the surface charge while steric stabilization is typically attained by the adsorption of long-chain organic molecules (e.g., surfactants). Large polymeric molecules also carry charges (e.g. polyelectrolytes) creating combined electrosteric repulsion and consequently enhancing ZVNI stability.
The attached stabilizer molecules are designed to provide strong interparticle electrostatic and/or steric repulsions to outweigh the attractive van der Waals and magnetic forces. To stabilize ZVI nanoparticles, two general strategies have been employed: (i) the application of stabilizers before the nanoparticles or aggregates are formed (pre-agglomeration stabilization) or (ii) to mechanically break down the formed nanoparticle agglomerates and add a stabilizer (post-agglomeration stabilization). As a result, to prepare more physically stable and chemically reactive ZVNI, the new processes are being investigated using stabilizers such as Cetyl Pyridinium Chloride (CPC), starch, hydrophilic carbon, Poly acrylic acid, as well as other surfactants and Polymers. Polyacrylic acid (PAA) was used for (pre-agglomeration) stabilizing Fe based nanoparticles and observed the improved transportability of PAA-stabilized ZVI nanoparticles in soils. He and Zhao employed a food-grade starch and sodium carboxymethyl cellulose (CMC) as preagglomeration stabilizers and obtained highly dispersed ZVNI. These supports prevented iron particles from agglomerating and thereby prolonged the reactivity of the particles. Generally, polymers such as CMC, guar gum, chitosan and PAA provide steric stabilization that exhibit a larger repulsion force than electrostatic repulsion [41], hence they can help to stabilize ZVNI particles.
2.3.4 Biosynthesis

Biogenic synthesis is useful not only because of its reduced environmental impact [42-44] compared with some of the physicochemical production methods, but also produce large quantities of nanoparticles that are free of contamination and have a well-defined size and morphology [45]. Biosynthetic routes can actually provide nanoparticles of a better defined size and morphology than some of the physicochemical methods of production [46]. The ability of plant extracts to reduce metal ions have been known since the early 1900s, although the nature of the reducing agents involved was not well understood. In view of its simplicity, the use of live plants or whole plant extract and plant tissue for reducing metal salts to nanoparticles has attracted considerable attention within the last 30-years. Processes for making nanoparticles using plant extracts are readily scalable and may be less expensive [47] compared with the relatively expensive methods based on microbial processes. Plant extracts may act both as reducing agents and stabilizing agents in the synthesis of nanoparticles [48]. The source of the plant extract is known to influence the characteristics of the nanoparticles [49]. This is because different extracts contain different concentrations and combinations of organic reducing agents [50]. Typically, a plant extract-mediated bioreduction involves mixing the aqueous extract with an aqueous solution of the relevant metal salt. The reaction occurs at room temperature and is generally complete within a few minutes. In view of the number of different chemicals involved, the bioreduction process is relatively complex.

Fig 2.9 Possible chemical constituents of plant extract responsible for the bioreduction of metal ions (Dubey et al [50]).
Synthesis of ZVNI nanoparticles using a tea leaf extract was reported by Nadagouda et al [51]. The polyphenols reduce the cationic iron to form nano-scale ZVI particles with three layers; (1) an inner core consisting of ZVNI, (2) an intermediate layer of iron oxides and oxyhydroxides and (3) an outer reductive cap consisting of polyphenols that are polymerized during the reaction. The reduction was ascribed to the phenolics, terpenoids, polysaccharides and flavones present in the extract.

**Fig 2.10 Various approaches for making nanoparticles and cofactor dependent bioreduction. (Amit Kumar et al [52])**

### 2.4 CHARACTERISATION METHODS OF ZVNI

#### 2.4.1 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a faster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and
other properties such as electrical conductivity. The types of signals produced by a SEM include secondary electrons, back scattered electrons (BSE), characteristic X-rays, light specimen current and transmitted electrons. These types of signals require specialized detectors. The signals result from the interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nanometers in size. Due to the way these images are created, SEM micrographs have a very large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

Fig 2.11 Schematic of Scanning Electron Microscopy

2.4.2 Energy Dispersive X-Ray Spectrometry (EDS)

If a sample is excited under high energy of electron beam or other electromagnetic radiation, the inner shell of electrons is ejected to vacuum creating a vacancy in that shell as shown in the fig. 2.12. Electrons from the outer shell jump into the vacant site for filling the inner shell. During this process, the sample fluoresces X-ray of energy, same as the energy difference between the initial state and final state. Since each atom has its unique and discretized energy levels, the X-Ray fluorescence is also the
characteristic of that atom. Energy dispersive X-ray spectroscopy is a technique that detects the x-ray fluorescence to characterize the elements present in a material.

Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images, can also be used for element mapping, and even point analysis, if an X-ray spectrometer is added. There is thus a considerable overlap in the functions of these instruments. Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition.

SiLi detectors operating at LN2 temperature are commonly used in EDX experiments. X-Ray striking the detector produces photoelectrons which in turn produces electron-hole pairs within the Si. These migrate to opposite ends of the detectors (via an applied electric field of 1.5 kV) producing a current pulse whose size is proportional to the energy of the incident X-Ray.

