



## Evaluation of Plant Biomass as Reducing Agent to Cr(VI) from Electroplating Effluent and Removal of Cr(III) by Adsorption on Hematite Ore

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The UV-visible absorption spectra of untreated electroplating effluent indicate that it contains Cr(VI) in the form of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ). Quantitative analysis indicated that effluent was acidic in nature and consists of about 146 ppm  $\text{Cr}_2\text{O}_7^{2-}$ . Primary experiment clearly indicated that fresh biomass of plants such as cabbage leaves, cauliflower leaves, *Sisuvium*, biomass of common agriculture weed, leaves of *Colocasia arum*, etc. can be used as reducing agent to Cr(VI). pH dependence study showed that acidic and low pH is essential for faster reduction of Cr(VI) to Cr(III). At pH of electroplating effluent and optimized effluent to biomass ratio 60 to 105 minutes were required for nearly 100 % reduction of Cr(VI) to Cr(III). After complete reduction of Cr(VI), it was removed as  $\text{Cr}(\text{OH})_3$  in presence of hematite ore. Applicability of bench scale experiment for large scale removal of Cr(VI) was tested and results of large scale experiment were found fascinating.

**Keywords:** Removal, Cr(III), Electroplating effluent, Hematite.

### INTRODUCTION

Chrome electroplating is one of the most common plating used for coating metal articles such as kitchen fittings, automobile parts, etc. to make them attractive as well as to protect them from corrosion. In chrome electroplating highly concentrated solution of chromic acid and sulfuric acid are used. Incomplete consumption of the chromic acid in electroplating process results into generation of effluent containing large quantity of Cr(VI), which is already proved to be highly toxic in nature<sup>1,2</sup>. As Cr(VI) is highly toxic in nature it must be removed before effluent is permitted to be released into the environment. There are number of methods recommended to remove Cr(VI) from industrial effluents which includes reverse osmosis, electrocoagulation, adsorption, reduction, precipitation, bioaccumulation<sup>3,4</sup>. But these methods have their own advantages and disadvantages. Some method are highly efficient towards removal of Cr(VI) but are not cost effective, while some of the methods are less effective when concentration is low or produces large amount of sludge and disposal of sludge is big problem<sup>5,6</sup>. When method is technologically less complicated and has low cost then it is easily accepted by industry for effluent treatment. In present study, we have tried to develop simple, low cost and efficient method in our laboratory for removal of Cr(VI) from chrome electroplating effluent. In this process, we have

used easily available cost less biomass of plants as reducing agent to Cr(VI) in place of chemical reducing agents such as Fe metal,  $\text{FeSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{Na}_2\text{SO}_3$ , etc.<sup>7,8</sup>. In this process waste produced in plant biomass which can be easily disposed as it is non-toxic in nature and biodegradable. In second step Cr(III) is removed by adsorption as chromium hydroxide on hematite ore. Finally Cr(III) is recovered from hematite ore which can be recycled. Such process was found to be very successful on lab scale as well on large scale. There are no reports on such process hence we are reporting work done on this method in our laboratory.

### EXPERIMENTAL

Untreated chrome electroplating effluent was compassionately obtained from electroplating unit located in Bhosari Industrial area, Pune (India). Fresh plant biomass of plants such as cabbage leaves, cauliflower leaves, *Sesuvium*, *Colocasia arum* (non edible) and common weeds were obtained from farmland. Biomass was crushed in the blender and used for different experiments. Hematite ore was purchased from chemical supplier. It was washed with distilled water to remove water soluble impurities and then dried at 200 °C for 3 h and used in further experiments.

**Primary experiment:** In 100 mL effluent, 6 g crushed biomass was added and stirred for 45 min at 200 rpm on

magnetic stirrer followed by filtration. From the filtrate Cr(VI) was analyzed by the spectrophotometry.

