

Hydrogen Peroxide and Activated Charcoal Mediated Removal of Chromium from Chrome Electroplating Effluent

Sujata S. Modhave, *Dnyaneshwar R. Shinde

Abstract— Analysis of untreated chrome electroplating effluent procured from electroplating unit showed that it was acidic in nature (pH=1.51) and it contains Cr(VI) at the concentration 70.74 ± 0.31 ppm. This effluent is used for further experiments. Removal of chromium from effluent was achieved in two steps. In first step Cr(VI) was reduced to Cr(III) by reaction with H_2O_2 and 0.6 ml 30% H_2O_2 was found sufficient for complete reduction of Cr(VI) from 1 liter of effluent. Then in second step Cr(III) was removed from effluent by precipitating it as $Cr(OH)_3$ in presence of activated charcoal. In absence of activated charcoal pH at which Cr(III) get precipitated, it has been observed that some quantity of Cr(III) oxidizes to Cr(VI) again. Removal of Cr(III) is governed by pH of solution and at pH 6.5 to 7.0 more than 99.00% of Cr(III) has taken place. By this process chromium removal efficiency was observed more than 99.00%. After bench scale experiment process was tried at pilot scale and designed process was found highly efficient on pilot scale for removal of chromium from electroplating effluent.

Keywords— Reduction, activated charcoal, H_2O_2 , Cr(VI), Cr(III), removal, electroplating effluent.

1 INTRODUCTION

CHROMIUM in +VI oxidation state is used in many industries such as leather tanning, electroplating, manufacturing of dyes, paint and paper, etc. These industries act as source of chromium in the environment [1]. Chromium in aqueous solution mainly exists in +III and +VI oxidation state [2]. Between these two valiancy state, Cr(III) is less toxic and required in very small amount as micronutrient for growth of plants and animals [3, 4]. However, Cr(VI) is highly toxic and long term exposure to Cr(VI) can cause damage to liver, kidney, nervous tissue, etc. [5]. As a result Agency for Toxic Substances and Disease Registry (ATSDR) included Cr(VI) in the list of toxic substances and ranked as 16th most hazardous substance [6]. Cr(VI) was reported as carcinogen and mutagen [5]. Due to toxic nature of Cr(VI) World Health Organization has recommended maximum allowable concentration of Cr(VI) in drinking water at the level of 0.05 mg L^{-1} , while maximum allowable concentration of Cr(III) in treated effluent is 2 ppm [7]. Untreated industrial effluent from industry like electroplating industry, leather tanning, etc. contains very high level of Cr(VI) [8]. Conventional methods like precipitation, reduction, evaporation, membrane filtration, electrochemical precipitation, etc. are used for the removal of Cr from industrial effluent [9, 10, 11]. However, some of these methods are less effective when concentration is low [12,13]. Cr(VI) exists as dichromate ($Cr_2O_7^{2-}$) in acidic medium [14] while as chromate (CrO_4^{2-}) in alkaline medium. Both of these forms of Cr(VI) are highly water soluble in acidic as well as in alkaline medium [14]. In contrast to Cr(VI), Cr(III) can be easily converted into insoluble form and can be removed from aqueous solution [15]. Toxic nature of Cr(VI) and its high water solubility make its removal difficult form aqueous solution. One of the alterna-

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tive to remove Cr(VI) is covert it to Cr(III) and then remove Cr(III) from aqueous solution. For conversion of Cr(VI) to Cr(III) reducing agents like Fe metal, $FeSO_4$, H_2S , Na_2SO_3 , H_2O_2 , etc. are recommended [1,15,16,17,18]. Use of some of these reducing agents results into the formation of side product which, increases load on the treatment process. Use of Fe as the reducing results into formation of $Fe(OH)_3$ while H_2S results into the formation of colloidal sulfur. Likely Na_2SO_3 results into the formation of Na_2SO_4 as side a product. Relative to these reducing agents, H_2O_2 is better reducing agent since except water any other side product is not formed during the reduction of Cr(VI) to Cr(III). In present research work we are reporting simple, low cost and two step alternative physicochemical process for removal of Cr(VI) from electroplating effluent. In this process we have used H_2O_2 as reducing agent to convert Cr(VI) to Cr(III) and then Cr(III) is removed as $Cr(OH)_3$ at pH 7 by adsorption on activated charcoal. Method was found efficient at high as well as low concentration of Cr(VI) in electroplating effluent.

