



Review Paper

An Overview on Research Trends in Remediation of Chromium

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Abstract

Chromium is one of the toxic heavy metals which needs ample attention in terms of soil and environmental degradation. Among the heavy metals and their toxicity, chromium toxicity was well studied by the researchers with the corresponding remedial measures. In the present review paper, the occurrence, transformation, in different environments and the possible and currently practicing remedial measures and the evaluation of their efficacy to minimize the toxic effects of chromium was thoroughly discussed.

Keywords: Chromium toxicity, transformation, environment, remedial measures, efficiency.

Introduction

Chromium is a steel-grey, lustrous, hard, brittle metal that takes a high polish. It dissolves readily in non-oxidizing mineral acids. The average crustal abundance of chromium is approximately 100 micrograms per gram. Chromium is a common water contaminant because of wide applications in metallurgy, staining glass, anodizing aluminium, organic synthesis, leather tanning and wood preserving industries. Cr (VI) affects human physiology, accumulates in food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma. Contrarily Cr (III) is nontoxic and an essential human nutrient, which does not readily migrate in groundwater since it usually precipitates as hydroxides, oxides, or oxyhydroxides¹. It is also quite soluble in aqueous phase over almost the entire pH range, thus it is quite mobile in the natural environment. Cr (VI) is more toxic than Cr (III). Therefore, reduction of Cr (VI) to Cr (III) is beneficial for the environment and is a feasible method for removal of Cr (VI). The removal of chromium from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, electrochemical treatment technologies etc. These processes have significant disadvantages, which are for instance, incomplete removal, high-energy requirements and production of toxic sludge². Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of waste water produced and to improve the quality of treated effluent.

Adsorption has become one of the alternative treatments, in recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified³. The adsorbents may be of mineral or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass and polymeric materials. Membrane separation has been increasingly used recently for

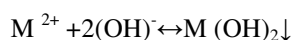
the treatment of inorganic effluents due to its convenient operation. Electro-treatments such as electro dialysis⁴ have also contributed to environmental protection. Photo catalytic process is an innovative and promising technique for efficient destruction of pollutants in water⁵. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level (MCL)(MCL for Cr =0.05 mg/L) standards established. This article presents an overview of various innovative physico-chemical treatments for removal of Chromium from industrial wastes. Their advantages and limitations in application are evaluated. To highlight their removal performance, the main operating conditions such as pH and treatment efficiency are presented well.

Reduction of Cr(VI) to Cr(III)

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 CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions⁶, 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 which processes are responsible for the reduction of metal contaminants. By comparing 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.

Chemical Precipitation: Chemical precipitation is an effective and by far 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 sulphurdioxide, sodium sulfite, sodium metabisulphite, ferrous sulphate, barium sulphite^{7,8}.

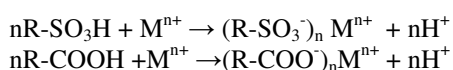
Hydroxide Precipitation: Lime and Limestone are the commonly employed precipitant agents due to their availability and low-cost in most countries⁹. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/l.



Maximum precipitation of Cr(III) occurred at pH 8.7 with the addition of Ca(OH)₂ and the concentration of Chromate was reduced from 30 mg/l. To enhance lime precipitation, fly ash was used as a seed material¹⁰. 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 problems¹¹. 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 solution iii. When complexing agents are in the waste water, they will inhibit metal hydroxide precipitation.

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 metals 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 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 sludge generated and the consumption of sulfide reagent.

Ion exchange: Among the physicochemical methods developed for 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 kinetics¹². This is a promising technique based on 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 (-SO₃H) 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.



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 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-divinylbenzene copolymer gel matrix. The total hexavalent chromium removed from the ground water as of October 8, 1995 was 660 grams¹³. The optimum pH for the removal is 6.5-8.5.

