Reviewing Remediation methods for efficient removal of Hexavalent Chromium (Cr6+) from Industrial Effluent

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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 Cr⁶⁺, Pb²⁺, Zn²⁺ etc.,) the presence of (CrVI) in industrial effluents has become a huge problem worldwide as (CrVI) is highly toxic to animals due to its ability to generate reactive oxygen species in cells. The excess amount of (CrVI) 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 (CrVI) in its effluents such as tanneries and electroplating industries, the (CrVI) contamination in the wastewater and aqueous solutions exceeds the tolerance limits. Many remediation processes for removal of (CrVI) have been researched and reviewed extensively. Many methods are used to remove the (CrVI) 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 bioabsorbant method, nano-technology application; and other remediation methods. For each method, information about major parameters affecting the efficiency of removal of (CrVI) from industrial effluent are stated. Brief discussion is included relating the different methods, in addition to some future aspects for the remediation process.

Keywords: (CrVI) Removal; adsorption; bio-treatment; nano-treatme

المستخلص:

المعادن الثقيلة هي واحدة من أكبر المشاكل البيئية والاحيائية في هذا العالم. يتسبب وجود المعادن الثقيلة في المياه ومياه الصرف في آثار سامة على الكائنات الحية والبيئة. مقارنة بالمعادن الثقيلة الأخرى (مثل ⁴⁶C + و¹C + و¹C وما إلى ذلك) ، أصبح وجود الكروم في النفايات السائلة الصناعية من أكبرلمخاطر في جميع أنحاء العالم لأن الكروم سداسي التكافؤ شديد السمية للكائنات الحية نظرًا لقدرته على توليد أنواع الأكسجين التفاعلية في الخلايا. تؤثر الكمية الزائدة من الكروم على الرئتين وتؤدي إلى اضطرابات في الجهاز التنفسي لدى البشر. كما أنه يلوث التربية والمياه الجوفية. نظرًا لقدرته على توليد أنواع الأكسجين التفاعلية في الخلايا. تؤثر الكمية التربية والمياه الجوفية. نظرًا لوجود عدد كبير من الصناعات التي تولد الكروم سداسي التكافؤ في النفايات السائلة مثل المدابغ وصناعات الطلاء الكهربائي ، فإن تلوث الكروم في مياه الصرف إلى النفايات السائلة مثل المدابغ وصناعات الطلاء الكهربائي ، فإن تلوث الكروم في مياه الصرف المحاليل المائية يتجاوز حدود التحمل. في هذه الدراسة تم بحث ومراجعة العديد من عمليات والمحاليل المائية يتجاوز حدود التحمل. في هذه الدراسة تم بحث ومراجعة العديد من عمليات والنفايات الصاعية السائلة. استعرضت هده الورقة طرق عداج مختلفة وهي: استخدام مادة ماصة طبيعية. طريقة الاخترال الكيميائي التقليدي ؛ طريقة الامتصاص الحيوي ، تطبيق تكنولوجيا والنفايات الصاعية السائلة. استعرضت هذه الورقة طرق علاج مختلفة وهي: استخدام مادة مات عليه أولياة الكروم سداسي التكافؤ. أستخدمت طرق عديدة لإزالة الكروم من المحاليل المائية والنفايات الصاعية السائلة. استعرضت هذه الورقة طرق علاج مختلفة وهي: استخدام مادة مات عليهية. إذلية الكروم سداسي التكافؤ. أستخدمت عنه ذكر معلومات حول العوامل الرئيسية التي تؤثر ماصة طبيعية. طريقة الاخترال الكيميائي التقليدي ؛ طريقة الامتصاص الحيوي ، مورق مان في على كفاءة إزالة الكروم سداسي التكافؤ (C+C)، من النفايات السائلة الصاناعية. تم تضمين مناقشة على كفاءة إزالة الكروم سداسي التكافؤ (C+C)، من النفايات السائلة الصناعية. عمليات المعالجة.

