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Polymers for the Extraction of Chromium—Role of Polymers in the Removal and Recovery of Chromium from Wastewater

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The present review discusses different possible routes of removal and recovery of chromium from industry and laboratory wastewater with special emphasis on the role of polymers in this context. Polymers can play a vital role in the easy, rapid and cost effective separation of chromium from aqueous solutions. Such studies of separation are important from the standpoint of identifying selective hosts and extractors for chromium. The use of suitable polymers in the removal and recovery of chromium from solutions is discussed.

Keywords: Polymers, chromium, extraction, elution, separation

1 Introduction

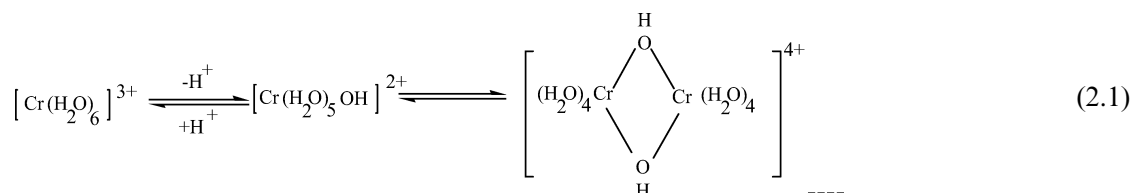
Chromium, an element of 6th group in the latest IUPAC version of periodic table, exists in the aqueous environment mainly in +III and +VI oxidation states. Cr(III) is non toxic and essential species to mammals that helps the body to control blood-sugar levels in trace concentrations, but toxic to fish (1) when present in water about 5.0 mg.L⁻¹. The Cr(VI) is more hazardous to animals (2–3) than the Cr(III). The permissible level of Cr(VI) (4) in water is less than 0.05 mg.L⁻¹. In India, about 150000 ton of chromium containing sludge is released into the environment from tannery industry effluent per year (4). Other industries and laboratories discharge wastewater into surface containing large amount of chromium. Thus removal and recovery of chromium from wastewater are highly important. In industrial wastewater treatment (5), the removal of Cr(VI) involves a two step process. The first step is the reduction of Cr(VI) to Cr(III) under acidic condition by a reducing agent. The second step is the precipitation of Cr(III) as Cr(OH)₃ using lime. The major drawbacks (5)

of the conventional treatment are lengthy process, high chemical cost, significant sludge production and higher disposal cost. As a result, emphasis in recent years has been given on methods for recovery and reuse of metals rather than disposal (6–8). The solid phase extraction (SPE) and ion exchange process based on reactive polymers play a vital role in removal and recovery of chromium from waste water in recent years (9–10).

The present review mainly aims to elucidate the role of polymers towards the removal and recovery of chromium from industrial and laboratory wastewater.

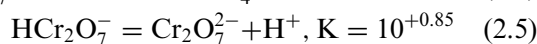
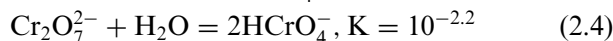
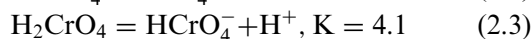
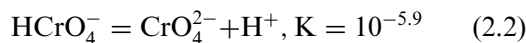
2 Aqueous Chemistry of Chromium

In aqueous solution, chromium remains mainly as +III and +VI oxidation states. In +III oxidation state, chromium remains as hex aqua ion [Cr(H₂O)₆]³⁺ in aqueous solution (11). The aqua ion is acidic (pK_a = 4), and the hydroxo ion condenses to give a dimeric hydroxo bridged species (11). The process of condensation through the formation of hydroxo-bridge is known as “olation” (Equation 2.1).

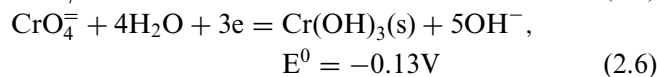
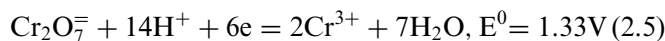


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In basic aqueous solution above pH 6, Cr(VI) forms tetrahedral yellow chromate ion (11), CrO_4^{2-} ; between pH 2 and 6, HCrO_4^- and the orange red dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ are in equilibrium (11); and at $\text{pH} < 1$, the main species is H_2CrO_4 . The following pH dependent equilibrium exist in aqueous solution (Eq. 2.2–2.5).



