

# Treatment of Electroplating Wastewater by Adsorption Technique

Debabrata Mazumder, Debabrata Ghosh and Pratip Bandyopadhyay

**Abstract**—The wastewater treatment process was evaluated in an Electroplating unit that practiced chrome and bronze plating. With a view to recycle and reuse the wastewater, adsorption process was adopted as single stage treatment instead of the existing chemical methods. Wastewater was collected from chrome and bronze plating unit and analyzed for the relevant parameters. On the basis of characteristics, adsorption process was selected and materials such as wood charcoal, coconut shell carbon, activated carbon etc. were not proved to be effective for acceptable removal of chromium and copper as well as colour. Later, Activated Alumina (AS 37 of grain size 0.6 mm – 0.9 mm) was opted and its performance was examined by several batch and column studies. The results showed that the chrome and bronze plating wastewater might be combined together and the composite sample could be treated with Activated Alumina to remove chromium, copper and colour appreciably. Under the existing pollution load in terms of chromium and copper, an adsorption column made of activated alumina was designed following the classical Bed Depth Service Time (BDST) relationship.

**Keywords**—activated Alumina, adsorption, chrome-bronze plating, electroplating wastewater

## I. INTRODUCTION

THE growth of civilization needs the manufacturing of materials, which are resistant to corrosive environment. Chrome and Bronze plating are two such methods to ensure longer durability of metallic substances. Such electroplating units have potential to generate the effluent consisting of heavy metals like chromium, copper, zinc, cadmium etc. The toxicity of the effluent obviously depends on the concentration of the respective metals as well as duration and type of discharge. With the increasing use of variety of heavy metals in electroplating industry problem may arise from potential toxicity in the environment to a great extent. Chromium is an essential element needed for human and other living organisms, which primarily involves in the action of insulin in glucose metabolism and helps transport of amino acids into the heart and liver. Its deficiency may disturb carbohydrate, lipid and protein metabolism [1].

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Water containing 0.5 mg/l or more chromium is considered highly toxic because it has carcinogenic and mutagenic properties [2]. Similarly copper is also an essential element of several proteins and enzymes. Deficiency of copper causes demineralization of bones, anemia, fragility of arteries, discoloration of skin as well as hair. High concentration of copper (above 3.0 mg/l) in water may lead to accumulation of copper in liver and lenticular nucleus of brain. Ultimately it may cause hepatic cirrhosis and brain necrosis. Renal damage may also occur due to accumulation of copper in kidney by means of consumption of water with high copper concentration in excess of permissible limit [1].

Faust and Ali (1987) [3] ascertained that removal of  $\text{Cr}^{+6}$  is extremely low while using Powdered Activated Carbon (PAC) in the pH range of 6.8 to 8.3. Tewari *et al.* (1989) [4] had shown that adsorption of chromium and copper reached to peak value at pH 5.5 and 8.0 respectively when activated carbon was used as an adsorbent. Shukla and Moitra (1994) [5] observed that acid charred waste of an oxalic acid manufacturing plant was capable of removing 98.6% of copper in 3 days. Bentonite immobilized in a polymer matrix of polysulfone in the form of special beads was effectively used in a column for the removal of copper [6]. Copper removal was possible from synthetic aqueous solution containing 5.0 to 100 mg/l of  $\text{Cu}^{+2}$  concentration using low grade rock phosphate [7]. Rice straw showed appreciable adsorption capacity than saw dust for the removal of  $\text{Cr}^{+6}$  and it could be used for the removal of the same in plating industry. In that study, at a pH 2 the maximum removal of chromium was around 95% [8]. Copper from wastewater was removed by using fly ash, with the efficiency of 62% and 98% at 60 mg/l and 2 mg/l copper concentration respectively [9]. Schmuhl *et al.* (2001)[10] established the effect of *chitosan* on adsorption of  $\text{Cr}^{+6}$  and  $\text{Cu}^{+2}$  and observed that  $\text{Cr}^{+6}$  removal was highest at pH 5.0 but pH did not affect the removal of  $\text{Cu}^{+2}$ . In presence of acidic pH ranging between 4 and 5.5 the “RAR” soil with greater amounts of exchangeable Aluminium and Iron oxides showed a low adsorption capacity but a high affinity for  $\text{Cu}^{+2}$  [11]. Aslam *et al.* (2004) [12] observed that the solution pH did not have a significant effect on the removal efficiency during adsorption of copper in sand.

The potential of mesoporous materials with MCM-41 type structure functionalized with different ratios of aminopropyl groups, namely  $\text{Na}_{50}$ ,  $\text{Na}_{25}$  and  $\text{Na}_5$  in removing nickel and copper from industrial electroplating wastewaters was evaluated. The observation revealed that reactive

aminopropyl-Si MCM-41 and similar materials could be used as a promising and alternative environmental technology in the future [13]. A batch study was conducted to remove hexavalent chromium ( $\text{Cr}^{+6}$ ) using scrap iron filings in both synthetic wastewater, containing 30 mg/L of  $\text{Cr}^{+6}$ , and chromium plating wastewater. Optimum condition for removal of  $\text{Cr}^{+6}$  was found to be at pH 3, iron particle sizes (35 – 200) mesh, agitating rate 250 rpm, contact time 180 minutes and iron dosage of 1 g. It was also observed that nickel and copper in the aqueous solution did not affect on the reduction of hexavalent chromium [14].

In order to purify electroplating wastewater with respect to Cr(VI) the adsorption behaviour of amorphous aluminium oxide was studied under batch method. With a varying Cr(VI) concentrations in the range of 10 to 200 mg/l, Langmuir model was found to best, showing a maximum adsorption capacity of 78.1 mg/g. Amorphous aluminium oxide also showed a high adsorption capacity in case of purification of Cr(VI) bearing electroplating wastewater [15]. A study on Fluidized zero-valent iron (ZVI) process was conducted to reduce hexavalent chromium (chromate,  $\text{CrO}_4^{2-}$ ) to trivalent chromium ( $\text{Cr}^{3+}$ ) from electroplating wastewater. ZVI process was selected because of (i) extremely low pH (1–2) in electroplating wastewater, (ii) production of ferric ion from the reaction of Cr(VI) and ZVI that can act as a coagulant to assist the precipitation of  $\text{Cr}(\text{OH})_3(\text{s})$  and (iii) higher ZVI utilization for fluidized process due to abrasive motion of the ZVI. In this study  $\text{Fe}^{2+}$  was considered as an indicator for complete reduction from Cr(VI) to Cr(III) [16].