**pH Dependant reduction of Cr(VI):** pH of 100 mL effluent was adjusted to requisite value  $\pm 0.1$  (1.5, 2 to 9 changed by 1 unit). To it 6 g crushed biomass of respective plant species was added and stirred for 45 min on magnetic stirrer, filtered and filtrate was analyzed for Cr(VI) content by spectrophotometry.

**Effect of biomass to effluent ratio on percentage of Cr(VI) reduced:** This experiment was performed at original pH of electroplating effluent. Biomass to effluent ratio (w/v) was varied from 2:100 to 12:100. The effluent containing biomass at particular ratio was stirred at 100 rpm for 45 min, filtered and filtrate was analyzed for Cr(VI) content by the spectrophotometry.

**Kinetics of reduction:** To 200 mL effluent optimized quantity of crushed biomass of respective plant was added and stirred till nearly 100 % reduction of Cr(VI) take place from effluent. At definite time interval 5 mL solution was withdrawn and analyzed for Cr(VI) content by spectrophotometry.

**Removal of Cr(III):** Plant biomass treated effluent was filtered and then passed through a bed of activated charcoal to remove dissolved organic matter. To this filtrate 1 mg mL<sup>-1</sup> hematite ore was added and stirred for 45 min and ore was allowed to settle. The supernatant was withdrawn and was analyzed for Cr(III) content by the spectrophotometric method.

**Experiment on large scale:** Large scale experiment was performed on 100 L synthetic effluent using the biomass of *Colocasia arum*. Cylindrical tank of 100 L capacity (polyethylene) equipped with the stirrer and the pump was used as reactor. To 100 L effluent 5 kg crushed biomass was added and stirred at 200 rpm still complete reduction of Cr(VI) take place to Cr(III). Then content of tank was taken out through outlet consisting of carbon filter To filtrate 100 g hematite ore and 1 g hydrazine sulfate was added and pH of resulted suspension was adjusted to 6.5. Resulted suspension was stirred for 45 min. Ore particles allowed to settle down at the bottom of tank and supernatant was withdrawn. Finally about 1.1 L suspensions containing hematite was filtered under vacuum. From hematite ore Cr(III) was recovered by washing it with 2 N H<sub>2</sub>SO<sub>4</sub>. Hematite ore was dried and reused. Washing of hematite ore generated about 900 mL solution containing Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

Absorption spectra of dilute electroplating effluent was recorded using double beam UV-visible spectrophotometer (Systronic (India) 2202 model) and further analyzed for Cr(VI) content by spectrophotometry using diphenyl carbazide (DPC) reagent<sup>9</sup>. 100 ppm standard solution of potassium dichromate was used as reference for the estimation. pH of the electroplating effluent was determined by standardized pH meter [Elico (India) LI 120]. Chromium(III) was analyzed by spectrophotometric method using diphenyl carbazide after oxidation of Cr(III) to Cr(VI) by potassium persulphate<sup>10</sup>.

## RESULTS AND DISCUSSION

**Characteristics of electroplating effluent:** UV-visible spectrum of untreated chrome electroplating effluent (Fig. 1) consists of one broad and strong peak at 350 nm and one weak

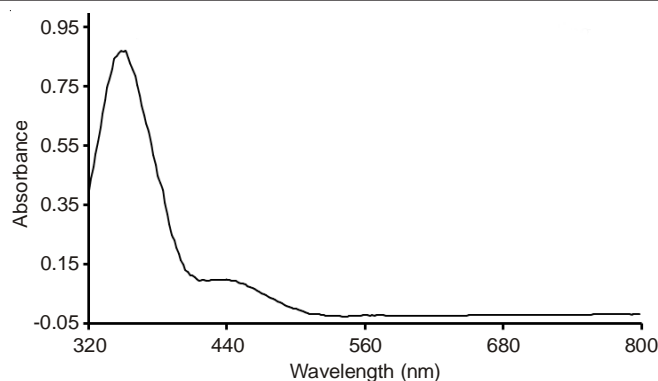


Fig. 1. UV-visible spectra of chrome electroplating effluent

broad peak at 440 nm. These are the characteristics of Cr(VI) in dichromate form (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>)<sup>10</sup>. These bands are due to charge transfer excitations from oxygen to Cr(VI)<sup>11</sup>. Chromium(VI) in the dichromate form and acid arise in effluent due to use of chromic acid in chrome electroplating process.