2 Experimental

All reagents used are of AR grade and prepared in AR grade solvents or in glass distilled water (whatever applicable).

2.1 Analysis of industrial electroplating effluent

Chrome electroplating effluent was procured from electroplating unit located in Chaken industrial area, Pune (India) and analyzed for Cr(VI) and acid content respectively by volumetry according to method described by Vogel [19].

2.2 Effect of pH on amount of Cr(VI) reduced

Reduction of Cr(VI) to Cr(III) was achieved by 30% H_2O_2 in acidic medium. Effect of pH on reduction of Cr(VI) was studied by variation of pH of effluent from pH 1.5 (original pH of effluent) to 9. pH of 200 ml effluent was adjusted to requisite value ± 0.1 by addition of dilute NaOH (pH was determined by pH meter), to it 0.1 ml 30% H_2O_2 was added and stirred for 30 minutes. After 30 minutes, reaction mixture was analysed for Cr(VI) content by spectrophotometry using diphenylcarbazide (DPC) reagent [19, 20]. Cr(VI) standard (200 ppm in

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distilled water) was used in this experiment which was prepared from AR grade dried (110 °C in an oven for 1 hr.) $K_2Cr_2O_7$. By this method Cr(VI) at concentration 0.01 µg per ml can be determined.

2.3 Time required for complete reduction of Cr(VI)

This experiment was performed on 200 ml effluent at original pH of effluent. In 200 ml effluent 0.1 ml 30% H_2O_2 was added and reaction mixture was stirred using magnetic stirrer at 200 rpm. Content from reaction flask was withdrawn at constant time interval and was analysed for Cr(VI) content by spectrophotometry. Reaction was monitored till reaction mixture gives negative test to Cr(VI) i.e. no visible red colour with DPC reagent.

2.4 Removal of Cr(III)

pH at which Cr(III) can be precipitated was obtained by turbidimetric measurement. pH of Cr(III) solution was varied from 5 to 9 at interval of 0.5 unit and turbidance was determined. For removal of Cr(III) pH of solution was adjusted to pH at which precipitation of Cr(III) take place completely (pH=7) followed by addition of activated charcoal (1 mg/ml). Resulted suspension was stirred for 45 minutes, filtered and Cr(III) was analysed by spectrophotometry by converting it to Cr(VI). For analysis of Cr(III), known volume of solution containing Cr(III) was treated with H_2O_2 in alkaline medium (pH=9.5 to 10) and diluted to definite volume. Absorbance of this was recorded at 370 nm against blank. Cr(III) content was calculated with respect to standard solution of Cr(VI). Standard Cr(VI) was prepared from AR grade dried $K_2Cr_2O_7$. Sample and standard was treated by same manner. Cr(III) at the concentration 0.01 µg per ml can be determined by this method.

2.5 Pilot Scale Process

Simple type of batch reactor was designed for pilot experiment. It consists of two tanks of 200 litre capacity. Both tanks were equipped with stirrer and pump. The outlets of tanks consist of carbon filter. Pilot scale experiment was carried out on 200 litre solution containing Cr(VI) at the concentration and pH of electroplating effluent. To it 120 ml 30% H_2O_2 was added and stirred at 200 rpm for 50 minutes. It is followed by addition of 200 g activated powdered charcoal. Then pH of resulted solution was adjusted to 6.5 to 7 with 10% $Ca(OH)_2$ suspension. Resulted suspension was stirred for 45 minutes and activated charcoal was allowed to settle at the bottom of tank. Then supernatant was withdrawn through outlet of the tank and analyzed for Cr(III) content. About 1.5 litre sludge containing activated charcoal was left behind in the tank which was finally filtered under vacuum. Activated charcoal was washed with 1 litre 2N H_2SO_4 to recover Cr(III). Finally activated charcoal was dried in an oven and reused for next batch process.

3 RESULTS AND DISCUSSION

Results present in this paper are mean of the three independent analysis ± standard deviation.