In the present study an Electroplating unit employing chrome and bronze plating was selected for process evaluation, removal of copper and chromium from wastewater and exploring the scope of recycling. The chemical treatment was planned to be replaced by physico-chemical process like adsorption. The wastewater emanated from bronze and chrome plating units were mixed together to prepare a composite wastewater sample. Later, activated alumina (AS 37 of size 0.6 mm - 0.9 mm) was utilized as an adsorbent for the removal of copper and chromium present in the composite wastewater. The study revealed that activated alumina performed very well as the adsorbing media for the removal of both chromium and copper.

## II. ELECTROPLATING UNIT UNDER THE PRESENT STUDY

The Study was performed with the effluent from rinsing tank of electroplating plant of M/s. Jessop & Co. Ltd., Kolkata, India.

### A. Plant description

M/s. Jessop & Co. Ltd., Kolkata was founded in 1788 and now it is engaged in the manufacturing of EMU Coaches, Wagons, Road Rollers, Cranes and Mining equipments. The plating operations, i.e. chrome plating and bronze plating are conducted for mining components. The components, susceptible to wear and tear, are chrome plated, whereas the components exposed to corrosive atmosphere are bronze

plated. The average monthly requirement of such plated components (as needed in India's mining industry) is approximately 50,000 sq. ft per month. M/s. Jessop & Co. Ltd. manufactures about 6000 sq. ft. of plated items per month out of which 2500 sq. ft. is chrome plated and 3500 sq. ft. is bronze plated.

### B. Existing treatment unit

The existing treatment unit follows chemical treatment to abate the heavy metal pollution arising out of chromium and copper. When appreciable sludge accumulation occurs in the rinsing bath, the entire rinsing water is changed and the wastewater is drained out to the equalization tank for treatment. Sodium meta-bi-sulphite is added to promote conversion of  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$  under pH range around 4.0 to 4.5. The wastewater from rinsing bath used for bronze plating is also drained out into another equalization tank when found unsuitable. The wastewater in the equalization cum storage tank contains  $\text{CN}^-$ , which is firstly made alkaline with Sodium hydroxide and then Sodium hypochlorite is added for cyanide destruction. As a result, cyanide is converted to cyanate and finally to  $\text{CO}_2$  and  $\text{N}_2$ , when pH is raised to above 7.5. The primary treated wastewater from both the tanks is mixed together in a separate neutralization tank for leveling the pH fluctuation. Then the neutralized wastewater comes to the clarifier and the settled solids are dewatered in a pressure filter. Solid wastes are sealed in a container for safe disposal and the effluent is discharged to the municipal sewer. The flow diagram of existing chemical treatment of the electroplating wastewater is shown in Fig. 1.

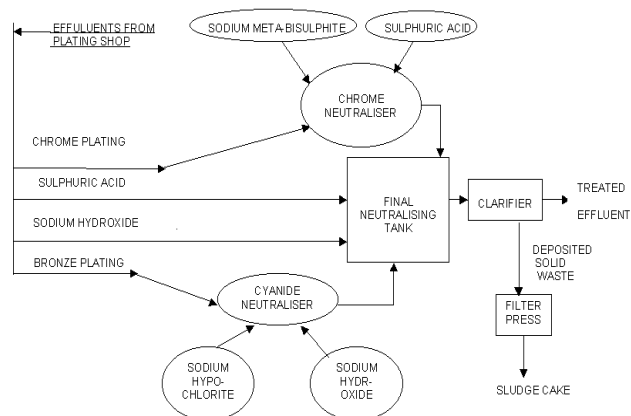


Fig. 1 Flow sheet of existing wastewater treatment unit

### C. Effluent Discharge Standards

In India the effluent discharge standards are laid down and monitored by Central Pollution Control Board, New Delhi, which is a statutory agency of Ministry of Environment and Forests, Government of India. The standards specify the desirable quality of effluent emanated from various industries. In case of Electroplating industry, the discharge standards for hexavalent chromium (as  $\text{Cr}^{+6}$ ), total chromium (as Cr) and copper (as Cu) are mentioned as 0.1, 2.0 and 3.0 mg/L

respectively [17].

#### *D. Major source of waste generation*

The rinsing of material after plating operation is required to remove any plating bath solution that may be left on material. Rinsing operation emanates the largest volume of wastewater from metal plating operations. Rinse waters finally become contaminated with varying concentration of heavy metals as per the type of rinsing scheme.

The tank capacity of rinsing bath was measured to be 4000 litres for both the chrome and bronze plating. Usually, the wastewater was discharged after a month period with an amount of (4000 + 4000) i.e. 8000 L. The plating bath liquid is changed occasionally when sufficient sludge is accumulated at the bottom. At this stage, the bath liquid is pumped and the sludge is removed. After cleaning operation, the bath is again filled with liquid that was kept aside. The appropriate bath composition is maintained by adding necessary amount of chemicals.

The chemical composition of Chrome plating bath and Bronze plating bath and current passed through them are as follows.

##### *Chrome plating bath*

- (1) Chromic Acid : 220 to 250 g/L
- (2) Sulphuric Acid : 1 in 100 ratio.
- (3) Current : 300 amps/sq. ft.

##### *Bronze plating Bath*

- (1) Bronze Salt A : Bronze Salt B in the ratio of 130 : 60 to keep the concentration of Copper ( $\text{Cu}^{+2}$ ) : 26 – 32 g/L and Tin ( $\text{Sn}^{+2}$ ) : 18 – 22 g/L.
- (2) Potassium Cyanide is added to get  $\text{CN}^-$  concentration 30 – 38 g/L. Potassium Hydroxide is also added with a concentration 4 – 8 g/L
- (3) Current : 25 amps / sq.ft.