Fig 2.12 Schematic diagram of Energy Dispersive X-ray spectroscopy (EDX).
2.4.3 X-Ray Diffraction

X-ray is a type of electromagnetic radiation with a wavelength in the range of $10^{-5}$ Å to 100 Å. X-rays are placed between gamma-ray region and the ultraviolet region on the electromagnetic spectrum. X-rays are nearly in the atomic scale and for this reason crystalline structures at atomic level can be determined using this radiation type. X-ray powder patterns can be used as fingerprints for crystalline solids, because each crystalline solid has its own characteristic X-ray pattern in the literature. Unknown materials can be determined with this pattern databases. A schematic diagram showing the components in an XRD instrument is given in Fig 2.13.

2.4.4 Zeta potential measurement

Many nanoparticles or colloidal particles have a surface charge when they are in suspension. When an electric field is applied, the particles move due to the interaction between the charged particle and the applied field. The direction and velocity of the motion is a function of particle charge, the suspending medium and the electric field strength. Particle velocity is measured by observing the Doppler shift in the scattered light. The particle velocity is proportional to the electric potential of the particle at the shear plane which is the zeta potential. Thus, this optical measurement of particle motion under an applied field can be used to determine the zeta potential.
2.4.5 Particle size measurement

Dynamic Light Scattering (DLS) is used to determine the particle size. DLS is the measurement of fluctuations in scattered light intensity with time. These fluctuations in intensity arise due to the random Brownian motion of the nanoparticles. Therefore, the statistical behaviour of these fluctuations in scattered intensity can be related to the diffusion of the particles. Since larger particles diffuse more slowly than smaller particles, one can readily relate particle size to the measured fluctuations in light scattering intensity.
2.4.6 Fourier Transform-Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption of a solid, liquid or gas. A FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made a dispersive infrared spectrometers but obsolete (except sometimes in the near infrared), opening up new applications of IR Spectroscopy. The goal of any FTIR is to measure how well a sample absorbs light at each wavelength. The most straight forward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed and repeat for each different wavelength. Fourier transform spectroscopy is a less natural way to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength.

2.4.7 UV-Visible Spectrophotometer

Ultraviolet–visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb.
Probably one of the most universally utilized spectroscopic techniques, the absorption of electromagnetic radiation in the range from ultraviolet to visible is still a versatile research tool. Just as in the case of FT-IR, UV-Vis can be used to analyze certain compounds used in the fictionalization of nanoparticles for dispersions and applications. Changes in the UV part of the spectrum can commonly be contributed to charge transfer (CT) bands between a surface metal cation and the functional ligand. In this region, although it can be difficult to distinguish between CT bands and typical $\pi$ to $\pi^*$ transitions, the information obtained can still be helpful in understanding and interpreting other data about the system of interest. Also, specific $n$ to $\pi^*$ transitions and the absence of absorption in the UV-Vis range can indicate the presence or change in certain functional groups. This can be helpful in illustrating the difference between a surface adsorption, absorption and a surface reaction. Nano-sized materials often present color changes when dispersed in a solvent that are correlated to the size of the particle or thickness of the shell in a core-shell particle. Gold for example has various color transitions related to size shell thickness, primarily due to changes in the surface curvature affecting the plasmon resonance. Most of these transitions occur in the visible portion of the spectrum and when used in certain cases, can give information.

### 2.4.8 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

The Raman effect is based on molecular deformations in electric field $E$ determined by molecular polarizability $\alpha$. The laser beam can be considered as an oscillating electromagnetic wave with an electrical vector $E$. Upon interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of
periodical deformation, molecules start vibrating with characteristic frequency $\nu_m$. Such oscillating dipoles emit light of three different frequencies (Fig 2.16) when:

(i) A molecule with no Raman-active modes absorbs a photon with the frequency $\nu_0$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $\nu_0$ as an excitation source. This type of interaction is called an elastic Rayleigh scattering. (ii) Part of the photon’s energy is transferred to the Raman-active mode with frequency $\nu_m$ and the resulting frequency of scattered light is reduced to $\nu_0 - \nu_m$. This Raman frequency is called Stokes frequency or just “Stokes”. (iii) Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\nu_0 + \nu_m$. This Raman frequency is called Anti-Stokes frequency or just “Anti-Stokes”.

Fig 2.16 Raman effect

2.5 Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

ICP-OES is one of the most powerful and popular analytical tools for the determination of trace elements in a myriad of sample types. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a RF (Radio frequency) discharge. Liquid and gas samples may be injected directly into the instrument, while solid samples require extraction or acid digestion so that the analytes will be present in a solution. The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core the inductively coupled plasma (ICP) sustains a temperature of approximately 10,000 K, so the aerosol is quickly vaporized.
Analyte elements are liberated as free atoms in the gaseous state. Further collisional excitation within the plasma imparts additional energy to the atoms, promoting them to excited states. Sufficient energy is often available to convert the atoms to ions and subsequently promote the ions to excited states. Both the atomic and ionic excited state species may then relax to the ground state via the emission of a photon. These photons have characteristic energies that are determined by the quantized energy level structure for the atoms or ions. Thus the wavelength of the photons can be used to identify the elements from which they originating element in the sample. ICP-OES can reach the detection limits in the ppb range.
2.6 REFERENCES