Quantitative analysis of effluent showed that it is acidic in nature (pH = 1.67) and contains about 146  $\pm$  0.24 ppm Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. This concentration of Cr(VI) is very high than permissible concentration of Cr(VI) in effluent which can be allowed to be released into environment<sup>12</sup>. Hence, treatment must be given to chrome electroplating effluent before it is being allowed to be released into natural water streams.

**Preliminary experiment:** Chromium(VI) in dichromate form is highly water soluble at all pH and can not be removed from aqueous solution easily<sup>13</sup>. Chromium(VI) can be precipitated as BaCrO<sub>4</sub> or PbCrO<sub>4</sub> in acidic medium<sup>10</sup>. But such method will generate sludge consisting of BaCrO<sub>4</sub> or PbCrO<sub>4</sub>. Both of these compounds are highly toxic hence disposal of such sludge will be a big problem. Hence alternative way is to convert Cr(VI) to less toxic form Cr(III) and then remove Cr(III) from effluent. Chromium(III) is less toxic as well as can be easily precipitated as Cr(OH)<sub>3</sub> under neutral to slightly alkaline condition<sup>14</sup> hence can be removed easily. Number of chemical reducing agents were reported to convert Cr(VI) to Cr(III) which include Fe metal, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, FeSO<sub>4</sub>, etc.<sup>15-20</sup>. In present investigation, we have explored easily available, costless and fresh biomasses of plants such as cabbage leaves, cauliflower leaves, *Sesuvium* (whole biomass), *Colocasia arum* (non-edible variety) and biomass of common weeds as reducing agent to Cr(VI) as an alternative to the chemical reducing agents. All these plant materials are easily available at farm land site or vegetable market site. Primary experiment was carried out to assess ability of plant biomass to reduce Cr(VI) to Cr(III). After 45 min. reaction time Cr(VI) content in solution was analyzed of which results are depicted in Fig. 2.

These results point out that at pH of electroplating effluent all the biomass of selected plants act as a reducing agent to Cr(VI). When more reaction time was allowed then complete reduction of Cr(VI) to Cr(III) was observed from all the flasks. The conversion of Cr(VI) to Cr(III) is clearly indicated by UV-visible spectra recorded after complete reduction of Cr(VI) to Cr(III) (Fig. 3) as well as by negative test to Cr(VI) with diphenyl carbazide. The effluent treated with plant material showed broad and weak peaks at 410 and 603 nm, which are the characteristics of Cr(III) in aqueous solution<sup>11</sup>.