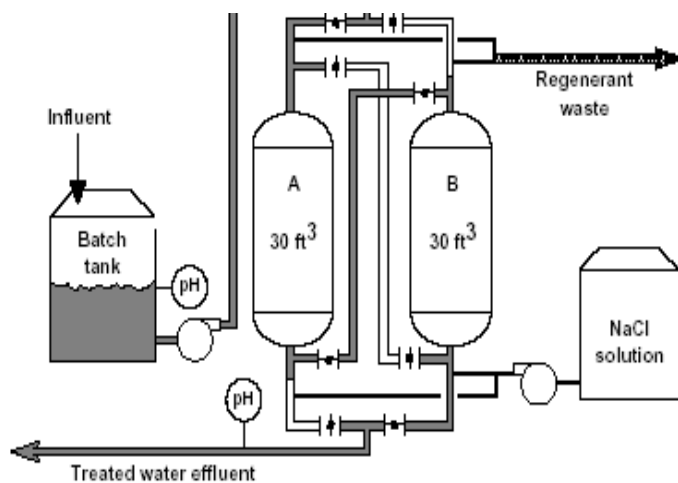


Figure-1
 Schematic representation for the process flow and regeneration of TFC Sally Bahawick; Lawrence Livermore Nat'l Laboratory

S.K.Sahu et al.¹⁴ investigated on extraction of chromium (III) from a model solution and from a tannery waste solution was studied by ion exchange using Indion 790 resin which is a

macro-porous strongly acidic cation exchange resin of sulfonated polystyrene group, which was found to be selective for the sorption of chromium(III) in the pH range 0.5-3.5 from a model solution containing 500 ppm Cr(III). Beyond pH 3.5 extraction of chromium (III) drastically decreased from 92% to 76%.

Chanda and Rempel¹⁵ reported the excellent performance of an epoxy-cross-linked poly ethylenimine gel coated silica(PEI) and Chelix-100 as resins for sulphate solutions. In the presence of NaCl, sorption of Cr (III) increased by 100% over gel coated PEI as compared to Chelix-100. The extraction of Cr(III) from the synthetic solution is studied by Pandey et al¹⁶ using cation exchangers viz. di(2-ethyl hexyl) phosphoric acid and bis (2,4,4-trimethyl pentyl) phosphoric acid. Synthetic Dowex 2-X4 ion exchange resin was employed to investigate the uptake of Cr(VI) from real plating waste water¹⁷. A 100% removal of Cr (VI) was achieved in the studies.

Kabey et al¹⁸ prepared a solvent impregnated resin (SIR) with aliquot 336 and used for batch removal of Cr(VI). It was reported that the sorption capacity of SIR increases with increasing impregnation ratio. Another synthetic ion exchange resin, Ambersep 132 was also prepared to recover Chromic acid from synthetic plating solution¹⁹.

The anion exchange resins extract Cr (VI) by an ion-pairing mechanism. IRA-900, a poly styrene matrix – divinyl benzene cross linking with trimethyl quaternary amine functionality- is a strongly basic exchanger whereas IRA-458, having a polyarylic matrix containing a quaternary amine, is a weak basic resin with lower chromate selectivity²⁰. These resins also remove other anions along with Cr (VI).

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 size exclusion, differences in diffusion coefficients, electrical charge and solubility. Membrane processes are often governed by 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 membrane²¹. Pugazhenth et al.²² prepared supported non-interpenetrating modified ultra filtration carbon membrane by gas phase nitration using NO_x and amination using hydrazine hydrate for separation of Cr(VI) from aqueous solutions. It was found that the effective pore radius of the unmodified, nitrated and aminated carbon membranes are found to be 2.0, 2.8 and 3.8 respectively. The

water flux of the modified membrane however has been found to increase by two times compared to that for the unmodified membrane. Separation experiments on the chromic acid solution have been carried out using unmodified (giving 96% rejection), nitrated (giving 84% rejection) and aminated (giving 88% rejection) carbon membrane.

The chitosan significantly increases the metal removal by 6-10 times compared to using membrane alone. This could be attributed to the major role of the amino groups of chitosan chain, which served as co-ordination site for metal binding. Increase in pH would enhance the formation of metal-chitosan complexes. To explore its potential to remove heavy metals, Saffaj et al²³ employed low-cost ZnAl₂O₄-TiO₂ UF membranes to remove Cr(III) ions from synthetic solution 86% Cr(III) rejection rates might be attributed to the strong interactions between the cations and positive charge of the membranes. UF presents some advantages such as lower driving force and a smaller space requirement due to its high packing density.