### III. EXPERIMENTAL

#### *A. Materials*

Activated Alumina of AS-37 grade with grain size 0.3 – 0.6 mm was used as adsorbing media, which was supplied by M/s. Oxide India Pvt. Ltd., Durgapur, West Bengal, India. Triple distilled water was employed for preparation of reagents whereas ordinary distilled water was used for other analyses. Initially, the wastewater volume generated from various major sources was noted and rinsing bath of both the chromium and bronze plating was found to be the principal source. Therefore, samples were collected from the respective rinsing baths and analyzed for the relevant parameters. To accomplish the simultaneous removal of copper and chromium, the chrome and bronze plating waste streams were mixed together to make a composite sample. The usual discharge of wastewater from chrome plating bath was 4000 L per batch and the bronze plating bath also discharged almost same quantity. Therefore, the mixture of two, i.e. composite

wastewater should contain wastewater from both the baths in 1 : 1 ratio. The total volume of wastewater in the composite bath was 8000 L. The composite wastewater sample was allowed to flow into the adsorption column with different flow rates, adjusted by the peristaltic pump.

#### *B. Method of analyses*

All the parameters were measured according to standard procedures suggested by Standard Methods (1985)[18] and Jeffery *et al.*, 1989 [19]. Chromium and Copper was determined by Colorimetric and Sodium Di-ethyl dithiocarbamate method respectively.

#### *C. Characterization of wastewater*

The wastewater collected from the rinsing bath of the Chrome and Bronze Plating unit were analyzed for the relevant parameters. A composite wastewater (1:1 Chrome and Bronze plating wastewater) was also analyzed.

#### *D. Batch adsorption study*

A batch study was performed with varying dosages of activated alumina (10, 20, 30, 40, 50 and 60 gm/L) in 100 ml of composite wastewater collected in the second phase and for the batch periods of 10, 20, 30, 40, 50 and 60 Min. Another study was carried out to determine the equilibrium concentration for the sorption of Chromium and Copper using Activated Alumina of dosage 50 g/L. 100 ml portion of the composite bath wastewater containing 13.6 mg/L of Chromium and 3.4 mg/L of Copper was added with the above dosage of Activated Alumina and was allowed for shaking for contact periods of 5, 10, 15, 30, 45 and 60 Min. Thereafter, effluent was centrifuged and the supernatant was analyzed for Chromium and Copper.

#### *E. Isotherm Study*

Isotherm study was performed with different dosages (10, 20, 30, 40, 50 and 60 gm/L) of Activated Alumina with the optimum contact period of 45 Min. Batch Isotherm Study was carried out at room temperature (average is about 25°C) using 100 ml composite wastewater with abovementioned dosages in separate bottles. The bottles were shaken in a rotary shaker at 25 rpm for a contact period of 45 Min. Later, the effluent was centrifuged and analyzed for chromium and copper. According to adsorption kinetics of different models the data were analyzed to establish the most appropriate Isotherm.

#### *F. Column Study*

Composite wastewater was fed through the column of height 100 cm and internal diameter (I.D.) 1.5 cm by a peristaltic pump with a flow rate of 4.98 ml/Min. The wastewater after 180 Min. was collected and analyzed for chromium and copper. The bed depth of the column was provided as 25 cm, 35 cm and 50 cm. The setup of the Column study is shown in Figure 2. The influent concentration of chromium and copper was observed to be 13.6 mg/L and 3.4 mg/L respectively. Effluent samples were collected at various time intervals and analyzed for Chromium

and Copper. From the results of analysis a set of breakthrough curves is developed and thereby the breakthrough times are obtained. The break-through concentration is taken as 0.1 mg/L as Cr<sup>+6</sup>, following the guideline of Central Pollution Control Board (CPCB), India. Although it laid down Cu<sup>+2</sup> discharge limit through wastewater as 3.0 mg/L, it was considered as 0.1 mg/L for reuse of water in rinsing bath either for chrome plating or in bronze plating purpose.

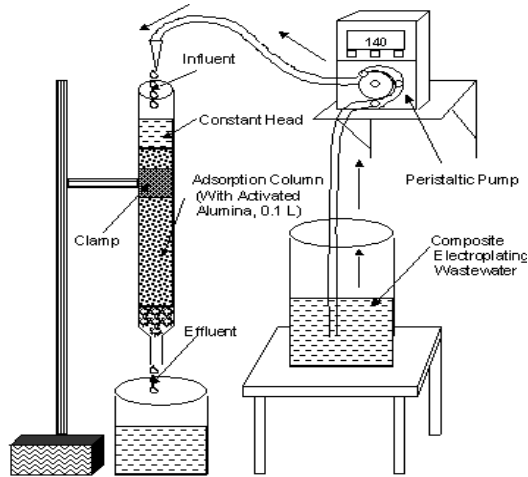


Fig. 2 Schematic arrangement of laboratory-scale Adsorption Column made of Activated Alumina (Grade AS 37)

beyond a dosage of 50 g/L. Although, the Copper concentration attained its desirable value at a dosage of 50 g/L, the Chromium concentration was yet to be 0.1 mg/L. Also the difference between the equilibrium Chromium concentration for 50 and 60 g/L of Activated Alumina was nominal (particularly for a contact period of 60 Min.). Therefore, a dosage of 50 g/L of Activated Alumina was taken for further kinetic study.