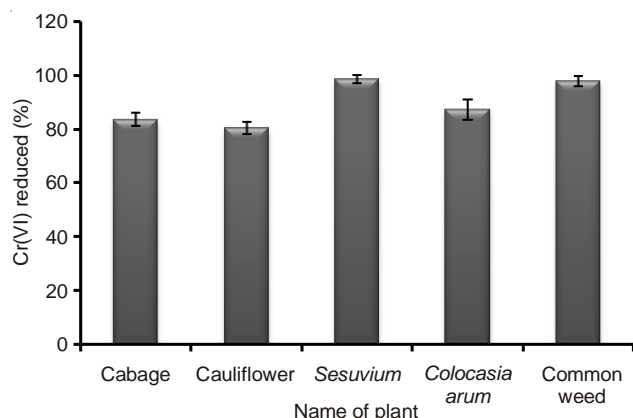


Fig. 2. Percentage of Cr(VI) reduced with 5 g biomass within 60 min

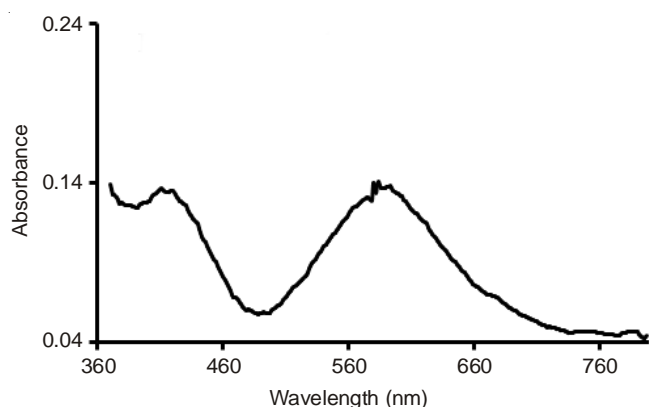
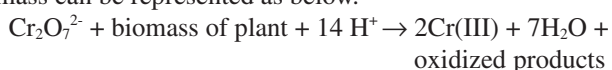


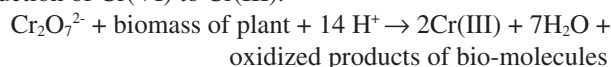
Fig. 3. UV-visible spectra of plant biomass treated effluent having Cr(III)

The primary experiment indicated that fresh biomass of selected plant are good reducing agents towards Cr(VI) and can be used in place of chemical reducing agents to convert Cr(VI) to Cr(III). Chromium(VI) is the strong oxidizing agent while plant material consists of variety bio-molecules such as proteins, carbohydrates, enzymes, chlorophyll, *etc.* which act as reducing agent. The reaction between dichromate ion and biomass can be represented as below.



**pH Dependant reduction of Cr(VI) by biomass of plant:** Results presented in Table-1 point out that percentage of Cr(VI) converted to Cr(III) within definite time goes on decreasing with increase in pH of the solution. For all plant materials highest per cent reduction of Cr(VI) to Cr(III) was observed at original pH of effluent. Per cent reduction observed at all other pH was found significantly lower than at pH 1.67.

It is well reported that acidic pH is required for reduction of Cr(VI) to Cr(III) by variety of reducing agents<sup>10,15-21</sup>. Dichromate consists of  $\text{O}^{2-}$  ion which on reduction of Cr(VI) to Cr(III) get converted to  $\text{H}_2\text{O}$ . Formation of water from dichromate is facilitated by  $\text{H}^+$  ions. Hence acidic and low pH favors reduction of Cr(VI) to Cr(III).



**Effect of effluent to biomass ratio on quantity of Cr(VI) reduced:** This experiment was performed to determine minimum quantity of biomass required for complete reduction of Cr(VI) from unit volume of effluent. Experimental results presented in Table-2 indicate that below 6:100 biomass to effluent ratio reduction of Cr(VI) remains incomplete by all biomasses. At 6:100 (w/v) ratios except *Colocasia arum* nearly 100 % reduction does not taken place by any other plant biomass. For all other plant materials ratio 10 to 12:100 was required for nearly 100 % reduction of Cr(VI). These results further indicate that among different biomasses quantity of *Colocasia arum* biomass required for complete reduction of Cr(VI) from unit volume of effluent is considerable low. This difference might be due to difference in inherent characteristics of plant biomass as well as content of cellulosic material in the biomass.

The quantity 6 g (for *Colocasia arum*) appears to be high as compare to chemical reducing agents ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  - 0.110 g,  $\text{Na}_2\text{S}$  (40 mg), Fe metal (40 mg) these are experimental evaluated value by us). This is due to characteristic of fresh biomass. Fresh biomass of plant consists of large quantity of water which results into greater weight of biomass. If this weight is expressed in terms of dry weight it is about 0.478 g for *Colocasia arum*. This quantity is not too high as compare to chemical reducing agents indicating that like that of chemical reducing agents plant biomass possess sufficiently high reducing capacity towards Cr(VI) hence can be utilized as reducing agent to Cr(VI) in place of chemical educing agent.