Another similar technique, complexation-ultrafiltration, proved to be a promising alternative to technologies based on precipitation and ion exchange. In the complexation-ultrafiltration process cationic forms of heavy metals are first complexed by a microligand in order to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained whereas permeate water is then purified from the heavy metals²⁴. Water soluble polymeric ligands have shown to be powerful substances to remove trace metals from aqueous solutions and industrial waste water through membrane processes. Barakat investigated the removal of Cr(III) from synthetic waste water solutions by using CMC and polyethersulphion ultra filtration membrane. The efficiency of Cr(III) rejection achieved is 99.1%. Aroua et al²⁷ investigated the removal of chromium species from aqueous dilute solutions using polymer enhanced ultra filtration (PEUF) process by the water soluble polymers, namely chitosan, polyethylenimine (PEI) and Pectin. High rejections approaching 100% for Cr (III) were obtained at pH higher than 7 for the three tested polymers.

The advantage of PEUF include high removal efficiency, high binding selectivity and high concentrated metal concentrate for reuse, etc. In addition the membranes should be compatible with the feeding solution and cleaning agents to minimize surface fouling.

Liquid membranes have been proved to be an effective and inexpensive method with 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 a Supported Liquid Membrane (SLM). Chiha et al.²⁸ used liquid emulsion membrane for the batch extraction of Cr(VI) from sulfuric acid aqueous solutions. Nanofiltration (NF) is a promising technology for the rejection of heavy metal ions. NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal.

Table-1
Comparative performance of various ion exchangers in remediation of chromium

Membrane characteristics	Chromium concentration	Experimental conditions	Removal efficiency	Reference
Ultra filtration, UF carbon membrane- Nitrated and aminated	-	-	96% rejection (unmodified) 84%rejection (nitrated)	23
Zn Al2O4-TiO2 Uf membrane	10 ⁻³ mol/l	pH 3.6	96% rejection	24
CMC and polyether sulphion-UF membrane	100 mg/l	pH≥7	99.1% rejection	25
UF made from PolyAcrylonitrile	0.07mg/dm3	17.6% PA, pH 6.0	98% retention	26
Liquid membrane Nanofiltration membrane NF-I NF-II	5-2000 mg/l	pH 2-11	84 -99.7% rejection(NF-I) 47-94.5% rejection(NF-II)	27

Table-2
Removal of chromium by various membrane separation process

Ion-exchangers	Chromium concentration	Experimental conditions	Removal efficiency	References
Indion-790	500 mg/l	acidic	100% removal	14
Chelax-100	2mM	Basic, saline	100% removal	15
Dowex 2-X4	9.8 mg/l	strongly basic	100% removal	17
Solvent impregnated resin (SIR) with aliquot 336	0.1 mg/l	acidic resin based on hydrophilic polymer	99.5% removal	18
Ambersep 132	750 mg/l	strongly basic	-	19

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. Rana et al.,²⁹ investigated the electrochemical removal of Cr(VI) ions from industrial waste water using carbon aerogel electrodes. It was found that the metal concentration in the waste water can be reduced by 98% under high charge (0.8 Ah) and acidic conditions (pH 2).

Electro coagulation (EC) involves the generation of coagulants in situ by dissolving electrically either aluminium or iron ions from aluminium or iron electrodes³¹. 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. Heidmann and Calmano³² studied the performance of the EC system with aluminium electrodes for removing chromium. Chromium ions are hydrolysed and co-precipitated as hydroxides. Earlier laboratory studies have found that, electroremediation of Cr(VI) in low buffering soils such as kaolin, the pH of the soil decreases to 2-3 near the anode and increase to 8-12 near the cathode due to the electrolysis of water at the electrode. Cr(VI) attempts to migrate toward the anode;

however it is absorbed to the soil in the region of low pH, thus hindering its complete removal from the soil³⁴. Control of pH may be a key for successful remediation.

Some studies using electrochemical precipitations (ECP) was carried out for the removal of Cr (VI) from real electroplating waste water. Kongsricharoern and Polprasert³⁵ 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 0.2mg/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.

Ana M. Nieto Castillo et al.³⁶ investigated on removal of Cr(VI) from soil using dimensionally stable titanium electrodes with an area of 10cm² and coated with mixed metal oxides were placed in the electrode compartments. Removal of chromium of 27% at 15V and 57% at 30V at pH <4 were achieved in 7-days treatments.