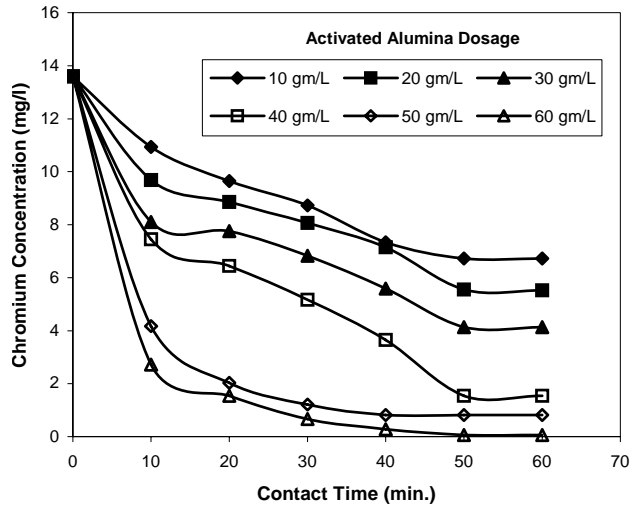


Fig. 3 Concentration of chromium at different dosages of Activated Alumina (0.3-0.6 mm) and contact period

IV. RESULTS AND DISCUSSION

A. Characterization

The results of characterization of Chrome and Bronze plating as well as composite wastewater are shown in Table-1. The characterization revealed that the wastewater contained heavy metals like Chromium and Copper. The value of Chemical Oxygen Demand (COD) is found to be low indicating low amount of oxidizable inorganic matter.

TABLE I RESULTS OF CHARACTERIZATION OF CHROME PLATING, BRONZE PLATING AND COMPOSITE WASTEWATER

Sl. No.	Source	Concentration of Parameters					
		pH	COD	Total Chromium	Copper	TDS	Iron
1.	Chrome Plating Bath	6.78- 6.86	24.0- 24.8	8.6-24.8	-	960-980	0.20
2.	Bronze Plating Bath	7.19- 7.68	0.0	-	5.0 - 6.5	1300 - 1330	0.13
3.	Composite Wastewater	7.33- 7.55	12.0- 12.4	6.82-13.6	2.36 - 3.34	1040- 1080	0.20

Note : All the parameters are expressed in mg/L except pH

B. Batch adsorption study

The effluent Chromium and Copper concentrations were analyzed by centrifugation of the sample and plotted in Figure 3 and Figure 4 respectively. The concentration profile of Chromium and Copper revealed that the removal was greatly affected by the dosage, but it was not significant

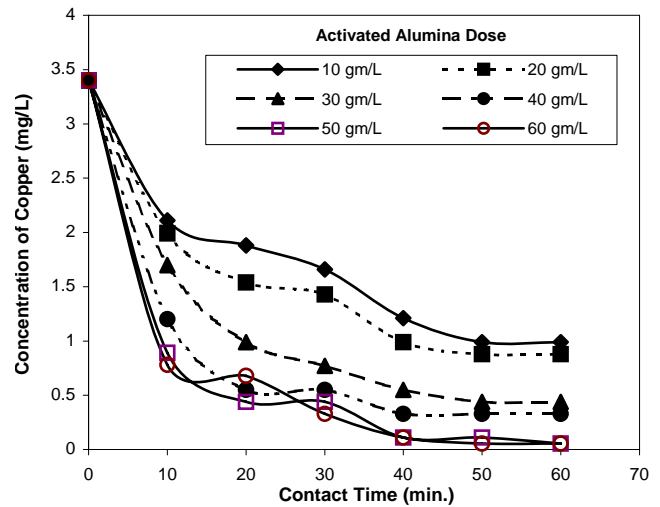


Fig. 4 Concentration of copper at different dosages of Activated Alumina (0.3-0.6 mm) at pH = 7.33

The percent removal of Chromium and Copper were evaluated with respect to the initial concentration as shown in Figure 5. It revealed that the percent removal of both Chromium and Copper increased rapidly up to a contact period of 15 Min. and almost ceased beyond this point. It was noted that this contact period for Chromium, i.e. time corresponding to the equilibrium concentration was less than that of the Copper. Therefore, the media was exhausted with chromium at a higher rate than Copper. Although, an

intersection of the removal curves of Chromium and Copper was observed, the most rational contact period for attaining equilibrium concentration was recognized as 45 Min. because it ensured more than 90 % of Chromium and Copper removal.

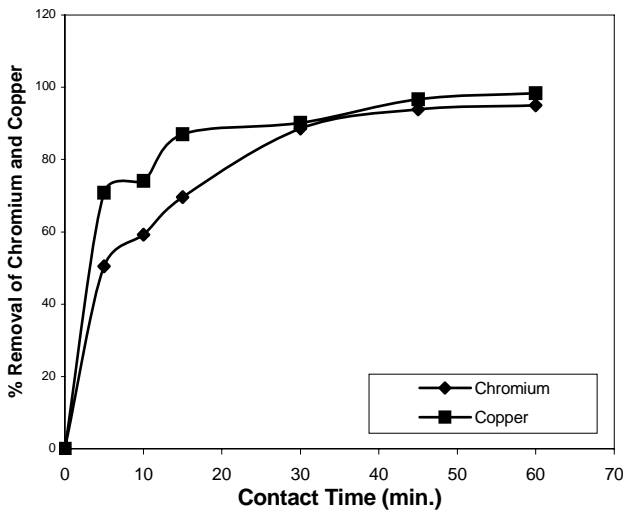


Fig. 5 Percent Removal of chromium and copper by adsorption on Activated Alumina from Composite Wastewater

C. Isotherm study

The result of analyses is presented in Table-2, which are used for development of different Isotherms.

TABLE II RESULTS OF ANALYSES FOR ISOTHERM STUDY

Sl. No.	Adsorbent Dosage (gm/L)	Chromium Concentration (mg/L)	Copper Concentration (mg/L)
1.	10	4.17	0.89
2.	20	2.04	0.44
3.	30	1.21	0.44
4.	40	0.83	0.11
5.	50	0.81	0.11
6.	60	0.81	0.055

(Note : The contact period is 45 Min. and Volume of sample is 100 ml)

Firstly, the values of equilibrium concentration of chromium as well as the mass of the activated alumina were used to fit with the Langmuir’s Isotherm. The relationship [3] has been developed with the following linear equation and a correlation coefficient ( $R^2$ ) value of 0.9838 is obtained. The equation of best-fit line is found as  $Y = 3.0977 X + 0.1702$ , where the slope and intercept are calculated as,  $X_m = 5.8754$  and  $b = 0.0549$ .