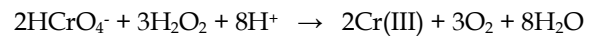
3.1 Analysis of Effluent

Analysis of Cr(VI) from untreated chrome electroplating ef-

fluent showed that effluent was acidic in nature (pH = 1.51) and it contains 70.74 ± 0.31 ppm Cr(VI). Incomplete consumption of Cr(VI) from electroplating bath and washing of the electroplated articles is a source of Cr(VI) in the effluent. Origin of acid in the effluent is chromic acid which is used as source of Cr(VI) in chrome plating process. Such effluent containing high quantity of Cr(VI) cannot be allowed to release directly into waste water streams or into natural water reservoirs without treatment.

3.2 Reduction of Cr(VI) to Cr(III) by H_2O_2

When effluent containing Cr(VI) was treated with 30% H_2O_2 at original pH of effluent then Cr(VI) get reduced to Cr(III). The reduction reaction taking place is given below [18].



Like H_2O_2 many other reducing agents such as elemental iron, ferrous sulfate, hydrogen sulfide, sodium sulfite, etc. can be used for reduction of Cr(VI) to Cr(III). However, use of H_2O_2 offer cleaner way of reduction of Cr(VI) than any other reducing agent. If reducing agents like Fe metal, $FeSO_4$, H_2S , Na_2SO_3 , etc. are used then along with formation of Cr(III) respectively formation of $Fe(OH)_3$, colloidal sulfur and Na_2SO_4 take place which increases load on treatment process [15-17]. H_2O_2 on reaction with Cr(VI) produces Cr(III) and H_2O i.e. do not produce side product which will increase load on the treatment process. If reducing agent like Fe metal is used then large quantity of sludge containing $Fe(OH)_3$ and $Cr(OH)_3$ is produced [21]. In contrast to Fe metal, if H_2O_2 is used as reducing agent then only Cr(III) will be formed after reduction of Cr(VI) and quantity of sludge produced will decrease by large amount. Therefore, we have used H_2O_2 as reducing agent in our process to convert Cr(VI) to Cr(III).

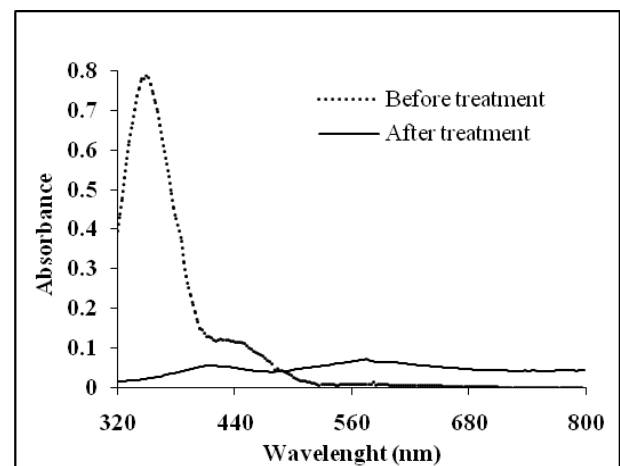


Fig. 1. UV-Visible spectra of effluent before and after treatment with H_2O_2 .

To 200 ml original effluent 0.1 ml 30% H_2O_2 was added and stirred for 45 minutes. In the process yellow solution containing Cr(VI) was converted to faint green colour which is a characteristic colour of Cr(III) in aqueous solution. The faint green coloured solution obtained after treatment with H_2O_2 showed

negative test for Cr(VI) i.e. no red colour obtained with DPC reagent. Further confirmation of reduction of Cr(VI) to Cr(III) was done by UV-Visible spectra of effluent before and after treatment (fig-1). Untreated effluent contains Cr(VI) and in acidic medium it exists as $\text{Cr}_2\text{O}_7^{2-}$. It shows characteristic peaks at 350 and 440 nm [19]. When effluent containing Cr(VI) was treated with hydrogen peroxide then two characteristic peaks of dichromate disappears and peaks at 340 and 576 appears. These peaks are the characteristic peaks of Cr(III) indicating that Cr(VI) from effluent is converted into Cr(III) by action of H_2O_2 [22].

3.3 Effect of pH on quantity of Cr(VI) reduced

Reduction of Cr(VI) to Cr(III) by H_2O_2 was found to be pH dependent. Experimental result depicted in figure-2 point out that percentage of Cr(VI) reduced from definite volume of the effluent in same time goes on increasing with decrease in pH of effluent.

