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# Chromium (VI) Removal Methods from Effluents – A Review Article

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**Abstract**: Heavy metal is one of the major environmental and ecological problems in this world. The presence of heavy metals in water and wastewater causes toxic effects to the living beings and the environment. Compared to other heavy metals (such as $Cr^{6+}$, $Pb^{2+}$, $Zn^{2+}$ etc.,) the presence of chromium in industrial effluents has become a major problem worldwide as hexavalent chromium is highly toxic to animals due to its ability to generate reactive oxygen species in cells. The excess amount of chromium affects the lungs and lead to respiratory disorders in the human beings. It also contaminates the soil and groundwater. Due to a large number of industries that generate hexavalent chromium in its effluents such as tanneries and electroplating industries, the chromium contamination in the wastewater and aqueous solutions exceeds the tolerance limits. Many remediation processes for removal of hexavalent chromium have been researched and reviewed extensively. Many methods are used to remove the chromium from the aqueous solutions and industrial effluents. This paper reviewed different remediation methods namely: the using of natural absorbent; the conventional chemical reduction method; the bio-absorbent method, nano-technology application; and other remediation methods. For each method, information about major parameters affecting the efficiency of removal of hexavalent chromium ($Cr^{6+}$) from industrial effluent are stated. Brief discussion is included relating the different methods, in addition to some future aspects for the remediation process.

***Keywords****: Chromium Removal; adsorption; bio-treatment; nano-treatment.*

## INTRODUCTION

Chromium most commonly occurs in trivalent/Cr(III) and hexavalent/Cr(VI) states. While the trivalent state of chromium is an important trace element, its hexavalent state is non-essential and toxic to animals and may cause dermatitis, lung cancer, kidney and gastric damage, irritation to respiratory tract and eyes [1;2]. At low or neutral pH values, the $Cr^{6+}$ compounds are the powerful oxidants. The mechanism of oxidation by $Cr^{6+}$ is presented in Equation1.

$$2[CrO_4]^{2-} + 2H^+ = [Cr_2O7]^{2-} + H_2O \qquad (1)$$

The toxicity level of the chromium ranges between 50-150µg/kg [3].

Removal of toxic level of the chromium content from the water and wastewater is a complicated process and the cost of this process is very high and considered as a challenging problem. The U.S. is one of the world's leading producers of **(CrVI)** compounds. There is no reliable data on local chrome production in Sudan, although it had targeted for 2011 a production of more than 50,000 tones but has released no final data yet. As waste (CrVI) uses and production the leather tanning industry plays the greatest role, there is round 23 mechanized tanneries and tenth of traditional ones. Round 150 employees per tannery are exposed to (CrVI). [4;5]

Due to rise in rigorous environmental policies, scientists all around the world are required to develop precise techniques to control the amount of heavy metal in waste water and drinking water. Chromium in particular has received a great deal of attention.

According to the dramatic evolution of the treatment methods, this review paper surveyed different remediation methods namely: general conventional methods, selected various natural adsorbents; bio-remediation, nano-remediation and other named methods. For each method a comparative summary is stated regarding the operating parameters and conditions, and the remediation efficiency so as to:

1. set a comparison study for each method with different parameters,
2. set a comparison study between the different remediation methods,
3. Recommendan appropriate method.

## REMOVAL METHODS OF ($Cr^{6+}$) FROM EFFLUENT:

### 1. Conventional Reduction Methods:

The conventional chemical reduction method comprises two steps—the reduction of Cr(VI) to Cr(III) by are ducing agent, at an acidic pH, and the precipitation of Cr(III) as an insoluble hydroxide at an alkaline pH. The chemical reducer can be any sulphur-based or iron-based salt. These two steps can be combined into a single step by the electrochemical addition of ferrous ion, rather than the addition of a ferrous salt ($FeSO_4$ or $FeCl_2$) which necessitates the use of an acidic and an alkaline pH, making it a two-step process. A summary of some conventional methods are listed below:

- *Physical Processes which includes:*

- Liquid–liquid extraction: like amine-based extractions and long-chain quaternary ammonium or tertiary amine-based compounds. [6:7].
- Adsorption: the most commonly used. Absorbent can be modified oxides, zeolites, waste slurry [8].Adsorption by hybrid clay material is reviewed as well like Organo modified clays such as natural red [9].
- Solid-phase extraction such as Solid adsorbents may be inorganic (silica, alumina, activated carbon, clay, ceramics) or organic (cellulose, grapheme oxide) [10;11].