Acid solutions of dichromate are strong oxidant (11). The mechanism of oxidation (12) has been studied in detail. During oxidation Cr(VI) is reduced to Cr(III) through the formation of intermediates, Cr(V) and Cr(IV). The chromate ion in basic solution, however, is much less oxidizing (11) as evident from E^0 values (2.5–2.6).



Cr(VI) does not give rise to extensive complex series of poly acids and poly anions (11,13) characteristics of the somewhat less acidic oxides of V(V), Mo(VI) and W(VI). The reason for this is perhaps the greater extent of multiple bonding (Cr=O) for the smaller chromium. Polymerization beyond the dichromate is apparently limited to formation of tri and tetra chromate ($\text{Cr}_3\text{O}_{10}^{2-}$) and ($\text{Cr}_4\text{O}_{13}^{2-}$) which can be crystallized as alkali as the dichromate, are formed by the corner sharing of tetrahedral CrO_4 (13), giving Cr-O-Cr angles very roughly in the region of 120° .

3 Biological Function of Chromium

In human beings, chromium(III) helps in glucose metabolism through activation of insulin (14–15). Severe malfunctioning of glucose metabolism in many cases (both children and aged person) has been checked with 100–250 mg of Cr(III) per day (14). Chromium(III) enters into our body mainly by food such as sugar, flour, broccoli, brewers yeast, liver, etc. (14). It is established that the Cr(III) is toxic to fish (3) when present in water above 5.0 mgL^{-1} . Although Cr(III) is essential in mg levels in human beings, Cr(VI) (in the form of chromate and dichromate) is now established as a carcinogen and a mutagen (2–3). The chromate enters into mammalian cells through the general anion channel. It produces several reactive intermediates such as Cr(V) and are susceptible to interact with DNA (14). The Cr(VI) toxicity includes lung cancer, liver, kidney and gastric damage, and epidermal irritation (15). The difference between biological activity of Cr(VI) and Cr(III) may be explained by the “uptake reduction” model (14).

Cr(III) hydrolyses smoothly at body pH to give insoluble hydroxide. Cr(III) is kinetically inert due to its electronic configuration (t_{2g}^3) (14). As a result, the ligand exchange process at Cr(III) is very slow. The transport of Cr(III) into the cell is also extremely slow. On the other hand, Cr(VI) can penetrate the cell membrane rapidly.

4 Source of Chromium in Wastewater

Tanneries, chrome plating, manufacturing industries and laboratories are the major sources of chromium in wastewater (16–17). The waste products from these industries normally contain Cr(III) and Cr(VI).

4.1 Leather Tanning Industry

Leather tanning is the process of converting raw hides or skins into leather. A significant amount of basic chrome sulfate (known as tanning powder, which is manufactured from the simple reduction of Cr(VI) to Cr(III) by sulfur dioxide) is applied in chrome tanning to convert polypeptide collagen strand in hide into cross-linked helix (18), which prevents penetration of water into leather pores (19) and provide thermal stability. The options for crosslinking are threefold: They are intra single helix, intra triple helix and inter triple helix (18–19). The Cr(III) fixation (crosslinking) can occur in two ways: (a) covalent reaction between one chromium ion and two carboxyl group of collagen (b) hydrogen bonding between chromium species (monomer, dimer, etc.) and the protein, specially along the polypeptide backbone. About 40% of used chromium is discharged in the effluent as Cr(VI) and Cr(III). The Cr(III) in soil may be oxidized to Cr(VI) in presence of manganese (1). Cr(VI) is formed in leather during photo aging (20).

4.2 Chrome Plating Industry

Chrome plating, often referred to simply as chrome, is a technique of electroplating a thin layer of chromium onto a metal (21). The chromed layer is decorative and provided corrosion resistance, easy cleaning and surface hardness. There are two types of chrome plating baths: hexavalent and trivalent. Trivalent chromium baths are not yet common. While hexavalent chromium baths are widely used. A typical bath composition of a hexavalent chromium bath (21) is as follows: (a) Electrolytic solution: chromic acid, CrO_3 (300 g.L^{-1}) or sulfuric acid (3 g.L^{-1}); (b) Anode: Lead with tin up to 7% (c) Operating temperature: $45\text{--}60^\circ\text{C}$; (d) Plating current: 1.5 to 3.0 kilo ampere per square meter. About 35% of used chromium is discharged in the effluent as Cr(III) and Cr(VI) (21).

