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Reduction of Chromium in Waste Water From Hard Chrome Plating Processes: A Review

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Abstract: Waste water from hard chrome is considered to be highly toxic due to the presence of chromium ions in hexavalent form and this hexavalent state of chromium is more toxic to animals and humans due to its ability to produce reactive oxygen species in cells. Such heavy metals are considered as carcinogenic to living organisms and hence either reduction of ions to trivalent chromium or removal of ions has to be done before ejecting the waste water into the environment. Many processes for reduction, neutralisation and removal of hexavalent chromium have been investigated and reviewed extensively. In the present review, studies and research carried out for the removal of chromium from waste water of hard chrome plating effluent are summarised. The study was carried out on the aspects such as percentage removal, efficiency and optimum operating conditions in chrome removal and reduction processes.

Key words: Hexavalent chromium, waste water, hard chrome, chrome plating, adsorbents.

Introduction

Waste water from the hard chrome plating industry has a major share of chromium compared to other elements. Hard chrome plating is the industrial process of deposition of a layer of chrome on the metal surface. The term 'Hard Chrome' is due to the fact that the chrome layer deposited by this process is thicker than any other chrome plating (Nikam, 2019). The waste discharged from this electroplating process mainly consists of chromic acid of hexavalent chromium ions. It may also contain other ions of heavy metals such as lead, copper, chromium, nickel, zinc, cadmium, etc., anionic compounds such as phosphates, sulphates, chlorides, etc. and other additives including oils, suspended solids, grease, etc. (Karegar, 2015).

Hexavalent chromium, Cr(+6) is highly carcinogenic in nature. But the trivalent form of chromium, Cr(+3), is a necessary micronutrient for carrying out normal metabolism in the human body (Owlad et al., 2009). However, contact with hexavalent chromium will cause acute and chronic health issues such as skin ulcers, eye damage, kidney failure and so on. There are numerous industrial methods of removing chromium ions from hard chrome waste water such as precipitation, oxidation, reduction, filtration, electrochemical evaporation and ion exchange resins (Singh, 2008).

This study summarises the research about various innovative processes and methods involved in the removal or reduction of chromium in waste water concentrating on the aspects such as percentage chromium removal or reduction, the efficiency of the

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operation and operating conditions of the process and these details are given in next sections.

Chromium Removal

Water is a universal requirement for commercial and industrial applications and has been increasing day by day. Lack of knowledge in utilising usable water from waste without treatment leads to water pollution, resulting in its scarcity. To overcome this problem, process industries need to adopt modern waste water treatment processes and methods for water purification. There are novel physical and chemical methods for the reduction and removal of chromium in waste water and are discussed in the next sections.

Electrocoagulation

The electrolysis setup invented by Peng et al. (2009) uses iron electrodes and a trial stock solution of acidic chromium solution as an electrolytic solution. Figure 1 summarises the reaction mechanism in an electrolytic cell. The anode which is made up of an iron electrode oxidises iron into ferrous ions (Fe^{2+}) in the first step and in subsequent steps hexavalent form of chromium is converted into trivalent by reacting with ferrous ions.

High reduction efficiency was observed at 70°C, the current density of 0.05A and electrolytic concentration of 0.50 mL H_2SO_4 (Peng et al., 2019). Further electro-reduction studies were carried out by Qin et al. (2018) and concluded that 99.96% of hexavalent chromium was reduced after direct coprecipitation methods of chromium trioxide. Dermentzis et al. (2013) also made studies on electro-reduction and precipitation methods and successfully reduced chromium ions and Chemical Oxygen Demand (COD) when 0.04A of electricity was supplied for 50 minutes.

It was observed that the reduction ability of hexavalent was greater at higher acidic conditions than in neutral conditions (Peng et al., 2019). Figure 2

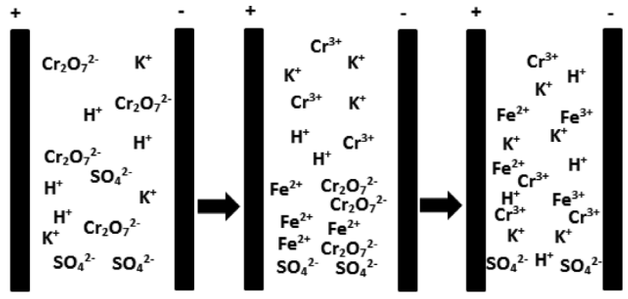

Figure 1: The reaction model for the electrochemical reduction process.