$$\frac{1}{X} = \frac{1}{X_m} + \left(\frac{1}{C_e}\right) \left(\frac{1}{b \cdot X_m}\right) \tag{1}$$

In order to develop the Freundlich Isotherm for chromium removal, the observed values of  $\log(x/m)$  and corresponding  $\log C_e$  are fitted in the following expression. of Freundlich [20]. The relationship is obtained as  $y = 0.7915 x - 0.4935$  having  $R^2$  value of 0.958 and the constants are determined as  $K = 0.3210$  and  $n = 1.2634$ .

$$\log\left(\frac{X}{M}\right) = \log K + \frac{1}{n} \log C. \tag{2}$$

To develop the BET Isotherm [3], the data have been arranged in accordance with the respective Isotherm equation as follows. The correlation of BET Isotherm yielded a straight line with a  $R^2$  value of 0.9477. The values of constants are calculated form the equation of Best-fit, i.e.  $Y = 0.8893.X + 0.1883$  as  $b = 5.7227$  and  $X_m = 0.928$ .

$$\frac{C_e}{X \cdot (C_s - C_e)} = \frac{1}{X_m \cdot b} + \frac{(b - 1)}{X_m \cdot b} \cdot \frac{C_e}{C_s} \tag{3}$$

Where,  $X = x/m$ , the amount of solute adsorbed, per unit weight of adsorbent  $m$ ;

$C_e$  = equilibrium concentration of solute;

$C_s$  = solubility of solute in water at a specified temperature;

$X_m$  = amount of solute adsorbed per unit weight of adsorbent required for monolayer adsorption;

and,  $b$  = a constant related to the heat of adsorption.

Similar isotherms have been plotted for adsorption of copper on activated alumina. The Langmuir isotherm for adsorption of copper on activated alumina has been developed with a relationship  $y = 0.7373x + 6.1328$  and  $R^2$  value of 0.825. The values of the constants are calculated as,  $X_m = 0.1630$  and  $b = 8.20$ .

The Freundlich Isotherm for copper removal is generated with a relationship  $y = 0.4997 x - 0.6754$  and  $R^2$  value 0.9057. The values of the constants are calculated as,  $K = 0.2111$  and  $n = 2.0012$ .

The BET isotherm for copper removal is also developed with a relationship  $y = 4.8181.x + 0.3128$  and  $R^2$  value of 0.9724. The constant parameters are determined as,  $b = 16.3993$  and  $X_m = 0.1949$ .

The most appropriate kinetics for adsorption of chromium and copper on activated alumina has been selected by comparing  $R^2$  values in different Isotherm correlations. Therefore,  $R^2$  values for Langmuir, Freundlich and BET Isotherms in case of chromium and copper are compared as shown in Table 3.

TABLE III VALUES OF CORRELATION COEFFICIENT ( $R^2$ ) IN VARIOUS ISOTHERMS

Isotherm	Values of $R^2$	
	Chromium	Copper
Langmuir	0.9838	0.8250
Freundlich	0.9580	0.9057
BET	0.9477	0.9724

It is evident from Table 3 that, Langmuir and BET Isotherms are most appropriate to express the kinetics of removal of chromium and copper respectively. The respective best-fit Isotherms for chromium and copper are shown in Figure 6 and Figure 7 respectively. As  $R^2$  value in case of chromium is more than 0.95 it can be concluded that there might be a heterogeneous surface offered by activated alumina during adsorption of chromium. The Isotherm for copper adsorption on activated alumina does not exhibit the monolayer nature. Moreover, the value of  $1/n$  less than 1 indicates that the adsorption capacity gets reduced at the lower equilibrium concentrations.

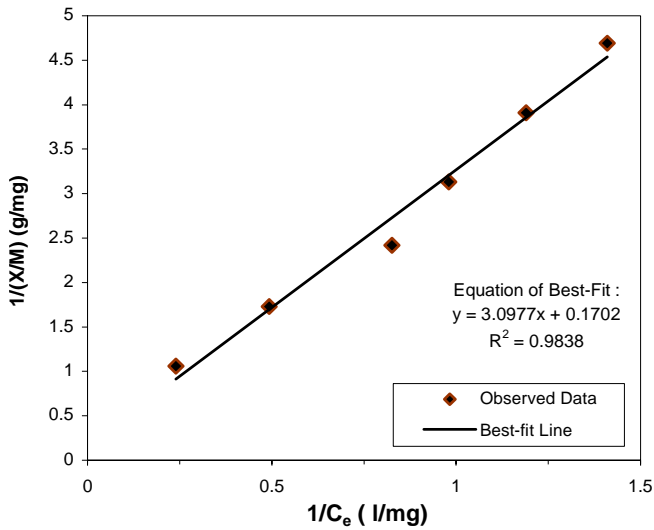


Fig. 6 Langmuir Isotherm for adsorption of chromium on Activated Alumina

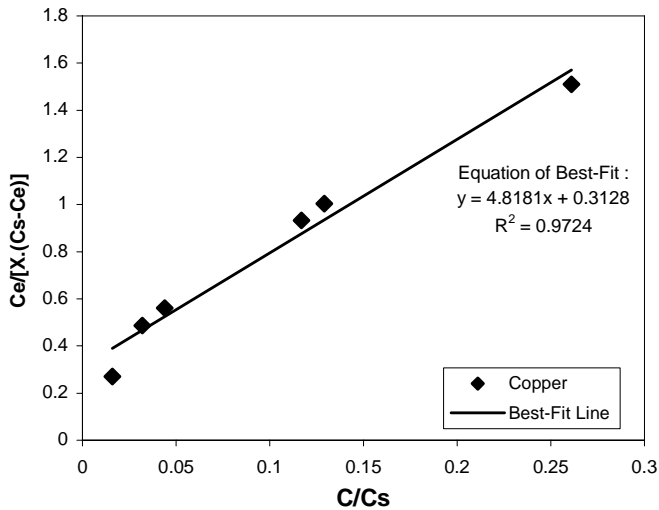


Fig. 7 BET Isotherm for adsorption of copper on Activated Alumina

*D. Shape of adsorption Isotherm*

The shape of the adsorption isotherm provides qualitative information about adsorption process and the extent of the surface covered by the adsorbate. Brunauer classified adsorption into five basic shapes, which are typically

developed by plotting the adsorption capacity ( $x/m$ ) with respect to the equilibrium concentration ( $C_e$ ). Following this, the chromium adsorption capacity of activated alumina is plotted against the respective values of  $C_e$  as shown in Figure 8, which resembles to Type I - Brunauer curve [21]. It also demonstrates that chromium adsorption on activated alumina does not proceed beyond monomolecular layer.