- *Chemical Processes*: processes such as reduction of chromium (IX) to chromium (III) are thoroughly studied. Additional processes are added such as physical and/or biological in order to increase the efficiency of the removal [12].

## 2. Usage of Various Natural Adsorbents

Adsorption is one of the cost effective methods being widely used for the removal of heavy metals from industrial and commercial wastewaters. It has been established as an important and economically feasible treatment technology for removing heavy metals, particularly chromium. A review of eight different kinds of natural adsorbent store duce the toxicity level of the hexavalent chromium ($Cr^{6+}$) was presented. The adsorption isotherms and kinetic studies were not considered. The papers reviewed have dealt only with adsorption at room temperature. Hence, the factors affecting the adsorption efficiency: (effects of pH, absorbent dose, contact time, concentration of chrome) have been tabulated in Table (2).

**Table .1.**Various natural absorbents versus recovery efficiency:

| Factor / Material | PH | Absorbent Dose (gm/L) | Initial Concentration | Time (min) | Particle Size | Recovery % | Reference |
|---|---|---|---|---|---|---|---|
| Saw dust | 1 - 6.9 | 4 - 24 | 100 – 400 (mg/L) | 250-1050 | Efficiency decreases as size increases | 99.9 - 81 | [13] |
| Cocount Shell Charcoal | 2 - 9 | 1.5 – 25.5 | 5 – 25 (mg/L) | 30 - 180 | 0.42-1.7 mm | 60-87 | [14] |
| Agricultur waste | 2-8 | 2-9 | 1.5 – 5(mg/L) | 100 | 100-200µm | 97-45 | [15;16;17] |
| Neem Leaves | 4.1 -6 | 2-10 mg/mL | 30mg/ 100mL | 80 | ND | 98-67.7 | [18;19] |
| Banana Peels | 3–8 | 1-5 | 0.5-3.5gm/10gm | 60-120 | ND | 96-60 | [20;21;22] |
| Grape Leaves | 1.5 -9 | 0.2 - 3 | 25-200 | 10-120 | Powder | | [23;24] |
| Groundnut Hull | 1-8 | 5 - 40 | 8.3 - 25 | 30-80 | 200-300 µm | 82-96 | [25] |

## 3. Bio-treatment

While reviewing there are some reports on the removal of heavy metals in effluent by complexion of dry biomass. Unfortunately, these methods were not employed on large scale. Many researchers have reported the methods of bio sorption on chemical modified solid surface [26], it takes some time for the adsorption of heavy metals in water bodies, especially, at ppm level.

Among the most promising types of bio sorbents studied is the algal biomass[27;28]. This is due to the presence of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding sites for metals [29]. In batch experiments both *Vetiveria* and *Anabaena* species were found to be cost effective bio sorbent for the efficient removal of Cr(VI) from the effluent and comparatively *Anabaena* species was found to adsorb maximum Cr(VI) (88.86%) at a low contact time of 60 min [30]. *Vetiveriazizanioides*, due to its unique morphological and physiological characteristics, and tolerance to high levels of heavy metal and adverse conditions, has also been successfully used in the field of environmental protection. It is excellent for the removal of heavy metals from contaminated soil and rehabilitating landfills [31]. Even though it is not an aquatic plant, *Vetiveria* can be established and survive under hydroponic conditions [32]. It can purify eutrophic water, garbage leachates and wastewater from pig farms [33]. Therefore, *Vetiveria* has high potential to be used for industrial wastewater treatment.