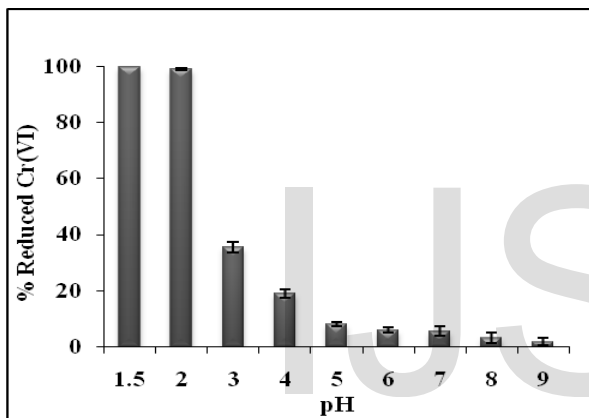


Fig-2: Effect of pH on % of Cr(VI) reduced in 30 minutes.

It has been further observed that pH 5 and above do not favours reduction of Cr(VI) to Cr(III) and very small quantity of Cr(VI) get reduced to Cr(III). Similar results were reported by W. van Niekerk et. al. on reduction of Cr(VI) by H_2O_2 [18]. At pH 4 and below rate of reduction of Cr(VI) to Cr(III) was observed high. As a consequence at pH 2, 99.01±0.35% reduction of Cr(VI) to Cr(III) was observed within 30 minutes reaction time while at pH of electroplating effluent nearly 100% reduction was observed within same time. The analysis electroplating effluent showed that it is highly acidic in nature (pH = 1.51). The observed results of effect of pH on reduction of Cr(VI) point out that such acidic pH of electroplating effluent is highly helpful for reduction of Cr(VI) to Cr(III) by H_2O_2 . H^+ ion act as catalyst in conversion of Cr(VI) to Cr(III) thereby high H^+ ion concentration favours this reduction reaction [19]. With decrease in pH of solution H^+ ion concentration goes on increasing logarithmically hence rate of the reduction reaction of Cr(VI) to Cr(III) goes on increasing with decrease in pH of solution. The reducing agents like sulphite, H_2S , Fe metal also requires acidic pH for complete reduction of Cr(VI) to Cr(III). Like H_2O_2 rate of reduction of Cr(VI) was found high at pH below 5 by sulphite and Fe metal [15,17].

3.4 Quantity of H_2O_2 for complete reduction of Cr(VI)

This experiment was performed to fix quantity of H_2O_2 required for complete reduction of Cr(VI) from unit volume of effluent at pH=2. Experimental results presented in Figure 3 indicate that 0.6 ml 30% H_2O_2 is sufficient for complete reduction Cr(VI) to Cr(III) within 60 minutes reaction time.

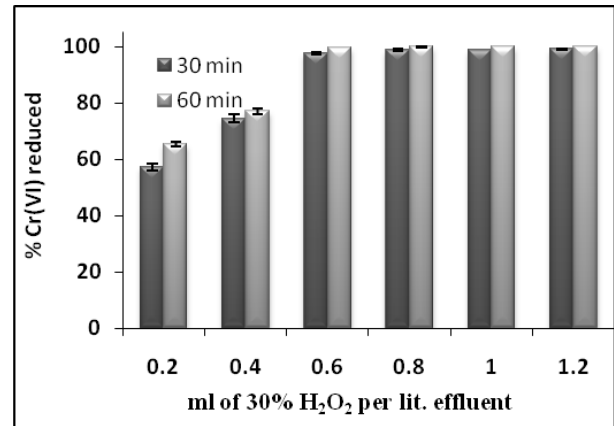


Fig. 3. Percentage of Cr(VI) reduced with different quantities of H_2O_2 in 30 and 60 minute time.

These results further indicate that quantity of H_2O_2 such as 0.4 ml 30% H_2O_2 per liter effluent is not sufficient for complete reduction of Cr(VI) within 60 minutes. Reaction mixture containing 0.2 and 0.4 ml 30% H_2O_2 was kept under observation for 24 hr. and it has been observed that complete reduction do not take place even after 24 hr. Thus, in further experiments we have used 0.6 ml 30% H_2O_2 per liter effluent for reduction of Cr(VI) to Cr(III).

3.5 Time required for complete reduction of Cr(VI)

This experiment was performed to obtain exact time required for complete reduction of Cr(VI) from unit volume of effluent containing Cr(VI). Results depicted in fig-4 point out that when 0.6 ml 30% H_2O_2 is used per liter effluent then 50 min observed to be sufficient for complete reduction of Cr(VI) to Cr(III).