4.3 Manufacturing Industry

Chromium compounds are used in paint pigments (1). Chromates of barium, lead and zinc gives us the pigments of lemon Cr, Cr yellow, Cr red, Cr orange, Zinc yellow and zinc green. Cr green is used in the making of green glass (21). Chromium chemicals enhance the colors of fabrics and are used to achieve the brightly colored Cr-based paints for automobiles and buildings. The chromate of Ba, Pb and Zn are toxic and these compounds are discharged in the wastewater (21). $K_2Cr_2O_7$ is applied in the manufacture of waterproof glues and photography (1).

4.4 Laboratories

Almost all chemical laboratories (academic, research and industry) discharges considerable amount of chromium in the environment (1). Chromium(VI) is used extensively in the laboratory as oxidant (13). Dichrometry is an important analytical tool.

5 Different Methods for the Removal and Recovery of Chromium

Several approaches have been used for the environmental removal of chromium. These approaches involve basic principle of chemical precipitation, electrochemical deposition adsorption, ion-exchange, complexation and magnetic separation. A wide range of technologies is available for removal of chromium from wastewater, some of which are well established methods that are discussed below.

5.1 Chemical Precipitation

The chemical precipitation method (22) involves a two-step process. The first step is the reduction of Cr(VI) under acidic conditions (usually pH 2–3), followed by the precipitation of Cr(III) hydroxide at a solution pH in the range 8–10. Commonly used reducing agents are sulfur dioxide, sodium sulfite, sodium bi-sulfite and ferrous sulfate. In addition to iron(II) being a reductant, the iron(III) that is formed is an effective precipitant for Cr(III). This effect of iron(III) appears to be due to formation of insoluble ferric hydroxide which co-precipitates with Cr(III) hydroxide. The solid $Cr(OH)_3$ - $Fe(OH)_3$ mixture can then be removed by flotation. Although Cr(VI) can be removed by reduction to Cr(III), followed by precipitation of $Cr(OH)_3$ at very low concentration of Cr(VI), the reduction is kinetically slow and does not result in zero levels of chromium in waters. Though the technology of chemical precipitation is quite satisfactory in terms of purging chromium from water, it produce solid waste residue (sludge) containing toxic compounds whose final disposal is generally done by land filling with related high cost and a still possibility of ground water contamination.

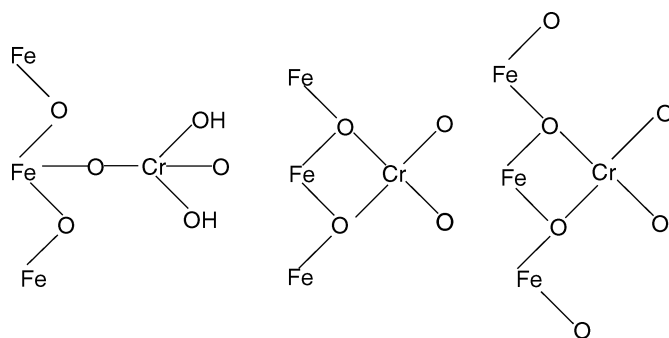


Fig. 5.3.1. (a) Monodentate; (b) Mononuclear bidentate; (c) Binuclear bidentate.

5.2 Electrochemical Precipitation

Electrochemical precipitation process (EPP) (23) has been used to remove chromium from electroplating wastewater. The chromium removal efficiencies by such method are greater than 99% and the residual chromium concentration is less than 0.5 mgL^{-1} . Though chromium removal efficiency by such method is very high, it consumes huge amount of power. The effectiveness of this method for dilute solution is very low.

5.3 Surface Adsorption

Surface adsorption (24–25) is found to be important basis for the treatment of toxic element contaminated water. Numerous adsorbents such as activated carbon (26), sawdust (27), goethite (28), zeolite (29), feldspar (30), hydrotalcite (31), hydrated oxides (ZrO_2 , TiO_2 and SnO_2) (32), fly ash (34, 35), rice hulls (35), etc. are reported to be good adsorbent for chromium (particularly hexavalent chromium). The surface adsorption depends heavily on the nature and level of adsorbent, pH and ionic strength of the solution, and concentration of Cr(VI) in aqueous solution. The disadvantage of the methods is the inability to regenerate the adsorbent for reuse. An analysis of the structural EXAFS data concluded that the three different surface complexes of chromate are formed on goethite (a mineral having chemical composition: α - $FeOOH$). The complexes are monodentate, mononuclear and bidentate binuclear (5.3.1a, 5.3.1b and 5.3.1c).