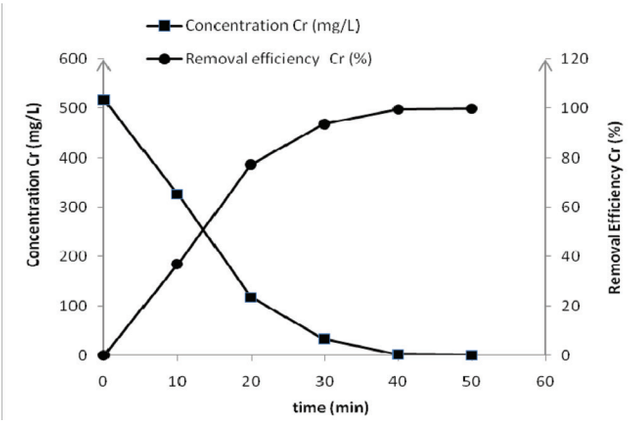

Figure 2: Plot of chromium concentration and chromium removal versus time for electroplating effluent water in electrocoagulation treatment (Dermentzis et al., 2013).

represents the relationship between reduction efficiency and metal ion concentration (Dermentzis et al., 2013). The only disadvantage is the corrosion of ferrous electrodes which results in frequent replacement of electrodes leading to added running and maintenance costs (Barakat, 2011). Chaudhary et al. (2003) found out that the electrocoagulation method does not require any external reducing agent while electrolytically reducing hexavalent chromium to trivalent chromium which can be recycled in other industrial processes. Velasco et al. (2016) observed that there was a decrease in current efficiency in reactions, oxygen reduction and hydrogen evolution in the reduction of hexavalent chromium ions at titanium electrodes. Table 1 summarises details regarding different electrocoagulation experiments.

Adsorption

Adsorption is found to have many advantages such as the availability of a wide range of adsorbents, operational ease and flexibility, and better efficiency, than the other conventional methods (Owlad et al., 2009). Various natural adsorbents for chromium removal include coconut shell charcoal, saw dust, bamboo waste, neem leaves and other agricultural waste (Yogeshwaran and Priya, 2016). Commercially available adsorbents include graphene, carbon nanotubes and activated carbon (Renu et al., 2017). Adsorption isotherms can best fit into Langmuir or Freundlich model (Panda et al., 2017).

Graphene is another form of carbon and is available as an adsorbent in oxide form, reduced form, nano size, etc. It possesses good chemical stability and high surface area due to its availability in nano size for the adsorption of a wide range of materials. Yang

Table 1: Optimum electrolysis conditions for chromium reduction

Electrode	*Electrolyte*	*Current supplied (A)*	*Time (min)*	*Temperature (°C)*	*Percentage removal/reduction*	*Reference*
Iron (Ferrous)	Stock solution of Potassium dichromate and Sulphuric acid	0.05	-	70	99.96	Peng et al. (2019)
Iron (Ferrous)	Stock solution of Potassium dichromate, Potassium chloride and Sodium Hydroxide	0.04	50	-	99	Dermentzis et al. (2013)
Iron (Ferrous)	Waste water consisting of nickel, chromium and copper from electroplating industry	0.04	40	25	99.95	Qin et al. (2018)
Titanium cathode and platinum anode	Stock solution of Potassium dichromate and Sulphuric acid	-	60	25	41	Velasco et al. (2016)
Graphite and platinum anode	Stock solution of Potassium dichromate and Sulphuric acid	-	60	25	49	Velasco et al. (2016)
Titanium cathode and Stainless steel anode	Stock solution of Chromium sulfate, Potassium dichromate and Sulphuric acid	0.25	360	-	98.6	Chaudhary et al. (2003)

et al. (2014) reported in their work showed that the maximum chromium adsorption capacity on the surface of graphene at pH 4 is 92.7 mg/g. The experimental study on the adsorption of chromium using graphene with cyclodextrin chitosan was reported by Li et al. (2013). Table 3 summarises various forms of graphene used in the separation of hexavalent chromium from waste effluent by adsorption.

Song et al. (2016) concluded that the maximum hexavalent chromium adsorption ability of wheat along with weed *Eupatorium adenophorum* at 308K was 89.22 mg per 1 gram adsorbent when pH = 1 and the time duration was 50 minutes. Tian et al. (2018) conducted experiments on the adsorption of ions using *Phyllostachys pubescens* biomass-loaded Cu-S nanospheres and where maximum adsorption was found at pH 1.9. In 2018, vesicular basalt was used as an adsorbent in experimental studies in chromium removal and it was found that the highest adsorption was 79.20 mg/kg for 50g/L of adsorbent for the 5 mg/L of initial concentration at pH 2 (Alemu et al., 2018).