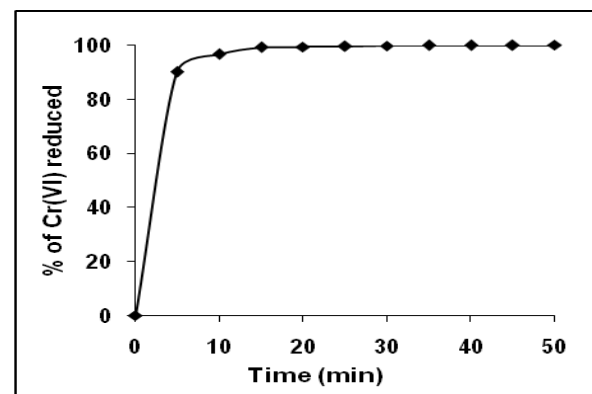


Fig-4: Effect of time on quantity of Cr(VI) reduced to Cr(III).

Within 50 minutes time percent reduction was observed 100%. The result presented in Figure 4 further indicates that initial rate of reaction is very high which goes on decreasing very rapidly with time. Within first 5 minutes about 90% reduction

of Cr(VI) take place while for 100 % completion it required about 50 minutes. It is well known fact that rate of a chemical reaction is directly proportional to conc. of reactants in reaction mixture at that time. In present reaction concentration Cr(VI) and H₂O₂ goes on decreasing with time hence rate of reaction goes on decreasing with time. In present reaction concentration Cr(VI) and H₂O₂ goes on decreasing with time hence rate of reaction goes on decreasing with time. This reflects in terms greater time for completion of reaction although about 90 % Cr(VI) is reduced in first five minutes. The observed time required for complete reduction of Cr(VI) to Cr(III) with H₂O₂ is considerably low than reducing agent like Fe metal [15], sodium sulphite [16], and H₂S [17]. This is one more advantage of use of H₂O₂ as reducing agent for Cr(VI) than other reducing agents.

3.6 Removal of Cr(III)

Cr(III) was removed as Cr(OH)₃ form effluent which was previously treated with H₂O₂. Determination of turbidance with respect to pH of Cr(III) solution (Figure 5) indicate that Cr(III) starts precipitating as Cr(OH)₃ above pH 6.5 which reflects in terms of rapid increase in turbidance of Cr(III) solution. However, it has been further observed that some quantity of Cr(III) get oxidized to Cr(VI) (Figure 6) at pH 7 and above.

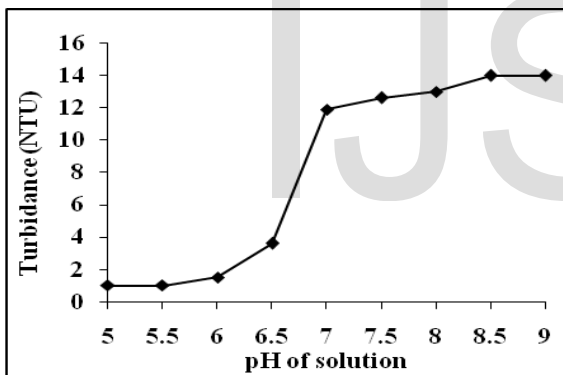


Fig.5. Graph - pH against turbidance of Cr(III) solution.

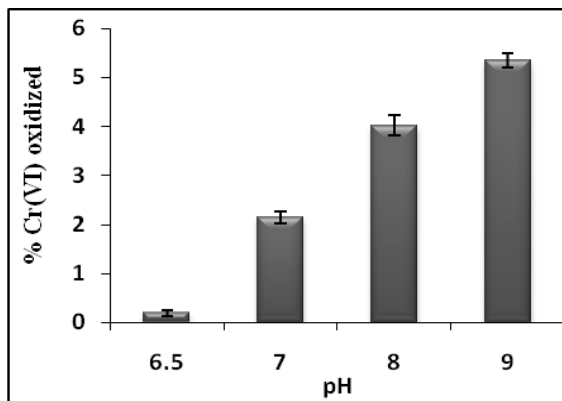


Fig. 6. Effect of pH on amount of Cr(III) oxidized to Cr(VI) in presence of H₂O₂ in 45 minutes.

