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## DETERMINATION OF SEXAVALENT CHROMIUM FROM THE EFFLUENTS OF VARIOUS ELECTROPLATING INDUSTRIES

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Sexavalent chromium has been determined from the effluents of some electroplating industries in and around Lahore. It has been found that the amount of this toxic ion in waste waters is quite high. Since this ion is carcinogenic it must be removed from water at all costs. Methods of its removal have also been discussed briefly.

*Key words:* Sexavalent chromium, Effluents, Electroplating industries.

### INTRODUCTION

For many years chromium compounds such as chromic acid, sodium dichromate, chromium sulphate and chromium chloride have been used in the metal treatment operations such as electroplating, conversion coatings, anodizing, corrosion inhibition, pickling, brightening and blackening. It is not customary to discard chromium bearing solution of high concentration into streams or water ways but many times such solutions as rinse waters with quite high concentration of chromium salts find their way into the water ways thus causing a serious pollution hazard. This water containing toxic sexavalent chromium is ultimately used for irrigation, drinking and washing purposes. Chromium reactions to the skin are generally classified as primary irritant and have allergic effects. Irritant effects include corrosive ulcers, scars, and eczematous and non-eczematous contact dermatitis. Sexavalent chromium is also known to be a strong carcinogenic which produces cancer of the lungs and stomach [1]. Workers who are involved in electroplating of nickel have approximately 150 times more cancer of nasal passages and sinuses than the general population. Similarly people who work in chrome plating shops have more probability of suffering from lung cancer. In 1981 Nippon Chemical Industries of Tokyo were ordered by a court to pay \$4.4 million as compensation to the families of persons who died and others were sick of lung, liver and stomach cancer due to chromium poisoning [2].

Since there are a number of electroplating shops in and around Lahore, it was felt necessary to undertake a study where by the level of the Sexavalent chromium could be evaluated in the effluents arising from these industries. This study is only limited to Lahore area but we believe that the situation in other cities may not be very different.

### EXPERIMENTAL

*Reagents.* All the reagents used were of analytical grade or of comparable purity. Distilled water was used to prepare the solutions of potassium permanganate (0.02M) and sodium azide (5%) and for diluting the concentrated sulphuric acid to 5N concentration. 0.5% solution of diphenyl carbazide was prepared in pure acetone. 1000 ppm aqueous hexavalent chromium stock solution was prepared using potassium dichromate.

*Procedure.* 10 ml of chromium solution (either synthetic or effluent water) containing 2-15  $\mu\text{g}$  of hexavalent chromium was taken in a flask. To this was added 1 ml of 5N sulphuric acid followed by 0.5 ml of potassium permanganate solution. The mixture was heated for 20 min. on a water bath. The excess of potassium permanganate was destroyed by adding sodium azide solution to the hot solution by adding dropwise after the interval of 5 to 10 seconds. Azide was added until all the brown colour had disappeared avoiding excess of azide. In the case of effluent waters, oxalic acid was added at this stage to mask Fe(III) ions. The solution was immediately cooled and transferred to a 25 ml measuring flask. 1 ml of diphenyl carbazide was then added to this mixture. The colour was developed within 1-2 mins. The absorbance was measured at 540 nm against a reagent blank.

*Calibration curve.* A calibration curve was prepared by taking different amounts of chromium in synthetic solutions as described in the procedure above and absorbance was measured at 540 nm. This graph obeyed Beer's Law from 2.0 to 20.0 ppm. The unknown quantities of Cr(VI) in effluents were determined from this calibration curve.

### RESULTS AND DISCUSSION

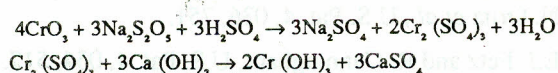
There are many plating shops, both, big and small in Lahore. Most of them are engaged in chrome plating along

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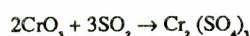
with other plating activities. Since hexavalent chromium is a toxic ion and is being thrown into the streams or sewer systems, it was felt necessary to determine its level in plating industry effluents.

Table 1 shows the level of sexavalent chromium in the effluents of a number of industries. It can be seen from this table that the amount of chromium which is being discharged into the sewer system is quite frightening. The samples were taken from the point where the effluent was being discharged into the city drainage system.

