Abstract

Chromium is the sixteen abundant metals in earth crust. Chromium is a transition metal, and has oxidation states ranging from Cr (-II) to Cr (+VI). Naturally it occurs in the form of metal oxide, metal sulfide but not in elemental state. Chromium is one of the toxic heavy metal of widespread use. Extensive use of chromium in many industries such as electroplating, steel production, wood preservation and leather tanning, results in releasing of chromium containing effluents in to the environment. Chrome electroplating industry, ore mining, and preparation of alloys containing chromium are the major sources of Cr(VI) and Cr(III) in environment. Electroplating is a process of deposition of thin layer of chromium onto a metal or plastics objects. The chromium layer can be decorative as well as provide corosions resistance, ease cleaning, or increase surface hardness, etc. Due to incomplete consumption of Cr(VI) from electroplating bath effluent large quantity of effluent containing Cr(VI) is generated at the end of electroplating process. Not only electroplating process but also leather tanning process generate large quantity of effluent containing Cr(VI).

Trivalent chromium is relatively less harmful and it is an essential trace element in mammalian metabolism. It is involved in glucose metabolism. It is assigned as essential micronutrient. Hexavalent chromium on the other hand is much more toxic due to its high water solubility and mobility. Under normal physiological conditions, Cr(VI) interacts spontaneously with the intracellular bio-molecules (e.g. ascorbate, glutathione, etc.) to generate the short lived intermediates such as Cr(V), Cr(IV), free radicals and the end product Cr(III). The process produces reactive oxygen species (ROS) that easily combines with DNA- protein complexes. This result in to carcinogenic activity of Cr(VI). From a health standpoint, hexavalent chromium is the most toxic form of chromium. In the U.S. it is heavily regulated by the Environmental Protection Agency: the EPA lists it as a hazardous air and water pollutant because it is a human Carcinogen, a "priority pollutant" under the Clean Water Act and a "hazardous constituent" under the Resource Conservation and Recovery Act.
Above discussion shows that, there is need for removal of chromium from industrial effluent before it is to be allowed to release into natural water resources. Present study deals with removal of chromium from aqueous solution especially in context to chrome electroplating effluent. Cr(VI) from effluent can be removed as Cr(VI) by precipitation or as Cr(III) after reduction of Cr(VI) to Cr(III). In present study we have adopted both types of strategy for removal of Cr(VI) from electroplating effluent.

Analysis of Cr(VI) was done by volumetric method and spectrophotometric method. Under volumetric method iodometric titration was carried out, whereas in spectrophotometric method used DPC reagent (method describe in Volgel, 1964. After analysis the average concentration of Cr(VI) in electroplating effluent was found to be 70.71±0.11 and pH 1.51±0.01. Thus, whole of the study was carried out at this concentration of Cr(VI) from aqueous solution. The UV-Visible spectra of electroplating effluent showed that Cr(VI) is present in dichromate form in effluent.

For removal of Cr(VI) as Cr(III), in first step reduction of Cr(VI) to Cr(III) was performed by different reducing agents such as, H₂O₂, FeSO₄.5H₂O, Na₂S₂O₃.7H₂O, Na₂S, NH₂NH₂.H₂SO₄, Fe-metal, different plant biomasses, activated charcoal. In this case for reduction of Cr(VI) to Cr(III) we are reporting some of the reducing agents that are not reported previously. Different parameters affecting reduction reaction by each reducing agent are studied independently and results are reported in thesis. The parameters studied were effect of pH, Effect dose of reducing agent, effect of time on quantity of Cr(VI) reduced, time required for completion of reaction, effect of temperature, effect of stirring rate, etc. We have found that plant biomass and activating charcoal are effective reducing agents like that of convection chemical reducing agents. Use of activated charcoal as reducing agent to Cr(VI) is the new investigation, where as many other researchers reported adsorption of Cr(VI) on activated charcoal. Among different chemical reducing agents H₂O₂ and Hydrazine sulfate provide cleaner method for reduction of Cr(VI). With these two reducing agents other than metal ion do get added into effluent. These method of reduction help to reduce formation of sludge as well as avoid contamination of Cr(III). Reactivity of different chemical reducing agents towards Cr(VI) was found different. The newly introduced reducing agents such as plant biomass, activated charcoal, sodium thiosulphate and
hydrazine sulphate showed same activity like that of previously reported reducing agents such as \( \text{H}_2\text{O}_2 \), elemental iron, \( \text{Na}_2\text{S} \), etc.

In the second step, complete removal of Cr(III) from resultant solution treated with different reducing agent was attempted either by using activated charcoal and hematite ore as an adsorbent or cation exchange resins. We observed that pH at which Cr(III) get precipitated as hydroxide i.e. above pH 7 it results into oxidation of Cr(III) to Cr(VI). Hence, removal of Cr(III) was carried out between pH 6 to 7 on activated charcoal and hematite ore as an adsorbent. In presence of both adsorbent nearly 100% removal was achieved without oxidation of Cr(III) to Cr(VI). From all reducing agents we observed that, in presence of hydrazine sulphate and activated charcoal Cr(III) can be precipitated as \( \text{Cr(OH)}_3 \) above pH 7 without allowing the oxidation of Cr(III) to Cr(VI). Activated charcoal posses relatively high cost hence we have studied hematite ore as low cost, non-toxic material as adsorbent and it is observed that hematite ore is equally effective like that of activated charcoal. Our study shows that, hematite ore is naturally available non-toxic, stable material, which provides alternative to activated charcoal.

Reduction of Cr(VI) to Cr(III) and then removal of Cr(III) as hydroxide is the beneficial than removal of Cr(VI) by precipitation. Since, in these methods recovery of Cr(III) in concentrated form and reuse is possible. This also avoids the problem of disposal of sludge.

In further studies chromium from aqueous solution was directly removed by precipitation method using Pb(II) and Ba(II) as a precipitating agents. Both precipitating agents were found successful and more than 99% removal was achieveved by optimization of different experimental parameters.

Along with Cr(III) we have studied the removal of Ni(II) and Cu(II) since like chromate electroplating Ni and Cu electroplating are most common. The method applicable for removal of Cr(III) by adsorption on activated charcoal as well as by hematite ore are found equally effective for removal of Ni(II) and Cu(II). It is also found that, simultaneous removal of all these three metal ions is possible by adsorption on hematite ore and activated charcoal. Different parameters affecting removal of these metal ions was studied which include, effect of pH, effect of quantities of different adsorbent, effect of time, effect of stirring rate, etc.
After the bench scale experiment performed the same experiment at pilot scale using some selective reducing reagents, include H$_2$O$_2$, Eichhornia biomass, activated charcoal and hydrazine sulphate. The pilot scale experiment was found equally successful towards removal of Cr(VI) like that of bench scale experiment. In conclusion we can say that the developed bench scale processes for removal of chromium from aqueous solution / effluent can be used for large scale removal of chromium effectively.