Table-3
Electrochemical treatment technologies used for removal of chromium

Electrolytes employed	Chromium concentration	Experimental conditions	Removal efficiency	Reference
Carbon aerogel electrodes	8 mg/l	pH 2.0	98.5%	30
Iron rotary	130 mg/l	pH 8.5	99.6%	31
Aluminium or Iron electrodes	Al=335.6mg (Ah) ⁻¹ , iron=1041 mg(Ah) ⁻¹	I=20-25Am ⁻²	-	32
Aluminium electrodes	50 -5000 mg/l	-	-	33
Stainless steel electrodes	1470 mg/l	I=7.4 A, applied time=70 min., pH 1.8	100%	34
Electrochemical precipitation units having six plates	215-3860 mg/l	I=3-6 A, EP=30-75V, pH>3.2	100%	36
Titanium electrodes	4056 mg/g	pH<4	27% at 15V, 87% at 30V	37

Photocatalysis

In the recent years, photocatalytic process in aqueous suspension of semiconductor has received 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, respectively³⁸. These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential.

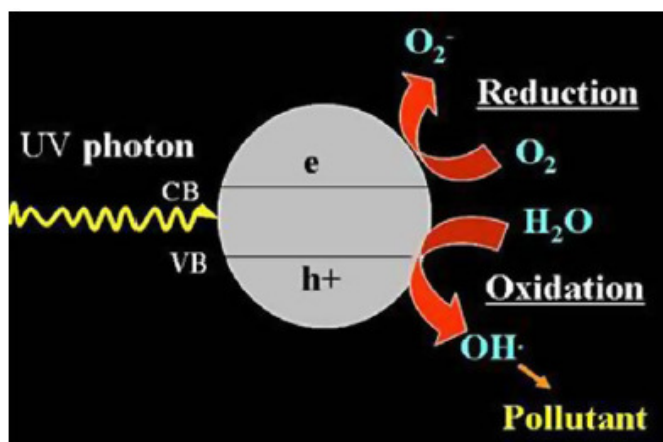


Figure-2

The conceptual reaction path of photocatalysis over TiO₂

The heterogeneous photocatalytic reduction of chromium in UV irradiated TiO₂/solution interfaces is done by the presence of various solution additives such as protons, ammonium ions³⁵. The maximum level of Cr (VI) adsorption is at pH of 4. TiO₂ modified with sulphate³⁹ and TiO₂ loading on Zirconium Phosphate (ZrP) and Titanium phosphate⁴⁰ were prepared and tested. Samples prepared at lower pH exhibit more surface area and higher reactivity than those prepared at higher pH.

Polyoxometalates (POM) PW₁₂O₄₃²⁻ or SiW₁₂O₄₀⁴⁻ as photocatalyst and an organic substrate (Salicylic acid or propan-2-ol) as electron donor were also investigated⁴¹. Increase of POM or Salicylic acid (SA) concentration accelerated, till a saturated value, with both the reduction of metal and the oxidation of the organic compound. The method is suitable for a range of chromium concentration for 5 to 10 ppm achieving complete reduction of Cr(VI) to Cr(III).

Photocatalytic reduction of Cr(VI) over TiO₂ catalysts was investigated in both the absence and presence of organic compounds⁴³. The results demonstrated that the photocatalytic reduction of Cr(VI) alone was dependent on both the specific surface area and crystalline structure of the photocatalyst in the absence of any organic compounds, but was dominated by the specific surface area of the photocatalyst in the presence of organic compounds because of the synergistic effect between the photocatalytic reduction of Cr(VI) and the photocatalytic oxidation of organic compounds.

Table 4

Photoreduction	Chromium concentration	Experimental conditions	Removal efficiency	Reference
PC-Polyoxometalates OS-Salicylic acid or Prapan-2-ol	5-100ppm	-	98%	39
Immobilized and anodized Titanium electrodes	2 ppm	pH<2	~98%	40

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.

Adsorption on natural materials: Natural Zeolites gained a significant interest, mainly due to their valuable properties as ion exchange capability. NaA zeolite is used for Cr(III) at neutral pH⁴⁴ 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 adsorption of Cr(VI) varies widely depending on 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 Al⁴⁵.

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. Sharma and Forster⁴⁶ studied the removal of Cr(VI) from aqueous solution using GAC type Filterasorb 400.

Selomulya et al.⁴⁷ used different types of activated carbons, produced from coconut shells, wood and dust coal to remove Cr(VI) from synthetic waste water. Karthikeyan et al.⁴⁸ used rubber wood sawdust –activated carbon for removal of Cr(VI) in a batch system. It was found that Cr(VI) removal is pH dependent and is maximum at pH 2.0. 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 al⁴⁹ 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 solution⁵⁰. 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.