Singh and Tiwari (1997) conducted studies on the adsorption of hexavalent chromium on carbon slurry obtained from chemical industry. The porous nature of these carbon particles helps in better adsorption due to more surface area. Table 2 shows the details of Langmuir isotherm constants and reaction equilibrium constants from studies conducted by Singh and Tiwari (1997). In Table 2, the values of equilibrium constant (K_c) in g/dm^3 and free energy change ($\Delta G°$) in kcal/mol is shown at different temperature. Langmuir constants Q^o and b in Table 2 indicate adsorption capacity and change in apparent heat during adsorption respectively. Figure 3 represents the plot of Langmuir isotherm of adsorption of hexavalent chromium by carbon slurry. Here C_e and q_e are, respectively, the concentration (g/dm^3) and quantity of solute adsorbed per unit mass of adsorbent (mg/g) at equilibrium conditions (Singh and Tiwari, 1997).

Singh et al. (1997) also recovered chromium by burning the used carbon slurry at 500-600°C. The obtained filtrate was filtered and reusable hexavalent

Table 2: Langmuir Constants at different Temperatures at pH =2.5 (Singh and Tiwari, 1997)

Values	*Temperatures* (± 0.5°C)		
	30°C	45°C	60°C
Langmuir Constants			
b	0.1779	0.2133	0.2661
Q°	24.05000	25.1515	25.6417
Equilibrium Constants			
K_C (g/dm^3)	6.0720	7.6577	8.9992
$\Delta G°$ (kcal/mol)	-1.0860	-1.2742	-1.4538

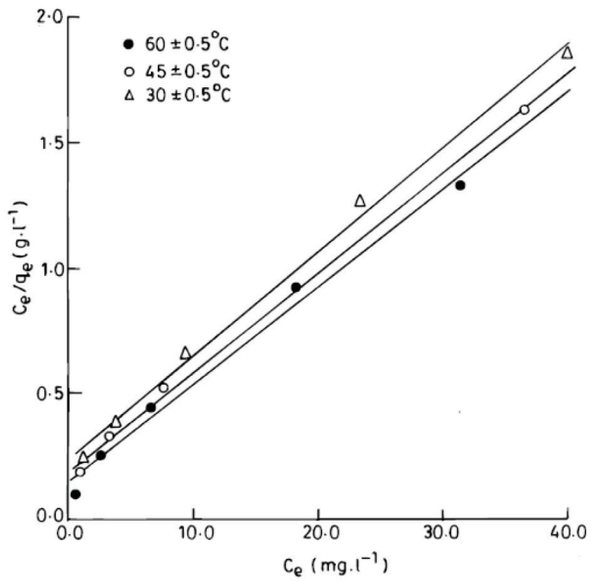

Figure 3: Adsorption isotherm for hexavalent chromium adsorption on carbon at different temperatures. pH: 2.5, contact time: 90 min (Singh and Tiwari, 1997).

chromium was obtained (Singh and Tiwari, 1997). Sunil et al. (2014) studied the effects of the amount of adsorbent and time of contact on the percentage removal of hexavalent chromium using activated charcoal. When the quantity of adsorbent was increased, the percentage of chromium adsorbed increased but the adsorptive capacity decreased. The amount of chromium removed was proportional to contact time (Sunil et al., 2014).

In fact, Sunil et al. (2014) concluded that many natural adsorbents such as wheat barn, neem leaves and groundnut shells showed maximum adsorption efficiency under high acidic conditions of pH 2.

Sharma et al. (2016) group utilised discarded potatoes (*Solanum tuberosum*) for adsorption at an optimum temperature of 25°C. When Berihun et al. (2017) studied chromium adsorption using coffee husk, they found that efficient adsorption of hexavalent chromium was 98.19% at 60 min contact time, 80 mg/L initial concentration, 2 pH, 3 g/L of adsorbent dose and at 200 rpm.