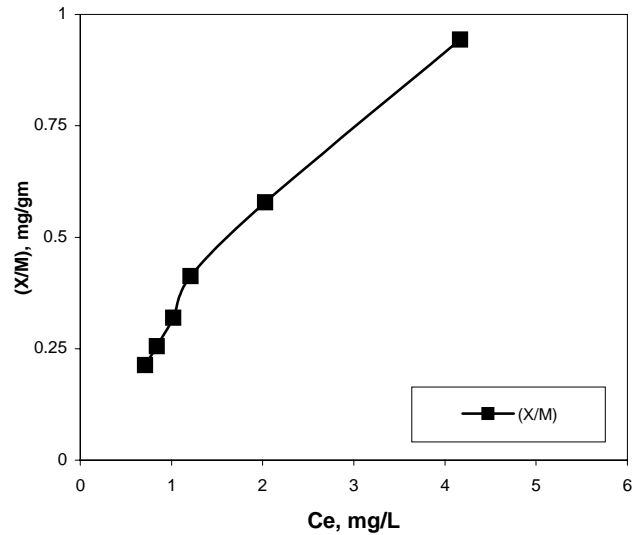


Fig. 8 Brunauer Isotherm for chromium adsorption on Activated Alumina

With a view to characterize the copper adsorption on activated alumina the values of  $(x/m)$  are plotted against  $C_e$ , as shown in Figure 9. It is observed that adsorption isotherm of copper satisfies Type IV - Brunauer Isotherm [21]. It depicts that surface of activated alumina is heterogeneous, not only in the surface structure but also in the distribution of surface energy. During the course of adsorption, the heat of adsorption did not remain constant for each incremental increase in adsorption.

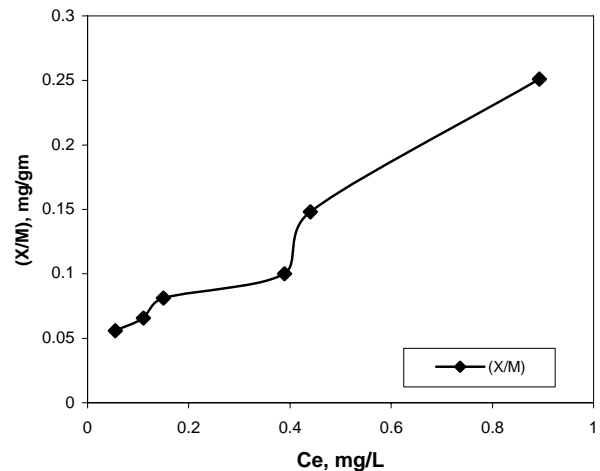


Fig. 9 Brunauer Isotherm for copper Adsorption on Activated Alumina

A steep initial drop of heat of adsorption with an increase of the material adsorbed indicates that the fast molecules arriving at the bare surface are preferentially adsorbed on the most attractive sites i.e. on the surface with minimum potential energy. As adsorption proceeds, the less active sites get occupied, which can be simulated as a case of multilayer adsorption.

*E. Relative adsorption of Chromium and Copper by Activated Alumina*

The efficiency of adsorption is directly proportional to the charge of ion and inversely proportional to the size of ion. It should be reflected in the relative adsorption of copper and chromium on Activated Alumina. Therefore, the percent removal of Chromium and Copper (from the Isotherm Study) are plotted along y and x-axis respectively as shown in Figure 10. The said graph depicts the percent removal of chromium expected for a specific percent removal of copper under the same condition. It is to observe that removal of chromium proceeds with a slow rate in comparison to the copper. It has also been observed that activated alumina could remove the colour almost completely from the composite wastewater.

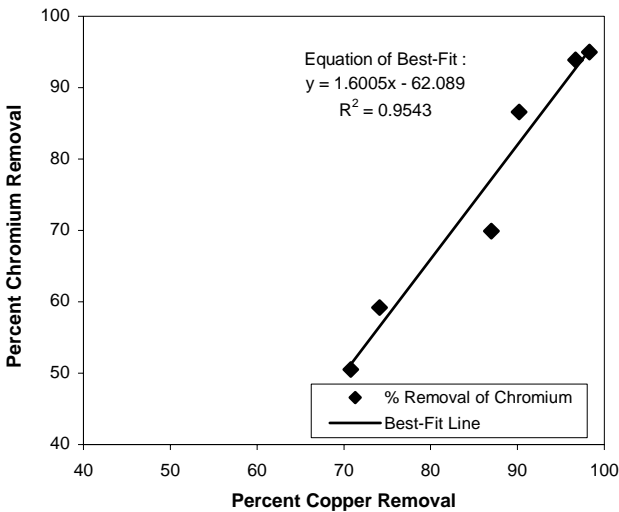


Fig. 10 Relative adsorption of copper in comparison to Chromium

*F. Column study*

The ratios of effluent to influent concentrations ( $C/C_0$ ) of Chromium and Copper are plotted against time as shown in Figure 11 and Figure 12 respectively and the respective breakthrough periods are also found out. The breakthrough concentration is considered as 0.1 mg/L for both chromium and copper as mentioned earlier. The Breakthrough times are determined from the intersection of the Breakthrough curve and Breakthrough concentration line. The Breakthrough times for different column depths of 25, 35 and 50 cm for Chromium and Copper are shown in Table 4.