5.4 Bio-sorption and Bio-remediation

The process of heavy metal removal by biological material is known as bio-sorption (7,36). It is a potential alternative to the existing physico-chemical technologies for detoxification and recovery of valuable metals from water. Many biomaterials (37) such as seaweed, mold, micro-algae, fungi, bacteria, crab, shells, lignocelluloses solid waste, husk, sugarcane and various other agricultural products have been studied for their chromium binding abilities. Most reports (37) related with the Cr(VI) bio-sorption with dead fungal

biomass have claimed that Cr(VI) was removed from aqueous systems by “anionic adsorption.” Zaho and Duncan (38) observed “partial reduction along with anion adsorption” in a column packed with formaldehyde cross-linked cerevisiae. Bioremediation is a technology that differs from the simple use of biomass for the adsorption of metals such as chromium (39–40). Instead, it is a technology that focuses on developing problem-specific organism. Although bioremediation is primarily used for organic pollutants, there are also possibilities for the development of biotechnologies that are focused on the remediation of chromate. The microbial reduction of Cr(VI) and its potential application for the removal of chromium from pollutant sites has been reviewed (41). Allied signal has developed a process for the bioremediation of Cr(VI) through the reduction of Cr(VI) to less toxic Cr(III) by sulfate-reducing bacteria. Chromium(VI) is removed from aqueous solutions by an entrobacter cloacae strain that reduces it under anaerobic conditions. Chromium(VI)-resistant fungal or bacterial microbes can be used to reduce Cr(VI) to Cr(III) (42). In order to be able to apply these technologies, a two-stage bioreactor has been designed where *Escherichia coli* cells are grown in a first stage, and then pumped to a second stage plug-flow reactor where the anaerobic reduction of Cr(VI) occur (43).

5.5 Magnetic Separation

A continuous flow hybrid field-gradient magnetic separation device (44) may be used for the removal of Cr(VI) from aqueous solution. Magnetic anion exchange resins (44) have been used for this method. Electrostatic interaction induced selectivity favors selective adsorption of Cr(VI) from mixtures. Thus, magnetic separation can tackle the issue of wastewater treatment in a much more elegant way.

5.6 Solvent Extraction

Solvent extraction (45) is a convenient technique for the removal of chromate ions from aqueous solution. Literature survey reveals that tertiary amine extractors, Aliquat 336 and Alamine 336 are effective reagents for the removal of Cr(VI). The major drawback of solvent extraction is the loss of solvent and it releases a waste solution which has the contaminated metals. This has to be stripped by another operation to avoid problems. Another option of Cr(VI) removal from aqueous solutions is the application of tertiary amines and quaternary ammonium salts as carriers in the membrane transport in micro porous hollow-fiber modules (46–49). The process, called also non-dispersive solvent extraction, offers a very large interfacial area per unit equipment volume without any dispersion.

5.7 Ion-exchange Method

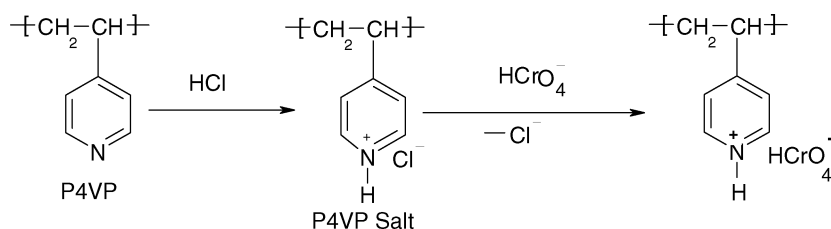
Anion exchange sorption process (50) can be used for the removal of Cr(VI) from the wastewater. The presence of sulfate makes the system less efficient. The adsorption capacity of chromate for commercially available polystyrene based anion exchangers in the pH range 2–5 is very high whereas at neutral to alkaline pH, the chromate removable capacity is drastically reduced (51). The strongly basic commercial anion exchangers AV-17(Cl) (containing-N⁺ (CH₃)₃ groups) and Varion AD (containing -N⁺ (CH₃)₂C₂H₄OH group) were reported to be excellent exchanger (52). The resins have a polystyrene-divinyl benzene matrix and are of gel type. The exchange capacity (51) is 3.5–4.0 miliequiv.g⁻¹. The strongly basic anion exchangers in certain conditions are able to retain Cr(III) ions through the formation of jarosite or alunite type mineral compounds in the polymer phase (52).