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. The interaction between chitosan and Cr(VI) was investigated by Udaybhaskar et al⁵¹. It was found that an adsorption capacity of 273 mg /g of Cr(VI) with chitosan was achieved at a pH of 4.0. Lee et al.⁵², prepared chitosan based polymeric surfactants (CBPS) and applied for removal of Cr(VI) commonly found in waste water. The CBPS maximum adsorption capacity of Cr (VI) was at pH 5.3. Spinelli et al⁵⁶, synthesized quaternary chitosan salt (QCS) and applied it to adsorb Cr(VI) at pH 9 was 30.2 mg/g while at pH 4.5 the capacity was 68.3mg/g. Shankaramakrishnan et al.⁵⁷ used chitosan cross-linked with gluteraldehyde, xanthate group and modified chitosan beads (CMCB) and flakes (CMCF) for the recovery of toxic Cr(VI). It was found that the sorption for both was optimum at pH 3.

Table-5

Various adsorbents used for the removal of chromium

Adsorbent	Adsorption capacities mg/g	pH	isotherm model	Reference
Activated carbon	Cr(VI) 315.6	3.0	Langmuir	1
Chitosan	Cr(VI) 273 mg/g	4.0	Langmuir	48
Fly ash	Cr(VI) 1.4	2.0	Langmuir	50
Fly ash impregnated Aluminium	Cr(VI) 1.8	2.0	Langmuir	50
Fly ash impregnated Iron	Cr(VI) 1.7	2.0	Langmuir	50
Japanese cedar	Cr(VI) 80.0	3.0	Langmuir	51
Sawdust	Cr(VI) 45	3.0	Freundlich	52

Effect of iron in remediation of chromium

Green rust-a very reactive iron oxide- can be used to reduce Cr (VI) to Cr (III) which is not soluble and less toxic than the mutagenic Cr(VI) .Y.H.Xu et al⁵⁸ reported that nano scale Fe(0) particles possess the advantage of a larger specific area and higher surface reactivity over microscale Fe(0), so they have a higher reducing capacity of chemical contaminants like heavy metals. Ritu singh et al⁵⁹ studied on zero-valent iron nanoparticles (nZVI) entrapped in calcium alginate beads as a potential remediation technology for the decontamination of Cr(VI) contaminated soil. Results of batch experiments conducted showed that 1.5 g of nZVI entrapped in alginate beads removes 98% Cr(VI) from spiked soil within a contact time of 60 min. Jo.S et al.⁶⁰ reported that FeS exhibited more Cr(VI) removal efficiency than zero valent iron and other oxide minerals due to the synergic effect of ferrous iron and sulphide.

The decrease of 100% Cr(VI) concentration with CMC stabilised Fe0 nano particles at the mass concentration even with 40 mg/L was studied by Madhavi et al.⁶¹. Fe(0) particles (NVZI) supported on a PAA/PVDF membrane were synthesized

by Shujing et al⁶² for the reductive immobilization of Cr(VI). The Cr(VI) removal capacity of NZVI-PAA/PVDF was 181 mg Cr/g Fe at pH 6.5± 0.1.

Bioremediation

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 *in situ* or *ex situ* in a range of bioreactor configurations. Microbes, especially bacteria capable of Chromium (VI) reduction exhibit plasmid-mediated chromate resistance and the reduction is enzymatically mediated⁶³.

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 reduced 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. Liyuan Chai et al⁶⁴ studied on *Pannonibacter phragmitetus* sp., an indigenous bacteria in soils contaminated by chromium-containing slag. The results showed that total Cr(VI) concentration declined from the initial value of 462.8 to 10 mg kg⁻¹ at 10 days and the removal rate was 97.8%.

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.⁶⁵ 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 process⁶⁶. Abubakr et al.⁶⁷ investigated the chromium(VI) reduction in *Methylococcus capsulatus*, a methane-oxidizing bacteria in which five candidate genes are responsible for the chromium(VI) reductase activity in this organism

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.flourosceus*, *E.coli*, *Achromobacter Eurydice*, *micrococcus roseus*, *enterobacter cloacae*, *desulphovibrio desulfuricans* and *D.vulgaris*. The radiation-resistant *Dienococcus radiodurans* RI⁶⁸, a close relative of *Thermoanaerobacter ethanolicus* isolated from deep subsurface sediments and *pyrobaculum islandicum*⁶⁹ have been found to reduce Cr(VI) at high temperature.

Phytoremediation: Phytoremediation is an ecofriendly approach for 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 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 permanent removal of metals from the site⁷⁰.