## 4. Nano-treatment

Using nanoparticles as adsorbents for the removal of hexavalent chromium from industrial effluents is recently investigated. Nano materials possess certain properties which make them an ideal adsorbent. Theseinclude a suitable particle size, large surface area, accessible pores and high stability [34]. Moreover, due to their extremely small size, they can be easily transported through a water body simply by Brownian motion, without the aid of any external force. As a result, the nanoparticles remain suspended longer to establish an in situ remediation zone [35]. Nanoparticles can be embedded in the bulk materials to overcome the problem of mass transfer resistance in the case of bulk adsorbents, thus facilitating the contact of contaminants to large surface area and encouraging internal mass transfer. These nanoparticles can be created by various physical, chemical and biological processes, and the adsorptive capacity of the particle varies according to the methodof production. Below are some of nan treatment processes:

**Table .2.**Various nanomaterials versus recovery efficiency:

| Material | pH | Initial Conc. | Recovery % | Reference |
|---|---|---|---|---|
| Magnetic-zeolite/polypyrrole composite | 2 | 300mg/l | 99.99 | [36] |
| nZVI in ion-exchange resin | 2.6 | --- | 99 | [37] |
| Carboxymethyl cellulose (CMC) as a stabilizer for nZVI | 3 | 10mg/l | 100 | [38] |
| Solar radiation ZnO nanoparticles | 2.7 | 200mg/l | 96 | [39] |
| Magnetite ($Fe_3O_4$) nanoparticles | 3 | 300mg/l | 97.6 | [40;41] |
| Cerium oxide nanoparticles | 3 | 300mg/l | 96.5 | [42] |
| chitosan as the polymer | 3 | 200mg/l | 98 | [43] |
| Nanoparticles applied on membrane | 3 | 350mg/l | 94 | [44] |

## 5. Other methods:

### 5.1 Coagulation

a. Electro coagulation: Electrocoagulation experiments were conducted using an electrochemical cell with iron electrodes immersed in a specific volume of tannery wastewater. Operating parameters, such as the initial chromium concentration, pH and current density as well as power consumption were evaluated to determine optimum chromium removal. The optimization was performed using Response Surface Methodology combined with central composite design. Analysis of variance (ANOVA) was used to determine the response, residual, probability, 3D surface and contour plots. The maximum chromium removal was 100% at the optimum values of 13 $mA/cm^2$, 7 and 750 ppm for current density, pH and concentration, respectively [45].

b. Chemical Coagulation: Ferric chloride produced better results than aluminum sulphate. The COD and chromium were removed mainly through coagulation: 38–46% removal of suspended solids, 30–37% removal of total COD from settled tannery wastewaters and 74–99% removal of chromium at an initial concentration of 12 mg/l can be achieved by using the optimum coagulant dosage (800 mg/l) in the optimum pH range (around 7.5). Coagulation combined with centrifugation improved the removal efficiency of suspended solids (70%). A high degree of clarification is attained as indicated by an excess of 85–86% colour removal [46].

### 5.2 Solvent Extraction :

The results demonstrated that 99.67% chromium could be extracted after six-stage countercurrent extraction, almost all impurity ions such as Na, *V*, Al and Mg could be removed from the loaded organic phase after three-stage cross-current scrubbing and 95.72% chromium could be stripped after six-stage countercurrent stripping respectively under the optimum conditions. The $Cr_2O_3$ product with 99.01% purity was obtained and total chromium recovery from the chromium (VI) waste solution was 95.40% [47].

### 5.3 Makeup and direct recycling:

a. Chemical makeup: The spent chrome tanning liquors were reused 5 times after they had been recharged with the reduced amounts of salt, acids and chrome. Savings in water, salt and chrome were 85%, 33% and 28% respectively. No significant changes were observed in the leather produced using the recycled liquors compared to the leathers produced using the fresh liquor [48;49].

b. Evaporation: Spent chromium liquor was concentrated by evaporation in a triple-effect evaporator. The concentrated liquor was blended with fresh make-up chromium and re-used in tannage. Although the energy cost of the evaporator, the leather produced by this make-up chromium has a normal properties and this is due to the strict control of pH, basicity and salt. [50].

## DISCUSSION

A wide range of treatment methods (Adsorption, Ion exchange, chemical precipitation etc.,) are available to reduce the heavy metal toxicity levels from the water and wastewater. Adsorption and Precipitation are the most efficient methods used to remove the heavy metals from the wastewater. Some other methods of Cr(VI) removal include membrane filtration, solvent extraction, leaching and electro kinetic procedures. These methods, though commonly used, have certain limitations. The major disadvantage of such conventional treatment methods is the high cost, which discourages many industries from adopting any remediation methods.