5.8 Liquid Membrane Technique

Recent years have seen a remarkable increase in the applications of liquid membranes in the separation process. These membranes include bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM). Ho and Sirkar provide a good overview of membrane process (53). BLM is practically a liquid-liquid extraction. ELMs are based on water immiscible emulsion dispersed in an organic phase (54). The emulsion is prepared from internal stripping agent, solvent, surfactant and carrier through stirring. This emulsion acts as liquid membrane. During the contact between aqueous solution and emulsions, solute transport occurs through the membrane phase into the internal stripping phase where it is concentrated. Extraction and stripping are carried out in a single stage and the mixture is allowed to separate. An SLM usually consists of an organic solution immobilized in the pores of a hydrophobic macro porous membrane that contains a complexing agent (carrier) that selectively binds one of the components from the feed solution (55). The SLM separates feed solution and strip solution by means of two interfaces. The species (chromate) are accumulated in the strip. The permeation of the species is due to a chemical potential gradient. High enrichment factors can be achieved using SLM in hollow fiber configuration.

6 Removal and Recovery of Chromium

For inorganic cations there is a wide range of extractants because they can be bound directly to a ligating group on a complexant. However, for inorganic oxoanions such as chromate, there is no direct interaction between the inorganic center and the complexant (22). As a consequence, although number of molecules act as complexants for cations, few molecules have been identified that act as selective hosts



Sch. 7.1.1. Extraction of Cr(VI) by poly(4-vinyl pyridine) salt.

and extractants for anions. Some polymer based materials can act as good sorbents for Cr(VI) and Cr(III).

6.1 Polymeric Sorbents

Several polymeric ligand exchange materials have been developed that removes trace concentration of Cr(VI) and Cr(III), even in the presence of sulfate, chloride, carbonate and bicarbonate ions (22). Some of the polymeric sorbents are discussed below.

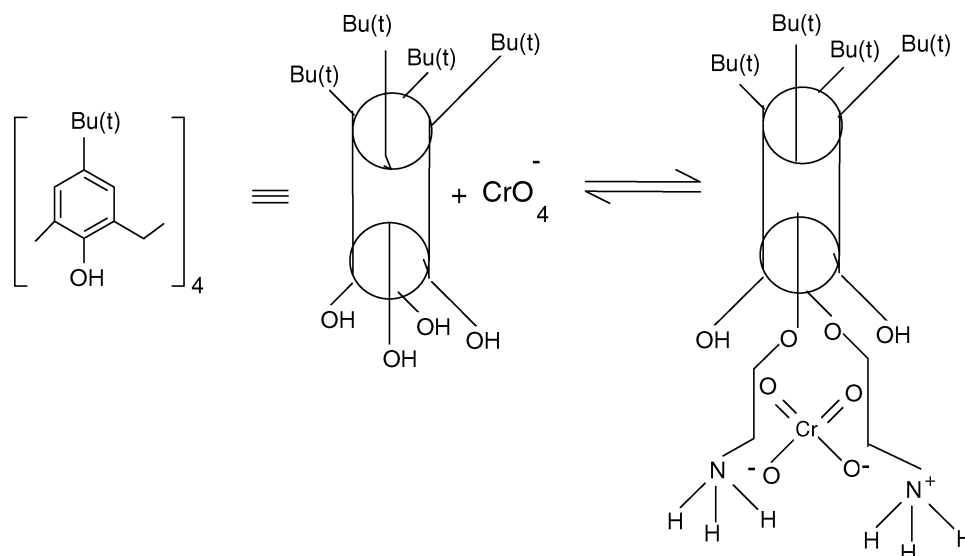
6.2 Poly(4-Vinyl pyridine)

Poly(4-Vinyl pyridine) (P4VP) has the suitable structure (Scheme 7.1.1) in acid medium to absorb Cr(VI) through anion exchange mechanism (56). Arslan et al. (56) described the sorption of Cr(VI) from aqueous using the batch method with poly(4-vinylpyridine). At pH 3, the maximum adsorption was achieved at 86.7 mg. g⁻¹ with 5000 mg. g⁻¹ Cr(VI) solution. The process of adsorption of Cr(VI) was described by the Langmuir isotherm. Yigitoglu et al. (57) grafted poly(vinyl pyridine) with poly(ethylene terephthalate) fibers to obtain better performance with respect to Cr(VI) adsorption. Gang et al. (58) modified poly(vinyl pyridine) coated silica gel through alkyl quaternization to

increase the surface area for Cr(VI) removal under very fast kinetics. Neagu et al. (50) produced anion interchange resins, using 4-vinyl pyridine and DVB functionalized with aliphatic groups such as methyl, ethyl and butyl moieties. The Cr(VI) removal capacity increased with decreasing aliphatic group size. Cardoso et al. (59) synthesized macro porous resins with specific surface areas by suspensions polymerization with 4-VP and DVB as co-monomers and various proportions of porogens (toluene and hexane) for removal and recovery of chromium.