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 1) extract large concentrations of heavy metals into their roots, 2) translocate the heavy metal into the surface biomass, and 3) produce a large quantity of plant biomass. Over 400 hyperaccumulator plants have been reported and include members of *Brassicaceae*, *Fabaceae*, *Euphorbiaceae*, *Asteraceae*, *caryophyllaceae*, *Lamiaceae* and *Scrophulariaceae*. Dushenkov et al⁷¹ observed that 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.

Chromium remediation was also examined by various plants including *Fagus orientalis* L., *Agave Lechiguilla*, *Atriplex canascens*, *Thuja orientalis*, *Larrea tridentate*, *Pinus sylvestris*. Romero-Gonzalez et al.⁷² reported Cr (VI) biosorption onto *Agave lechiguilla* biomass. The maximum absorption of Cr (VI) is at pH 2.0 due to either electrostatic attraction to Cr (VI) oxyanions by positively charged ligands such as protonated amines or through Cr (VI) to Cr (III) reduction, subsequently resulting in the binding of Cr(III) to the biomass.

Rhizosphere, as an important interface of soil and plant, plays a significant role in 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 potential to enhance phytoremediation processes. Some rhizobacteria can exude 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% Cr, siderophore producers with 78.5% Cr and finally for acid producers with 63.5% Cr. Park⁷³ reported that a strain of *Ps. Maltophilia* was shown to reduce the mobile and toxic Cr (VI) to nontoxic and immobile Cr (III). An experiment on rhizofiltration by Karkhanis et al.⁷⁴ was conducted in a green house, using *Pistia*, duckweed and water Hyacinth to remediate aquatic environment

contaminated by coal ash containing heavy metals. The results showed that *pistia* has high removal capacity of uptake of Cr, Duckweed and Hyacinth also showed good potential for uptake of Cr next to *Pistia*.

Comparative study of evaluation of treatment methods: One of the important features that distinguish heavy metals from other pollutants is that the former are not biodegradable. Once metal ions enter the environment, their chemical form largely determines their potential toxicity. The interest in chromium is governed by that its toxicity depends critically on its oxidation state. In the environment, chromium, a redox active metal element, usually exists as Cr (III) or Cr (VI) species. Hexavalent chromium, Cr (VI), is a well-documented carcinogen, mutagen and redox active species. However, the use of chromium in industrial processes including corrosion inhibition, metal finishing, tanning and pigment production is still prevalent. Pollution due to Cr(VI) is a considerable problem due to its extremely hazardous nature and the relative ease with which it may contaminate the environment.