**Effect of contact time on percentage of Cr(VI) reduced:** This experiment was performed to investigate minimum time that can be taken by known quantity of the biomass for complete reduction of Cr(VI) from unit volume of effluent. The experiment was carried out on optimized pH and quantity of biomass for 100 mL effluent. The result presented in Fig. 4 indicate that time 60 min is sufficient for complete reduction of Cr(VI) to Cr(III). The time required by plant biomass is not comparatively high than chemical reducing agents such as  $\text{H}_2\text{O}_2$  (45 min), Fe metal (45 min), sodium sulfite,  $\text{H}_2\text{S}$  (60 min)<sup>15-21</sup>. Such high time may be required due to heterogeneous nature of reducing agent in biomass of plant materials.

TABLE-1  
EFFECT OF pH ON QUANTITY OF DICHROMATE REDUCED BY DIFFERENT PLANT BIOMASS

Name of Plant	% of Cr(VI) reduced with 6 g biomass of different plants				
pH	Cabbage	Cauliflower	Sesuvium	Colocasia arum	Common weed
1.67	53.59 ± 1.57	60.31 ± 1.24	68.49 ± 0.34	97.25 ± 1.28	77.77 ± 0.86
2	46.15 ± 3.30	57.83 ± 1.45	62.86 ± 4.1	79.41 ± 0.86	74.20 ± 1.79
3	31.02 ± 3.48	34.44 ± 1.71	44.41 ± 4.11	74.05 ± 0.86	65.24 ± 1.05
4	20.16 ± 2.15	20.33 ± 3.17	33.11 ± 3.17	71.44 ± 0.86	51.12 ± 1.56
5	18.26 ± 1.93	6.62 ± 1.42	28.72 ± 3.86	67.32 ± 0.86	30.9 ± 2.77
6	14.21 ± 4.44	2.38 ± 1.74	17.07 ± 3.03	47.52 ± 0.86	18.84 ± 2.21
7	2.39 ± 1.86	1.26 ± 1.44	3.26 ± 1.12	21.54 ± 0.86	8.45 ± 1.89

TABLE-2  
EFFECT OF BIOMASS TO EFFLUENT RATIO ON QUANTITY OF DICHROMATE REDUCED BY DIFFERENT PLANT BIOMASS

Biomass to Effluent ratio	Percentage of Cr(VI) reduced with biomass of different plants				
	Cabbage	Cauliflower	<i>Sesuvium</i>	<i>Colocasia arum</i>	Common weed
2:100	32.61 ± 2.85	31.86 ± 3.7	42.74 ± 1.29	59.05 ± 1.01	49.23 ± 2.51
4:100	49.86 ± 2.62	46.34 ± 1.41	64.09 ± 1.66	78.22 ± 2.13	71.31 ± 1.58
6:100	51.02 ± 2.48	56.99 ± 3.84	74.14 ± 2.64	99.02 ± 0.11	87.43 ± 1.90
8:100	63.57 ± 1.82	70.55 ± 0.58	80.82 ± 3.47	100 ± 00	94.84 ± 1.15
10:100	79.65 ± 2.86	89.22 ± 0.34	91.64 ± 1.42	100 ± 00	98.81 ± .26
12:100	85.66 ± 2.04	94.34 ± 0.08	98.48 ± 0.78	100 ± 00	100 ± 00

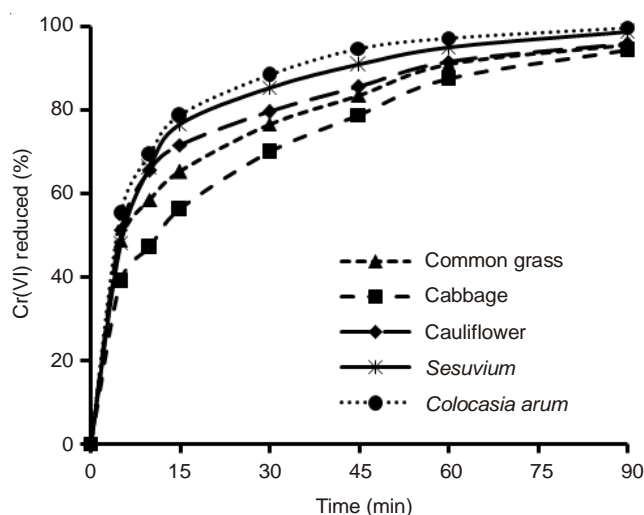


Fig. 4. Percentage of Cr(VI) reduced with time by 10 g biomass of different plants