Although the concentration of copper is less than that of chromium, the Breakthrough time is observed to be higher in case of chromium. It may be attributed to the fact that the

activated alumina adsorbs chromium with a faster rate than the copper. It might be due to higher affinity of activated alumina to chromium than the copper. It is also supported by literature that ionic radius of  $CrO_4^{2-}$  (where Chromium is in  $Cr^{+6}$  form) is about 3.5 times that of Copper [21].

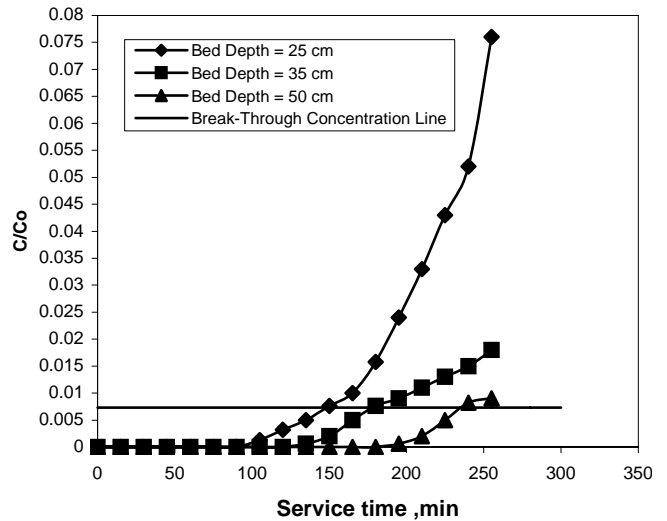


Fig. 11 Breakthrough curves for chromium on Activated Alumina columns with Composite Wastewater

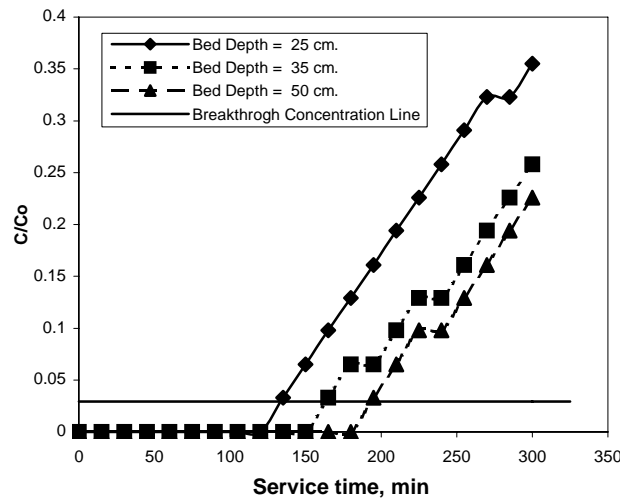


Fig. 12 Breakthrough curves for Copper on Activated Alumina columns with composite wastewater

TABLE IV BREAKTHROUGH TIMES FOR CHROMIUM AND COPPER USING COMPOSITE WASTEWATER

Bed Depth (cm)	Breakthrough Time (Min)	
	Chromium	Copper
25	150 min	135 min
35	180 min	165 min
50	235 min	195 min

During the column study chromium concentration in the effluent was traced earlier than the copper for all the cases, which indicates the more service period for the copper removal. While Breakthrough time is considered for any element, it must be checked whether the concentration of the other element remains within the desirable limit. In the present study, the Breakthrough time for chromium (from Figure 11) can be used in Figure 12 to determine the respective effluent concentration of copper. Consequently, the  $(C/C_0)$  values are obtained for 25, 35 and 50 cm depth of the column as 0.065, 0.065 and 0.098 giving copper concentrations of 0.221, 0.221 and 0.333 mg/L respectively, which are appreciably lower than the permissible value of 3.0 mg/L. In the present case the breakthrough times are determined corresponding to a hydraulic loading rate of  $1.69 \text{ m}^3/\text{m}^2/\text{h}$ .

*G. Process design of Adsorption Column by Bohart-Adams Model*

The Bed Depth-Service Time (BDST) method as proposed by Bohart and Adams has been used for designing the Activated Alumina Column [3] for the removal of chromium and copper from the real wastewater. To develop the BDST relationship the data obtained from three columns are plotted with Breakthrough time as Service time along abscissa and the column depth along ordinate. Two linear graphs are obtained for chromium and copper as shown in Figure 13 and Figure 14 respectively corresponding to three column depths. The BDST curve for chromium is represented by the equation,  $y = 3.4211x + 62.895$  with  $R^2$  value of 0.9972, whereas BDST curve for copper is expressed by the equation,  $y = 2.3684x + 78.158$  with  $R^2$  value of 0.9868.

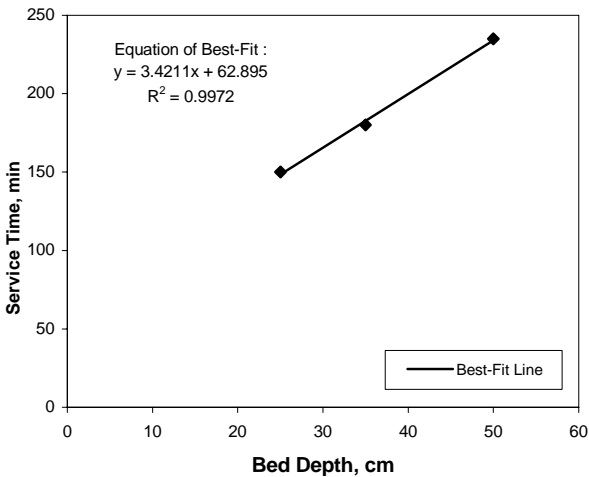


Fig. 13 Bed Depth Service Time (BDST) curve for chromium on Activated Alumina

The usual concentration of chromium and copper in composite wastewater in an identical electroplating plant is observed as 90 to 100 mg/L and 8 to 10 mg/L respectively. For the sake of design of a suitable Adsorption column for simultaneous removal of chromium and copper, their respective concentrations in real wastewater are considered as

100 mg/L and 10 mg/L. It is to simulate the fact that the physico-chemical treatment is undertaken only when the wastewater in the storage tank almost attains the abovementioned concentration of chromium and copper.