6.3 Poly(ethylene glycol)

An aqueous solution of poly(ethylene glycol) is a biphasic system that has been used as a medium for the phase transfer recovery of metals from salt solutions (22). When ammonia is bubbled through an aqueous solution having the Cr(VI) in the upper PEG-rich layer, the chromium is transferred to the lower layer. Similarly, passing carbon dioxide through the system in aqueous ammonium with Cr(VI) in the lower layer results in transfer of chromium to the upper layer (22). Subsequent addition of ferrous sulfate leads to reduction of Cr(VI) to Cr(III), followed by an essentially quantitative transfer of the chromium from the PEG to the salt layer. A combination of electrolytic



Sch. 7.3.1. Extraction of Cr(VI) by Calix (4)arenes.

methods coupled with the iron (II, III) redox system can be used to reduce Cr(VI) to Cr(III). The system succeeds because after oxidation of the added iron(II) to iron(III) by Cr(VI), the iron(III) is electrolytically reduced back to Iron(II). The iron(II), therefore, needs to be present in only catalytic quantities.

6.4 Calixarens

Calixarens (22), which are cyclic oligomers prepared by condensation reaction between para substituted phenols and formaldehydes, are excellent phase transfer agents. Calix(4)arene have both a wide and narrow rim. They have tert-butyl groups on the wide rim and phenol functionalities on the narrow one (Sch. 7.3.1). Calix(4)arenes diamine has been found to be a pH switchable extractant for Cr(VI) [60]. The reaction scheme is shown below (Sch. 7.3.1). A limitation to calix[4] arenes amine is that they are susceptible to oxidation by Cr(VI). Calix(4) arenes amide, however are more resistant to oxidation and shows significant liquid-liquid extraction of chromate from water into a chloroform phase (61–63). The amides have the advantage in that they have both amide nitrogen and carbonyl oxygen functionalities for hydrogen bonding with the chromate.

6.5 Poly(acrylamide) Based Copolymers

Poly(acrylamide) homo-polymer is a water soluble polymer. So it is not suitable for chromate extraction. Therefore it is necessary to make it co-polymer (block and graft) with other monomer. Bajpai et al. (64) prepared poly(acrylamide-co-maleic acid) hydro-gels to extract Cr(VI) from aqueous solution. The polymer removes Cr(VI) from aqueous solution effectively. The possible reasons for the adsorption of Cr_2O_7^- ions onto the hydrogels seems to be the hydrogen bonded interaction between the electronegative oxygen atom of dichromate ions and hydrogen atom present in carboxylic groups of maleic acid and amide groups of acrylamide. Iron(III) complex of a carboxylated polyacrylamide grafted sawdust is an adsorbent for the removal of Cr(VI) from aqueous solution (65). Up to 99% removal is possible in the pH range 2–3 (22). The Cr(VI) is adsorbed as chromate (HCrO_4^-). Over 95% of the chromium can be desorbed with 0.1M NaOH solution. Amine-modified polyacrylamide-grafted coconut has been studied (65) for the adsorption of chromium from aqueous solution.

6.6 Polyamines and Polyanilines

One approach in designing specific extractants for chromate is to seek cationic hosts with tetrahedral cavities (22). These cations can have metal centers that bind the oxo functionalities of the oxoanions or cationic groups that can interact by hydrogen bonding (Eq. 7.5.1 and Eq. 7.5.2). Amines meet many of these requirements and reversibility

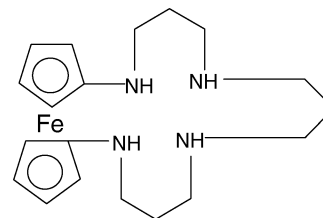
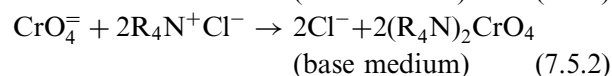
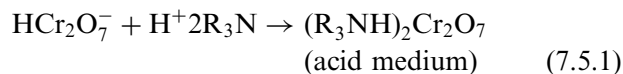


Fig. 7.5.1. Cyclic polyamine.

of anionic binding can be achieved by switching between the free amines and its protonated form (22).