Formation of Cr(VI) is clearly indicated by pale yellow colour to the solution of which intensity goes on increasing with time.

Further it is confirmed by uv-visible spectra of solution (Figure 7). Cr(III) in aqueous solution shows characteristic peaks at 310 and 576 nm but when precipitation of Cr(III) is carried out above pH 7 characteristic peak appears around 370 nm which is a characteristic of Cr(VI) i.e. CrO₄²⁻. This indicate that in presence of residual H₂O₂ oxidation of Cr(III) take place to Cr(VI). Residual H₂O₂ arises in treated effluent due to incomplete consumption of H₂O₂ from the reaction mixture. In alkaline medium Cr(III) is unstable and get easily oxidized to Cr(VI) by H₂O₂ [19]. This observation showed that in presence of residual H₂O₂ complete precipitation of Cr(III) as hydroxide from effluent is not possible. After trial and error we have noted that if precipitation of Cr(III) is carried out in presence of powdered activated charcoal then oxidation of Cr(III) to Cr(VI) do not take place even up to pH=9. Activated charcoal provides reducing environment and thereby avoids oxidation of Cr(III) to Cr(VI). Therefore, we have used 1 mg ml⁻¹ (optimized quantity) powdered activated charcoal during precipitation of Cr(III). We have observed that one more advantage of activated charcoal in our process that it act as an adsorbent for Cr(OH)₃. When precipitation was carried out in presence of activated charcoal and after settling of charcoal supernatant was analyzed for Cr(III) content then it do not showed positive test for Cr(III). When separated activated charcoal was treated with 2N H₂SO₄ Cr(III) was released into washing solution. In washing process 10 ml 2N H₂SO₄ was required for complete removal of Cr(OH)₃ from 1 g activated charcoal.

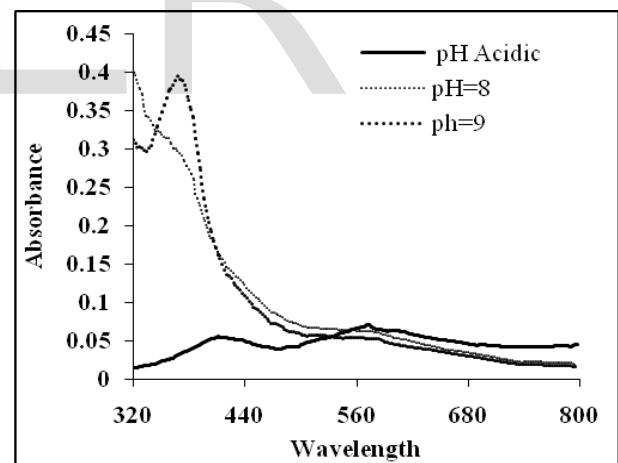


Fig. 7. Spectra of Cr(III) containing solution at different pH in presence of H₂O₂.

3.7 Pilot Scale Experiment: After bench scale experiment pilot scale experiment was performed so as to test feasibility of process for large scale treatment of effluents. Experiment was carried out on 200 litre solution containing Cr(VI) at the conc. and pH of electroplating effluent. For complete reduction of Cr(VI) to Cr(III) from 200 litre solution 120 ml 30% H₂O₂ was found to be sufficient. Within 50 minutes time 100 % reduction of Cr(VI) to Cr(III) was observed and this was confirmed by test with DPC reagent and by UV-Visible spectra. At pH = 7 and in presence of activated charcoal Cr(III) was removed and

analysis shows that 99.11% chromium get removed from the solution. This proved that the designed process is highly efficient and even effective at large scale. As activated charcoal is reused cost of the process decreases by large amount. After washing of activated charcoal we get Cr(III) as $\text{Cr}_2(\text{SO}_4)_3$ in concentrated form, which can be reused in electroplating process.

4 Conclusions

Cr(VI) from chrome plating effluent can be successfully reduced to Cr(III) by H_2O_2 and Cr(III) from effluents can be removed as $\text{Cr}(\text{OH})_3$ using activated charcoal as an adsorbent. The designed process by our self allowed more than 99% remediation of chromium from effluent. Bench and pilot scale experiments are equally effective for removal of chromium from industrial effluent and designed process can be used for large scale treatment of effluent containing chromium in both oxidation states.

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