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Efficient methods for the removal of Chromium from Textile effluents – A Review

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Abstract: Chromium is a metal that exists in several oxidation or valence states, ranging from Cr(-II) to Cr(+VI). Many effluents from leather industries, textile, dye industries, cement industries give away these toxic heavy metals that disturb our eco system. This paper includes the methods to remove this hexavalent chromium. Chemical precipitation, adsorption and biosorption, reverse osmosis, ion exchange, electrodialysis and photocatalysis. We here compare the six methods and analyse which is better.
Keywords: Chemical precipitation, adsorption & biosorption, reverse osmosis, ion exchange, electrodialysis and photocatalysis.

Introduction

Chromium compounds are very stable in trivalent state and occure naturally in this state in ores such as ferrochromite or chromite ore. Chromium III is an essential nutrient for maintaining blood glucose levels. Hexavalent chromium is the second most stable compound that rarely occurs in nature.It is generally toxic and man made. It is used in many industrial application for its anti corrosive properties and it is used in electroplating. The sources of chromium are aircraft painting, leather tanning, textile manufacturing,dyeing and cement industry. But it is hazardous to health. It is erosive to stomach, causes hemorrhage. Direct eye contact with chromic acid or chromate dusts can cause permanent eye damage. Hexavalent chromium can irritate eye, nose and throat. It can also cause ulcers, allergic reaction, skin rashes and is carcinogenic. It even causes death.

Methods

Chemical Precipitation

Formation of seperable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it. The removal of chromium can be accomplished by the addition of ferrous sulphate and lime. Ferrous ion first reduces hexavalent chromium to trivalent chromium by simultaneous oxidation of ferrous ion to ferric. The resulting forms can be precipitated as hydroxides by lime. Chromium is precipitated as hydroxide:

$Cr^{3+} + (OH)^- \rightarrow Cr(OH)_3$

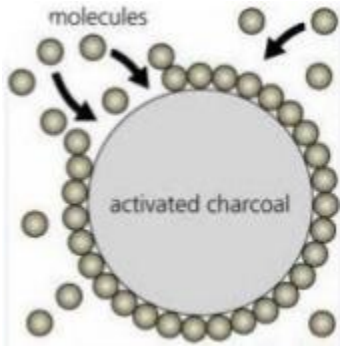
The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Its efficiency is affected by low pH and the presence of other salts(ions) and is ineffective in removal of the metal ions at low concentration[1].

Adsorption and Biosorption

Defined as accumulation of liquid or gas phase on the surface of a solid phase. The material that absorbs is called adsorbent and the substance getting adsorbed is called adsorbate. Adsorption may be physical

adsorption or chemical adsorption or a combination of both (Figure- 1). Sometimes the adsorbent materials have negatively charged ligands that can form complexes with metal ion via electrostatic interactions. If we have to remove soluble material from the solution phase, but the material is neither volatile nor biodegradable, we often employ adsorption processes. Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. It is particularly the cell wall structure of certain algae, fungai and bacteria which was found responsible for this phenomenon. The advantages of biosorption process are that these are cost effective, technically feasible and eco-friendly. This method suffers from low adsorption capacity and less intensity of biosorption[2].

Figure 1: Adsorption of chromium by using activated charcoal



Reverse Osmosis

Reverse osmosis is filteration process that is often used for water. It works by using pressure to force a solution through a membrane, retaining the solute on one side and allowing the pure solvent to pass to the other side. This is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. A semi permeable membrane, like the membrane of a cell wall or a bladder, is selective about what it allows to pass through, and what it prevents from passing. These membranes in general pass water very easily because of its small molecular size; but also prevent many other contaminants from passing by trapping them. Water will typically be present on both sides of the membrane, with each side having a different concentration of dissolved minerals. Since the water with the less concentrated solution seeks to dilute the more concentrated solution, water will pass through the membrane from the lower concentration side to the greater concentration side. Eventually, osmotic pressure will counter the diffusion process exactly, and an equilibrium will form. The semi permeable membrane can be fabricated by a variety of materials in a way to support a high transmembrane pressure.