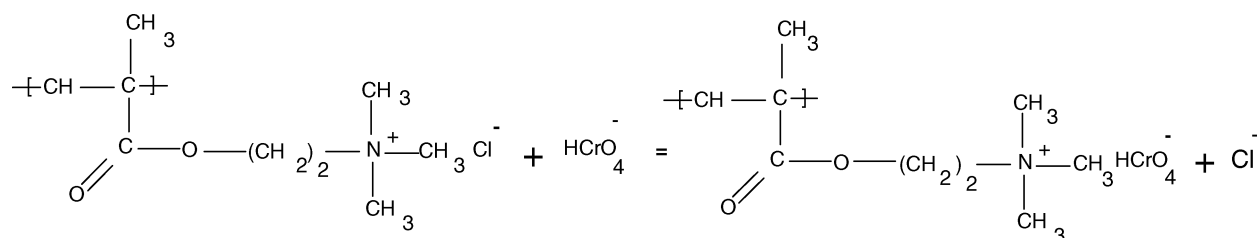
[R_3N = Simple long chain alkyl amine]; [$\text{R}_4\text{N}^+\text{Cl}^-$ = Alkyl ammonium salt]

Another approach is to use cyclic polyamines. These compounds are cationic in acid solution, have cavity sizes that can be modified to be specific for tetrahedral chromate and have multiple hydrogen bonding sites (66). An example of cyclic polyamines is given below (Fig. 7.5.1). Water soluble polyazaferrocene macrocycle has been employed as an oxoanion sensor by making use of the reversible 1-electron oxidation of ferrocenyl moiety (67).

The chemical structure of polyaniline (PANI) in acid medium is suitable for adsorbing chromate (68). However, very few works (69) on Cr(VI) adsorption by PANI has been reported. Ansari (70) reported the application of PANI (HCl doped, half oxidized emeraldine form) composite with sawdust in acid medium for adsorption and desorption of Cr(VI). Eisazadeh (71) reported removal of chromium from wastewater using PANI (H_2SO_4 doped, emeraldine form) composites. The reduction of Cr(VI) on PANI surface (72–73) and needs of acidic medium are the major drawbacks of using PANI in removing Cr(VI). Fully oxidized PANI (pernigraniline) may be used to avoid the drawbacks (36). The addition of formaldehyde to aniline in acidic medium forms a rubbery thermoplastic resin spontaneously, which is known as aniline formaldehyde condensate (AFC). It is extremely used in adhesive industry and also useful to bind Cr(VI) effectively in acid medium (74). AFC is effective even at low concentration of Cr(VI) (9 mg. L^{-1}) and reduces Cr(VI) level by 70% at pH 3 (74).

6.7 Poly(2-methacryloyloxyethyl trimethyl ammonium chloride) Resin

Crosslinked poly (2-methacryloyloxyethyl trimethyl ammonium chloride) (PMETAC) can act as “ion-specific resin” under proper operating condition (75). Crosslinked PMETAC binds chromates selectively at wide pH range through ion exchange mechanism as given below



Sch. 7.6.1. Extraction of Cr(VI) by PMETAC.

(Sch. 7.6.1). Rivas et al. (76) co-polymerized METAC with acrylic acid and then cross-linked by *N,N*-methylene bisacrylamide to obtain specialty resin. This specialty resin has the property of binding both Cr(III) and Cr(VI) simultaneously. The polymer uptakes Cr(III) and Cr(VI) through cation-exchange and anion exchange mechanism, respectively.

6.8 Solvent Impregnated Resins

Solvent impregnated resins (SIR) are simply prepared by immobilization of solvent extraction reagent having a complexing group within a highly porous polymer adsorbent by a physical contact (77–78). Aliquat 336 (tri-octyl methyl ammonium chloride) is a well known extraction reagent for removal of chromate ions from solutions (79) (Sch. 7.7.1). Kabay et al. (80) impregnated Aliquat 336 with amberlite XAD-4 for Cr(VI) extraction from aqueous solution in presence of chloride and sulfate ions. Arda et al. (81) prepared SIR using Diaion HP-20 and HP-2MG as polymer adsorbents, Aliquat 336 as extractants, and poly(vinyl alcohol) (cross-linked with vinyl sulphone) as protector (81) are used for the selective extraction of Cr(VI). Guibal (82) et al. reported Cr(VI) extraction using Aliquat 336 in a hollow fiber module made of chitosan.