Table 3: Hexavalent chromium removal using various graphene based adsorbents

Type of adsorbent	*Concentration of metal (mg/L)*	*pH of solution*	*Contact time (min)*	*Adsorbent taken (g/L)*	*Adsorbent load (mg/g)*	*Percentage Cr(IV) removal (%)*	*References*
Graphene oxide prepared from graphite	10-80	4.0	40	0.005-0.01	-	92.8	Mondal and Chakraborty (2020)
Chitosan grafted graphene oxide	10-125	2.0	420	2	104.4	96	Pradeep et al. (2019)
Graphene nanosheets coated by iron	12–34	3.0	90	1	-	70	Li et al., 2016
Graphene oxide coated with nickel ferrite	10-100	4.0	120	0.125-2.5	45	-	Lingamdinne et al., 2015
Graphene oxide with acrylate co polymer of dimethylaminoethyl methacrylate	-	1.0	45	-	82.4	93	Ma et al., 2015
Graphene sand composite (GSC)	10-20	1.5	90	10	2859.4	93	Dubey et al., 2015
Graphene-magnetitenanocomposites	45–100	3.0	120	-	101	83.	Lu et al., 2014
Graphene	10-52	5.0	12	-	43.7	96.65	Yang et al., 2014
Modified Graphene with Cetyltrimethyl ammoniumbromide	50-100	2.0	60	400	21.57	98.2	Wu et al., 2013

A new composite comprising glucosamine, chitosan and ceramic alumina was prepared and experimented on chromium waste water and reported 153.85 mg/g of optimum adsorption capacity by adopting the Langmuir model (Boddu et al., 2003).

Ion Exchange

In 2015, a research group experimented on chromium using an ion exchange method with Tulsion A-27(MP) resin and it was reported that 80.5% of Cr(VI) removal from waste water by using 14 cm bed height at the flow of 1 mL/min within the flow concentration of Cr(VI) was 1145 mg/L (Karegar, 2015). But this process cannot be used for waste water of chromium concentrations as it fouls the resins (Barakat, 2011).

Membrane Separation

Kocurek et al. (2014) studied reverse osmosis using the membrane separation method for chromium removal. RO98pHt membrane, made of a thin polyamide layer on a polypropylene support material, was used in the process of reverse osmosis. The rejected liquid from membrane separation had almost 100% of chromium ions when 100 mg/L model solution was processed at 20°C and a pressure of 1.5 MPa (Kocurek et al., 2014). Table 4 gives details on the relationship of operating pressure with the pore size of the membrane and the type of filtration used in membrane-based separation of chromium removal.

Table 4: Pressure-driven membrane separation processes (Kocurek et al., 2014)

Method of separation	*Size range (nm)*	*Operating pressure (MPa)*
Microfiltration	>100.0	<0.5
Ultrafiltration	10.0-100.0	0.5-1.0
Nano filtration	1.0-10.0	1.0-4.0
Reverse osmosis	0.1-1.0	3.0-10.0

Advancements and New Methods

Several research works are being conducted based on membranes doped with adsorbents. One such research by Nayak et al. (2020) on polyvinyl chloride polysulphone doped with TiO_2 nanoparticles revealed that a maximum of 87 ± 5 % rejection of Cr (VI) was obtained at 100 kPa pressure in an acidic medium. The membrane was reusable upto three cycles with the capability of 70% rejection of chromium ions (Nayak et al., 2020). TiO_2 nanoparticles used were synthesised by the method of functionalising 4-amino benzoic acid with polyvinyl chloride using sol-gel process and later PVC was spread equally over matrix of polysulphone. The final membrane colour was yellowish saffron and porous in nature thus providing better efficiency (Nayak et al., 2020).

But nanoparticles may add up to the cost of membrane fabrication. Hence cheaper adsorbents such as carbon and graphene could be used in a matrix of cellulose acetate-polystyrene membrane. Reverse osmosis using these membranes may be industry efficient and could be applicable to continuous processes.

Conclusions

This review investigates potential methods to remove chrome from wastewater by the electroplating process. The electro-reduction studies report that high efficiency of up to 99.96% of hexavalent chrome was reduced by direct precipitation methods at 70°C with a current density of 0.05A. The adsorption techniques have advantages due to the wide range of commercially available adsorbent materials. The graphene based adsorption is capable of up to 96 % of chrome removal from waste water by maintaining pH 2 and a contact time of 420 min. Ion exchange lacks chrome removal due to the limitations of resins. Membrane-based hexavalent chrome separation research work reports that 100% of chromium ions separation at 20°C and operating pressure 1.5 Mpa is possible. Advanced methods such as membranes doped with adsorbents have revealed that a maximum of 87% hexavalent chromium separation is possible. There are many techniques for hard chrome waste water treatment, further studies have to be conducted for the implementation of methods at a large scale in industries. Desorption and regeneration of adsorbent are observed to be a bottleneck for various adsorption techniques. Also, disposal of adsorbents, electrodes and ion exchange resins is a serious problem for the environment and further research is needed for safe disposal.

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