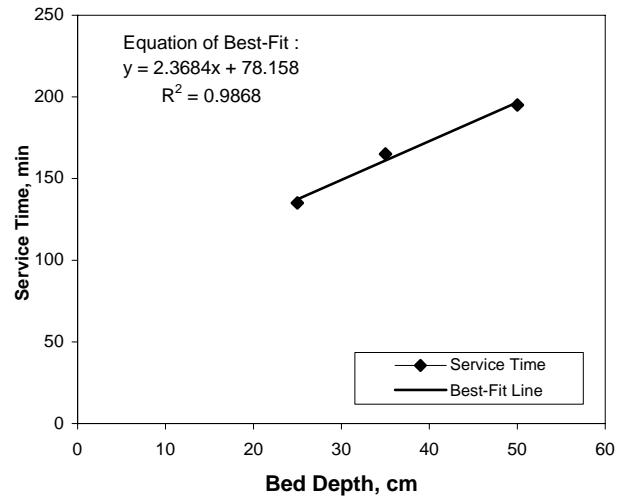


Fig. 14 Bed Depth Service Time (BDST) curve for Copper on Activated Alumina

The necessary calculation for designing the adsorption column is shown hereunder.

The BDST relationship for Chromium gives

$$\text{Service Time in min.} = 3.4211(\text{Bed Depth in cm.}) + 62.895 \quad (4)$$

Whereas, The BDST relationship for Copper is

$$\text{Service Time in min.} = 2.3684(\text{Bed Depth in cm.}) + 78.158 \quad (5)$$

The wastewater volume is observed as 8000 litres in a month as a single discharge. On a higher side it may be considered that the wastewater is discharged @  $1 \text{ m}^3/\text{day}$  for one 8 hours working period and this is to be treated and recharged again in the rinsing bath. The activated alumina column having a diameter of 500 mm is firstly considered for which the changed hydraulic loading rate would be  $0.51 \text{ m}^3/\text{m}^2/\text{h}$ .

As a result, the change in the flow rate will cause a change in slope.

$$\begin{aligned} a' (\text{New Slope}) &= \frac{V}{V'} * a (\text{old slope}) \\ &= \frac{1.69}{0.51} * 3.4211 = 11.33 \end{aligned}$$

Also, the changed feed concentration for designing the adsorption column can be expressed as

$$a'' = \frac{C_0}{C_1} * a'$$

$a''$  can be considered as the new slope due to new feed concentration, where  $C_0$  and  $C_1$  are the old and new feed concentrations respectively and  $a'$  is the slope obtained with changed loading rate. Therefore, for a Chromium concentration of 100 mg/L in the feed waste stream

$$a'' = \frac{13.6}{100} * 11.33 = 1.54$$



As a result of change in the feed concentration there will be a change in the intercept, which is calculated as

$$b' = b \left( \frac{C_0}{C_1} \right) \cdot \frac{\ln \left[ \left( \frac{C_1}{C_F} \right) - 1 \right]}{\ln \left[ \left( \frac{C_0}{C_B} \right) - 1 \right]}$$

$$= 62.895 \left( \frac{13.6}{100} \right) \cdot \frac{\ln \left[ \left( \frac{100}{0.1} \right) - 1 \right]}{\ln \left[ \left( \frac{13.6}{0.1} \right) - 1 \right]}$$

$$= 11.97$$

Therefore, the new equation correlating service time and bed depth for a continuous 8 hrs of operation will be

$$\begin{aligned} \text{Service time in min.} &= 1.54 \cdot (\text{Bed Depth in cm.}) + 11.97 \\ 8 \times 60 &= 1.54 \cdot (\text{Bed Depth in cm.}) + 11.97 \\ \text{Bed Depth} &= (480 - 11.97) / 1.54 = 304 \text{ cm.} \end{aligned}$$

Similarly, the bed depth is also evaluated for new applied concentration of copper with a changed flow rate i.e.  $0.51 \text{ m}^3/\text{m}^2/\text{h}$  as  $167 \text{ cm.}$ , which is lower than that required for chromium. Therefore, the Adsorption column having diameter  $500 \text{ mm}$  requires bed depth of  $304 \text{ cm}$ , which is capable to adsorb both chromium and copper concentration up to  $0.1 \text{ mg/L}$  in both cases. However, regeneration of the bed would be required after every 8 hours operation period.

#### H. Conclusions

The present study reveals that the batch discharge from Chrome and Bronze Plating unit can be treated by adsorption in Activated Alumina, when two waste streams are mixed together as a composite waste sample. However, prior to go for adsorption process, chemical treatment of bronze plating waste stream for cyanide destruction is essential to prevent toxic hazard. Activated Alumina (Grade AS 37) shows a good performance at existing pH for substantial removal of chromium and copper from the composite wastewater (prepared with chrome and bronze plating wastewater in 1 : 1 ratio) within a short contact time. The adsorption kinetics follows mostly Langmuir Isotherm for chromium and in case of copper, BET Isotherm appears to be best. With regard to simultaneous removal of chromium and copper, Activated Alumina provides a considerable breakthrough time at different column depths. The adsorption kinetics for chromium and copper is influenced by each other and therefore it may necessarily not be used for the synthetic solution of copper and chromium independently.

The Bed Depth Service Time (BDST) relationship, developed from continuous operation in the column study shows a good correlation co-efficient (near about 99%) and it

can be successfully utilized for prediction of bed depth for a given influent concentration and hydraulic loading rate. According to the present practice of discharge and subsequent chemical treatment, an adsorption column of Activated Alumina (AS 37 Grade,  $0.3 - 0.6 \text{ mm}$  size) is designed for a chromium and copper concentration of  $100 \text{ mg/L}$  and  $10 \text{ mg/L}$  respectively and a flow rate of  $1 \text{ m}^3/\text{day}$ , using the BDST relationship. The dimension of the proposed adsorption column (Diameter  $500 \text{ mm}$  and height  $304 \text{ cm}$ ) provides a viable solution towards the replacement of existing chemical treatment method.

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