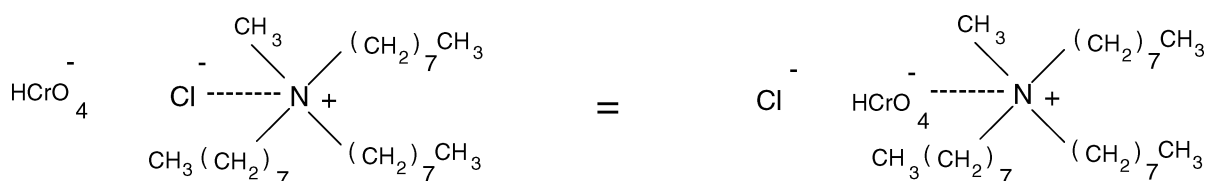
6.9 Biopolymers

It has been found that (83) biopolymers beads composed of crosslinked sodium alginate and crosslinked gelatin are effective adsorbent for the removal of dichromate ions from aqueous solution. The chemical composition of beads greatly influences their adsorption capacity. The adsorption of Cr(VI) increases with the increasing concentration of sodium alginate, gelatin and glutaraldehyde. It is quite sensitive to the pH of a suspension and shows an optimum

uptake value at pH 8.9 (iso-electric point of gelatin). Chitosan based polymeric surfactants prepared by partial *N*-acylation of amine groups on chitosan with acid anhydrides were also used for the removal of Cr(VI) from wastewater (84). The maximum adsorption capacity of Cr(VI) was 180 mg/g at a final pH of 5.3. Starch is a low cost natural renewable polymer that can be highly cross-linked with epichlorohydrin to make them water-insoluble and modified with various reagents to yield ionic products. Ionic products can be used to remove heavy metal ions from wastewater. It has been reported that water insoluble cross-linked amphoteric starch containing phosphate group and tertiary amine group can remove Cr(VI) from solutions (85). The adsorption of the chromate ions follows the Langmuir adsorption isotherm, and it was confirmed that Cl^- of tertiary amine groups are exchanged by chromate ions. The adsorption of Cr(VI) on the cross-linked starches with cationic quaternary ammonium and anionic carboxymethyl groups was also investigated (86–88).

7 Application of Polymeric Materials in Real Cases

A typical industrial wastewater (89) containing Cr(VI) analyzed before and after passing through the PANI-packed column (Table 8.1). As the sulfate ion showed an adverse effect in adsorbing Cr(VI), it was removed from the wastewater by drop wise addition of BaCl_2 in acidic medium and filtration. The sulfate free filtrate was passed through the PANI-packed column (0.8 cm \times 8 cm) with down flow rate 5 mL.min⁻¹. It was found that the specified columns could remove Cr(VI) to the level of less than 0.02 mg.L⁻¹. The adsorbed Cr(VI) was eluted from the column by passing 250 mL of 2.5M NaOH solution followed by washing with 50 mL water. Both the regenerates and washing were collected in same container and Cr(VI) was recovered as BaCrO_4 .



Sch. 7.7.1. Binding mechanism of HCrO_4^- ions by Aliquot 336.

Table 8.1. Some water quality parameters of synthetically prepared wastewater before and after passing PANI-packed column

Parameter	Sample	After passing through column
pH ^a	7.3	5.0
Temperature (°C)	25	25
Color	Yellow	Colorless
Suspended solids (mg.L ⁻¹)	750–760	620–680
Cr(VI)(mg.L ⁻¹)	18–19	0.01–0.02
Chloride (mg.L ⁻¹)	690–700	750–760
Sulfate (mg.L ⁻¹)	190–200	0.7–0.8
Ni ²⁺ (mg.L ⁻¹)	40–41	40–41
Fe ³⁺ (mg.L ⁻¹)	1.5–1.6	1.45–1.52
Mn ²⁺ (mg.L ⁻¹)	0.9–1.0	0.86–0.98

^apH was adjusted to 4 before feeding into column using HCl;
 b) The chloride value is a result of addition of HCl for pH adjustment.

The mother liquor left after BaCrO₄ separation was found to contain Cr(VI) at concentration below 0.05 mg/mL, which was disposed of safely into the surface water.

8 Conclusions

The review has attempted to explain the role polymers (both synthetic and natural including bio-polymers) in the removal and recovery of chromium from wastewater. The role of polymers in the extraction of chromium is important with respect to high adsorption capacity, selectivity, rapid extraction, wide pH range of extraction, satisfactory desorption and regeneration. The polymeric materials may be applied in real samples including wastewater on the commercial basis.

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