### 1. Conventional Remediation

Among the conventional remediation methods, adsorption is the most effective and economical solution to remediation of Cr(VI), especially if it is coupled with proper regeneration of the adsorbent. Activated carbon (AC) is one such highly effective adsorbent, which resembles granular or powder charcoal and possesses high porosity, internal surface area and mechanical strength. AC is especially useful in remediation of low concentrations of effluent stream. However, commercially available ACs are not economically feasible, and hence, any material with a high organic content and low inorganic content can be used for manufacturing of AC. The major limitation of chemical adsorption method is the formation of toxic solid sludge during the precipitation of Cr(III). Moreover, in the treatment of soil contaminated by Cr(VI) from industrial effluents, it is disadvantageous as the contaminated soil needs to be physically mixed with the reducing agent, making the entire process labor-intensive.

The feasibility and efficiency depends on the physical properties of the effluent, the size of the industry producing the effluents and the availability and friendly-environmental of the agents.

### 2. Natural Adsorbent

According to this review, it is concluded that sawdust is the best adsorbent to remove the Hexavalent Chromium ($Cr^{6+}$) with an efficiency of 99.9%. Here, the saw dust plays a major role in adsorption and accumulation of heavy metal contents from the wastewater, due to its organic nature and high amount of carbon content. Also, the Banana Peels (98%), Bamboo waste (98%) and Agricultural waste (98%) had given their best adsorption rate of Hexavalent Chromium ($Cr^{6+}$). However, these efficiencies are obtained from the aqueous solutions, not industrial effluents (Because of high concentration). Combination of these adsorbents in equal or different ratios will give the maximum efficiency (100%) of removal of Hexavalent Chromium ($Cr^{6+}$) from the industrial effluent such as tanneries, electroplating industries etc.

### 3. Bio-remediation:

The key factors for preparation for bioadsorbent depend on its morphological properties such as particle size and shape, binding surface area, and overall effluent removal capacity. For bio-remediation there are five operating parameters that govern the adsorption efficiency; pH; agitation time; bioadsorbent dose; elution agent and adsorption isotherm.

The pH of the metal solution is the most influential factor as it affects surface properties of the adsorbent and metal speciation. The uptake of the metallic cations by adsorbent is reduced at pH below 3 and above 8.

Variation in bioadsorbent dosage increased the removal of Cr(VI). This is to be expected because for a fixed effluent concentration increasing total adsorbent doses, provides a greater surface area or adsorption site.

The low elution efficiency of $HNO_3$ solution can be attributed to the greater affinities of divalent cations for the negative charged sites on the bioadsorbent than monovalent cations. HCl and EDTA showed the maximum efficiency for the desorption process. This result obtained with EDTA can be attributed to the strong complexion ability to Cr(VI). HCl was selected as an effective desorbing agent due to the similar result with EDTA, and low cost of HCl .

### 4. Nano remediation

To overcome the problem of mass transfer resistance in the case of bulk adsorbents, nanoparticles can be embedded in the bulk materials, thus facilitating the contact of contaminants to large surface area and encouraging internal mass transfer. Nanoparticles can also be applied on membranes used to enhance removal of chromium ions from an aqueous solution. Nanoparticles tend to get accumulated in the liver, kidney and lungs, where they exert their toxic effects. In the liver, these nanoparticles induce oxidative stress and may also trigger the inflammatory cytokines cascade, resulting in inflammatory cell.

## FUTURE ASPECTS

Natural absorbents revealed to be the most efficient in removing the chromium oxide, but still more researches are needed for the regeneration of the absorbents and reuse of the chromium.

With regard to Nano-technology in today's society of unstable economy, industries are reluctant to spend adequate money on remediation processes. Industrialists should be aware of such remediation processes and their benefits in the long run. The capital cost of cleaning industrial effluents may be high, but with the use of cost-effective techniques, such an investment may be profitable for the industry.

Using greener and eco-friendly techniques, such as use of biogenic nanoparticles, may reduce the cost even more with a simultaneous increase in efficiency. Future research should focus on developing less toxic, more efficient, cost-effective and increasingly reusable nano adsorbents.

Thermal and electro remediation can be of promising process, if the energy cost can be minimized.

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