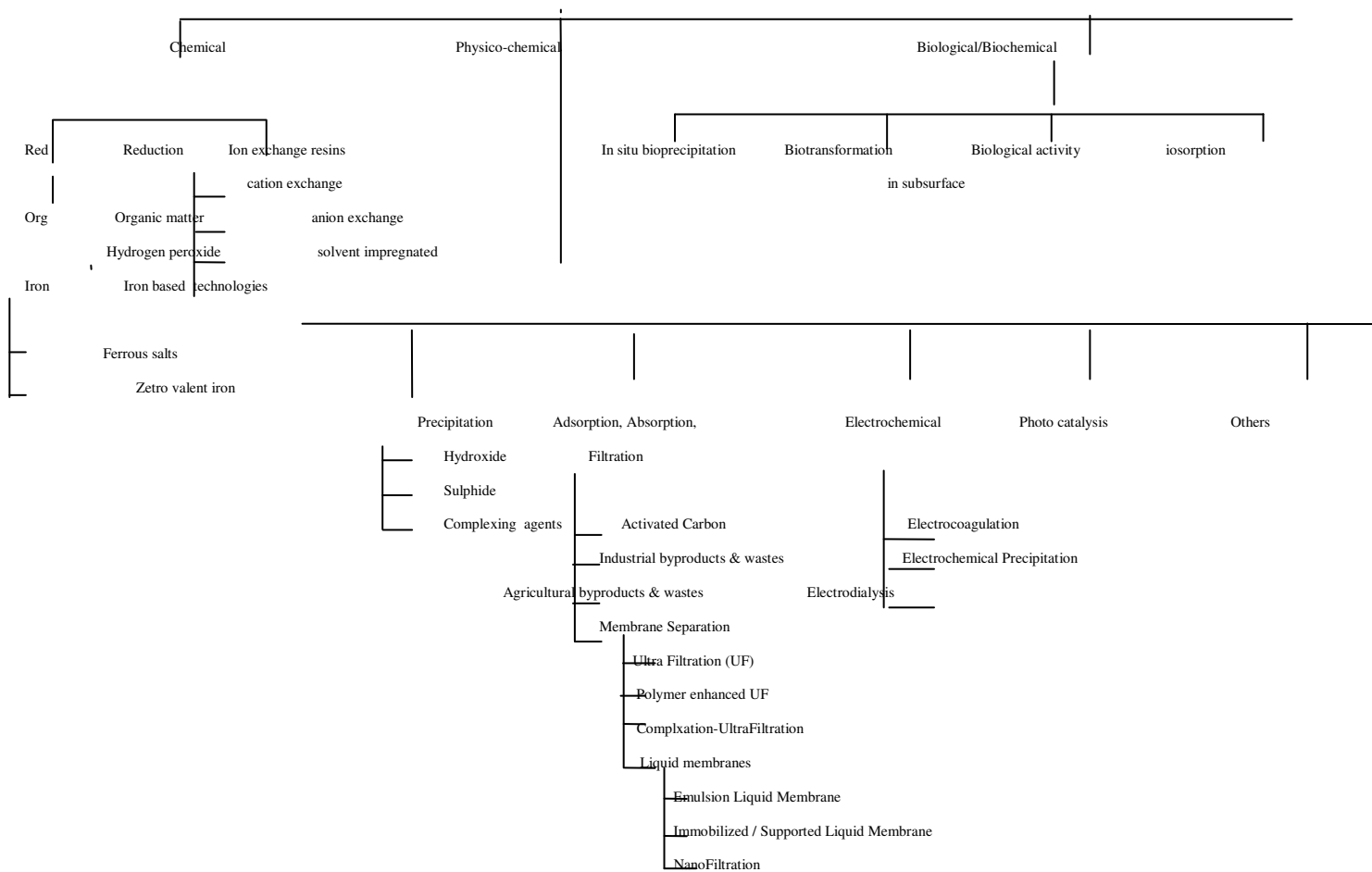


Figure-3
Chromium remediation technologies

This review shows that the various techniques for Cr(VI) removal has been studied widely and has attracted the attention of scientists. Various methods exist for the removal of heavy metal ions from waste water which include chemical precipitation, membrane filtration, ion exchange, adsorption, photo catalysis, bioremediation etc. In general physicochemical treatments offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. In addition, the treatment system requires a lower space and installation cost. Their benefits however are outweighed by a number of drawbacks such as their high operational costs due to their chemicals used, high-energy consumption and handling costs for sludge disposal.

A comparative analysis of the various process technologies that are currently in use and are in the developmental stage is just done for the advantages and disadvantages of the discussed removal methods.

The most widely used method for removing heavy metals from solutions is by precipitation at increased pH, thus converting the soluble metal into an insoluble form (ie., its hydroxides). Chemical precipitation has been traditionally carried out for its simplicity and inexpensive capital cost. Precipitation by adjusting the pH value is not selective and any iron present in the effluent will be precipitated initially, followed by other metals. Consequently, precipitation produces large quantity of solid sludge for disposal, which again created a burden for its disposal. Ion exchange is the second most widely used method for heavy metal removal from aqueous streams. During removal, recovery, or processing of metals, ion exchange acts as a concentrator of metals. Despite, the advantages, ion exchange also have some limitations in treating waste water. Ion exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration causes serious secondary pollution. Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only heavy metals, suspended solids but also organic compounds associated with them. However its problems such as high cost, membrane fouling, limited flow rates have limited their use in heavy metal removal.

Electrochemical heavy metal waste water treatment techniques are regarded as rapid and require fewer chemicals, provide high selectivity and produce less sludge. However, electrochemical techniques involve high initial capital cost and production of dendrite, loose or spongy deposits.

Adsorption is one of the most popular and effective processes for the removal of heavy metals from waste water. The adsorption process offers flexibility of design and operation and in many cases produces treated effluent suitable for re-use, free of color and odour. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metals. However, the adsorption efficiency depends on the type of adsorbents and requires chemical derivitisation to improve its sorption capacity.