**Removal of Cr(III):** The effluent treated with fresh biomass of plant consists Cr(III) and dissolved matter of plants biomass. Removal of Cr(III) from effluent was achieved by precipitation of Cr as  $\text{Cr}(\text{OH})_3$  in presence of hematite ore. pH dependent study showed that in presence of hematite ore at pH 6.5 to 8 maximum removal of Cr(III) take place from the solution (Fig. 5). However, if precipitation is carried at pH above 7 then it has been observed that some quantity of Cr(III) oxidizes to Cr(VI) at pH 8. Formation of Cr(VI) in solution is clearly indicated by UV-visible spectra of effluent (Fig. 5). The spectra at pH 8 shows strong absorbance band around 370 nm which is characteristic of Cr(VI) in chromate form<sup>10</sup>.

To avoid oxidation of Cr(III) to Cr(VI) then different strategy was adopted. Solution containing Cr(III) was passed through of bed of activated charcoal to remove dissolved organic matter. Then,  $\text{Cr}(\text{OH})_3$  was precipitated in presence of hematite ore and maintaining 5 ppm hydrazine sulfate. Hematite ore acts as an adsorbent to  $\text{Cr}(\text{OH})_3$  and help to remove Cr(III) from the solution. Hydrazine sulfate is good reducing agent and thereby avoids oxidation of Cr(III) to Cr(VI).

**Large scale experiment:** Large scale experiment was carried out on 100 L of synthetic effluent. The strategy for complete removal was decided from bench scale experiment. In first step biomass of *Colocasia arum* was used as reducing agent and complete reduction was achieved at pH of electroplating effluent which required about 65 min. After separation of biomass removal was achieved as  $\text{Cr}(\text{OH})_3$  by adsorption on hematite ore and experimental results showed that in the process of 98.37 % Cr get removed from the electroplating

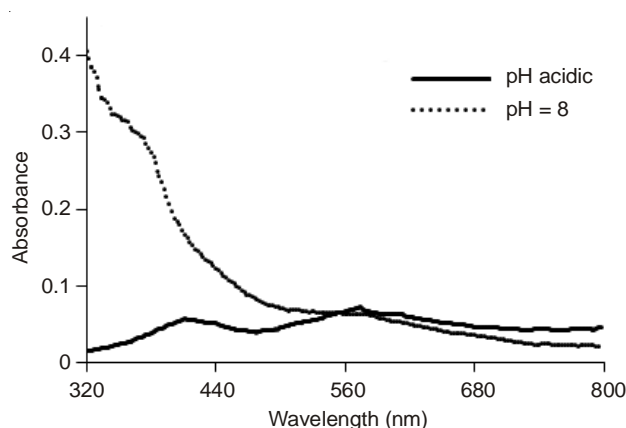


Fig. 5. Spectra of Cr(III) at pH = 2 and at pH = 8 in presence of biomass

effluent. Large scale experiment demonstrated that the designed method by utilizing biomass and hematite ore can be used for large scale removal of Cr from electroplating effluent.

## Conclusion

Plant biomass possess sufficiently high reduction capacity towards Cr(VI) and it is best alternative to conventional chemical reducing agent for reduction of Cr(VI) to Cr(III). Another naturally occurring low cost material *i.e.* hematite ore was evaluated as an adsorbent to  $\text{Cr}(\text{OH})_3$  and results showed that hematite ore can be used as an adsorbent for removal of Cr(III). As designed process showed high efficiency towards removal Cr from effluent hence it can be adopted for large scale treatment and will be cost effective.

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