It is very important that such effluents be treated prior to their disposal into the streams or drain. A number of technologies are available for the treatment of electroplating waste water containing Cr(VI). One of the most common method of treating chromium waste is chemical reduction and precipitation. This was recommended by EPA [3]. In this method sexavalent chromium is first reduced to trivalent chromium and then at a definite pH it is precipitated as chromium hydroxide. The most common reducing agents used are sodium metabisulphite, sodium sulphite, sodium hydrosulphite, sulphur dioxide and ferrous sulphate. Reduction and then precipitation takes place according to the following equations:



Batch or continuous treatment system can be adopted. Similarly when chromic acid wastes are treated with sulphur dioxide. The following reaction takes place

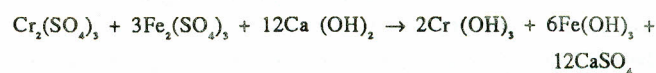


the precipitation is again done by calcium hydroxide because this is a cheaper material.

When ferrous sulphate is used as reducing agent the following reaction takes place



precipitation is done by  $\text{Ca}(\text{OH})_2$  again.



This reaction is pH dependent and the reduction of sexavalent chromium takes place at pH 3.0.

The second method of reducing sexavalent chromium is electrolytic reduction. In this method the electrolytic cells employes a semi conductive bed of carbonaceous particles between the electrodes. When direct current is applied to all the particles of the semi-conductive material shows bipolar character and maintain higher conductivity than that of the water being treated. Waste water containing 100 to 200 ppm of sexavalent chromium when enters the cell at a flow rate of 5 to 10 gallons per minute under a potential of 12 volts at pH 2.0-3.0, it gets reduced. The precipitation is again done by addition of alkaly.

In a third method chromium from waste water is removed as barium chromate by adding barium carbonate to it [4]. Another method which is not very common has also been reported in literature [5]. In this method activated carbon has been used for the removal of sexavalent chromium from waste waters. Number of deionization techniques can also be used to remove sexavalent chromium from waste water. In this technique ion exchange resins are used quite effectively [6]. This method is quite useful because rinse water can be passed first through a cation exchanger and then an anion exchanger. In this way all the undesirable ions are removed and this water can again be used for rinse purposes. A recent development with improvement has been reported where chromic acid waste has been passed through a very efficient ion exchange unit having three beds [7]. Electrodialysis is another technique which has been used to deionize rinse water. In this procedure ions are

Table 1. Concentration of chromium in industrial waste water.

Industry	Conc. ppm zero time	Conc. after 15 days	Conc. after 30 days	Conc. after 45 days	Conc. after 60 days	Conc. after 75 days	Conc. after 90 days	Average Conc. of Cr <sup>6+</sup> ppm
Capital Industries	270	260	300	290	270	290	280	280
PECO	75	65	70	50	70	60	86	68
Reilaghy	225	225	190	200	170	210	180	200
Rustam Sohrab	150	128	130	149	130	145	135	138
Lahore Cycle Works	155	170	175	166	160	149	146	160
Naeem Electroplating	240	200	270	230	296	230	245	244
Bhatty Electroplating	200	210	180	200	170	190	198	192
Saleem Eelectroplating	250	290	287	240	260	255	212	256
Saeed Electroplating	210	230	190	200	170	214	240	208
Lahore Electroplating	300	270	285	255	265	240	260	268
Shehbaz Electroplaiting	160	180	160	155	165	190	195	172

made to pass through an ion selective membrane under the influence of direct current. Two types of membranes are generally used (i) cation selective membrane (ii) anion selective membrane. This method is quite expensive due to the cost of membranes [9]. Details of such methods could be read in a number of articles [10-15]. These are the few methods which have been discussed here but the point is that the water coming out of such factories should not be allowed to be put in the sewer or stream without treatment. Any of the above methods can be chosen for this purpose. The choice of the method will be course depend upon number of factors such as:

(i) Average volume of the effluent coming out of the electroplating shop; (ii) The maximum concentration of chromium in the effluent; (iii) pH of the waste; (iv) Other ions associated with chromium waste; (v) cost of the methodology applied; (vi) Available space for the waste equipment; (vii) Whether or not it can be locally fabricated; (viii) Water cost; (ix) Space for sludge disposal; (x) Minimum sludge formation; (xi) Cost of treatment chemicals; (xii) Manpower to be employed; (xiii) Last but not the least is Federal or Provincial regulation for waste disposal.

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