The most promising method to treat industrial waste water is the photo catalytic ones which consume cheap photons from the UV-Visible region. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Thus, they induce both degradation of organic pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds. But the limitations involve long duration time and limited applications. Iron plays a major role in remediation of chromium. Iron (II) is an important natural reductant of Cr(VI) that transforms Cr(VI) essentially to non-toxic Cr(III). Earlier developments in the remediation of chromium include iron-based materials such as iron oxides and sulphides, scrap iron, iron filings, zero valent iron and iron nano particles. In spite of many advantages using iron nano particles including high reactivity and short time interval when compared to the other iron based materials, nano particles have been shown to remain reactive in soil and water up to 8 weeks and can flow with the ground water for >20m.

Bioremediation can be effective in removing chromate from the environment. Several bacteria possess a chromate-reducing capacity that can convert chromate to Cr(III), thus, reduction by enzymes affords a means of chromium bioremediation. Biosorption would be incorporated to detoxify the waste streams and chromium effluents. Thus, chromium remediation through micro-organisms or plants may be the best suited technology to clean-up Cr-contaminated sites. These technologies are eco-friendly and cost-effective. Most plants, even when grown in Cr-rich soils, the food chain is well protected against Cr toxicity. The use of Cr-hyper accumulator plant species or Cr-reducing micro-organisms represents a cost-efficient and highly effective technology for the removal and detoxification of the toxic forms of chromium. However, the problem arises as membrane damage of cells due to high oxidation power of Cr (VI).

Among the several techniques discussed in this review to employ for Cr (VI) removal, selection of the most suitable treatment techniques depends on some basic parameters as pH, initial Cr(VI) concentration, plant flexibility and liability, environmental impact as well as economic parameter such as the capital investment and operational costs.

Conclusion

Over the past two decades, environmental regulations have become more stringent, requiring an important quality of treated effluent. In recent years, a wide range of treatment technologies such as chemical precipitation, ion exchange, membrane filtration, adsorption, electrochemical methods, photo catalysis, bioremediation have been developed for heavy metal removal from the contaminated waste water. It is evident from the literature survey of 190 articles that: chemical precipitation has been found as one of the most effective conventional means to treat inorganic effluent. Ion exchange, adsorption, membrane filtration electrochemical treatment methods are frequently

studied and widely applied for the treatment of heavy metal contaminated waste water; photo catalysis is a promising innovative technique for a clean and efficient treatment. Efficient removal of Cr(VI) from industrial waste water can be done by iron-based materials. Bioremediation is an emerging technology for cleaning up of contaminated sites, which is cost

effective and has aesthetic advantages and long term applicability. Though the knowledge of chromium removal-disposal serve the purpose of satisfying water pollution norms, it is necessary to better understand that they produce solid sludge. Therefore, processes based on recovery-reuse are to be increased in future.

Table-6

Comparative performance characteristics, advantages and disadvantages of various methods in remediation of chromium

Performance characteristics						Advantages	Disadvantages
	pH range	Metal selectivity	Influence of suspended solids	Tolerance of organic molecules	Working level (ppm)		
Chemical Precipitation Hydroxide	Tolerant	Non selective	Tolerant	Tolerant	>1000	low capital cost, simple operation.	Sludge generation, extra operational cost for sludge disposal.
Sulphide	Limited Tolerant	Limited selective, pH dependent	Tolerant	Tolerant	>10	no secondary waste generation.	Toxic gas intermediate, gas delivery to aquifer is difficult.
Adsorption	Limited tolerant	moderate	fouled	Can be poisoned	<10	wide variety of target pollutants, low cost, fast kinetics	performance depends on type of adsorbent, production of waste products.
Electrochemical treatment	tolerant	moderate	Can be engineered	Can be accommodated	>10	no additional chemical reagents required, high selectivity, low cost	spongy deposit, production of sludge, filtration process for flocs
Photocatalysis	-	Limited selective	-	Tolerant and removed	>100	removal of metals & organic pollutants simultaneously, less harmful byproducts	long duration time, limited applications
Membrane filtration	Limited tolerant	Non selective	fouled	-	>10	low solid generation, low chemical consumption, small space requirement	high initial capital cost, high maintenance cost, limited flow rate.
Bioremediation	Limited tolerant	Non selective	tolerant	Tolerant & degrade		high initial capital cost, high minimization of chemical mud, heavy metal recovery	not applicable to synthetic waste, no recycling
Phytoremediation	tolerant	nonselective		tolerant	>100	eco-friendly, high accumulation rate.	Long duration time, phytotoxic at high Concentrations.

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