Generally membranes made up of polyamide are used for the treatment of chromium containing effluent [3]. The reverse osmosis technique has been successfully used in the treatment of electroplating rinse waters, not only to meet effluent discharge standards, but also to recover concentrated metal salt solutions for reuse. Its main demerits are high priced equipment and/or expensive monitoring system, high energy requirement, sludge generation.

Ion Exchange

It is based on the exchange of cations or anions on synthetic resins with essential characteristics of its regeneration after the elution of ions. Resins are classified based on the type of functional group they contain:

Cation Exchangers:

Strongly acidic-functional groups derived from strong acids e.g., R-SO_3H(sulfonic).Weakly acidic-functional groups derived from weak acids, e.g., R-COOH(carboxylic).

Anionic Exchangers:

Strongly basic-functional groups derived from quaternary ammonia compounds, R-N-OH.Weakly basic- functional groups derived from primary and secondary amines, R-NH_3OH or R-$R^{'}$-NH_2OH.

About 100% removal of Cr (V1) was achieved in the studies.Its advantages over other processes are the

recovery of the metal's value, high selectivity, less sludge volume produced and the ability to meet strict discharge specifications. Its limitations are and high operating costs compared to other treatment systems. There can be incomplete removal of the chromium from the salt solution

Electrodialysis(ED)

Electrodialysis is an electro membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. Applying a voltage between two end electrodes generates the potential field required for this. Since the membranes used in electro dialysis have the ability to selectively transport ions having positive or negative charges[4]. The ion permeable membranes used in eletrodialysis are essentially sheets of ion exchange resins. They usually contain other polymers to improve mechanical strength and flexibility. The resin components of a cation exchange membrane would have negatively charged groups chemically attached to the polymer chains. Polymer chain forms anion permeable membranes, which are selective to transport of negative ions, because the fixed –NR3+ groups repel positive ions. The recovery percentage of chromium is quite good, the chromium concentration is not high enough to be cycled to the tanning process. Other problems with electrodialysis are high capital and operating costs involved and the requirement of highly trained human resources. The fouling and scaling of membranes is another drawback which can be controlled to an extent by employing flushing step

Photo catalysis

Photo catalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor producing electron hole pairs [5].

$TiO_2 \rightarrow e^-_{cb}(TiO_2) + h^+_{vb}(TiO_2)$

Oxidation of water by the hole produces the hydroxyl radical. Similarly O_2 radical also formed. OH radicals rapidly attack pollutants in solution. The oxidation pathway is not yet fully understood. But OH radical can be formed in two different manners.

$TiO_2(h_{vb}^+) + H_2O_{ads} \rightarrow TiO_2 + HO^*_{ads} + H^+$
$TiO_2(h_{vb}^+) + HO^-_{ads} \rightarrow TiO_2 + HO^*_{ads}$

Cr(VI) will be reduced to Cr(III) and precipitated out. Photo catalysis has large capability for the removal of trace metals. The drawback of this method is that of being slow compared with traditional methods but it has the advantage not leaving toxic by product or sludge to be disposed

Result and Discussion

500ml of effluent water is taken for each analysis, the methods are considered in the order for the removal of maximum chromium percentage. The first method, the chemical precipitation shows that it removes 69% of chromium and the second method, adsorption and biosorption to remove 72% of chromium. The further study shows from that reverse osmosis method the chromium removal of 76% is the highest chromium removal method among ion exchange, electrodialysis and photocatalysis method which is discussed in (Table- 1)

Table 1: Removal of chromium using various method in %:

S.No	Method	% present	% removed
1.	Chemical precipitation	80	69
2.	Adsorption and biosorption	80	72
3.	Reverse osmosis	80	76
4.	Ion exchange	80	75
5.	Electrodialysis	80	74
6.	Photo catalysis	80	68

Conclusion

Each method has its own merits and limitation. The versatility, simplicity, cost effectiveness and technical feasibility are a few factors that must be considered while selecting a particular method. High cost and technical complication are the problem associated with reverse osmosis and electrodialysis.

Ion exchange is also comparatively costly whereas chemical precipitation leads to sludge generation and involve high capital costs. Photo catalysis process is still in the developmental stage. Adsorption and biosorption are found to be technically uncomplicated as well as economical but the desorption studies on the adsorbents need to be carried out before going for large scale applications.

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