Introduction

Chromium most commonly occurs in trivalent/Cr(III) and / Cr(VI) states. While the trivalent state of (CrVI) is an important trace element, its state is non-essential and toxic to animals and may cause dermatitis, lung cancer, kidney and gastric damage, irritation to respiratory tract and eyes. Hexavalent chromium, also called (CrVI), is hemotoxic, genotoxic, and carcinogenic. When (CrVI) enters the bloodstream, it damages blood cells by causing oxidation reactions. This oxidative damage can lead to hemolysis and, ultimately, kidney and liver failure. Patients might be treated with dialysis. [1-2].

At the low or neutral pH values, the Cr^{6+} compounds are the powerful oxidants. The mechanism of oxidation by Cr^{6+} is presented in Equation 1.

 $2[CrO_4]^{2-} + 2H^+ = [Cr_2O7]^{2-} + H_2O \qquad (1)$ The toxicity level of the (CrVI) ranges between 50-150 µg/kg [3].

(CrVI) compounds, such as (CrVI), are widely **used** in electroplating, stainless steel production, leather tanning, textile manufacturing, and wood preservation. 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] Objectives:

Removal of toxic level of the (CrVI) 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. Due to rise in rigorous environmental policies, scientists all around the world are desired to develop precise techniques to control the amount of heavy metal in waste water and drinking water. Due to the dramatic evolution of the treatment methods, this article, based on survey of previous used methods aims to:

- 1. set a comparison between the different removal methods,
- 2. recommend for the appropriate methods,
- 3. set a comprehensive article as reference in the field.
- 4. Remediation Methods for removal of (Cr⁶⁺) from industrial effluent:

A wide range of treatment methods is (Adsorption, Ion exchange, chemical precipitation etc.,) 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 electrokinetic procedures. These methods, though commonly used, have certain limitations. The major disadvantage of such conventional treatment methods is the high cost, which dissuades many industries from adopting any remediation methods. [4-7]

Different remediation methods are summarized in this review article: general conventional methods, selected various natural adsorbents; bio-remediation, nano-remediation and other named methods, comparing different operational parameters with remedy percentage. [8-11]

1. Conventional Reduction Methods:

The conventional chemical reduction method comprises of two steps—the reduction of Cr(VI) to Cr(III) by a reducing agent, at an acidic pH, and the precipitation of Cr(III) as an insoluble hydroxide at an alkaline pH. The chemical reductant 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 (FeSO₄ or FeCl₂) which necessitates the use of an acidic and an alkaline pH, making it a two-step process. The major limitation of this 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, the chemical reduction method is disadvantageous as the contaminated soil needs to be physically mixed with the reducing agent, making the entire process labour-intensive. An alternative method which can be used in this situation is electrokinetic remediation, which involves passing of low-voltage direct current through the soil, thus providing in situ remediation [12-13]. A summary of some conventional methods are listed below:

Physical Processes: this includes

• Liquid–liquid extraction: like amine-based extractants and long-chain quaternary ammonium or tertiary amine-based compounds. [14-19].

• Adsorption: the most commonly used. Absor-

bent can be modified oxides, zeolites, waste slurry [20-25]. Also biopolymers are used [26-27]. Adsorption by hybrid clay material is reviewed as well like Organo modified clays such as natural red [28-35]. • Solid-phase extraction such as Solid adsorbents may be inorganic (silica, alumina, activated carbon, clay, ceramics) or organic (cellulose, grapheme oxide) [36].

- Chemical Processes: processes such as reduction of (CrVI) (IX) to (CrVI) (III) are thoroughly studied. Additional processes are added such as physical or/and biological in order to increase the efficiency of the removal [37-44].

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 (CrVI). Herewith, a review of eight different kinds of natural adsorbents to reduce the toxicity level of the (CrVI) (Cr⁶⁺). Here, adsorbents (a substance which adsorbs another) [45-46] have been used to receive the metal ions from the water and wastewater. 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).

Factor Material	рН	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	[46-48]
Cocount Shell Charcoal	2 -9	1.5 - 25.5	5 – 25 (mg/L)	30 -180	0.42-1.7 mm	60-87	[49-58]
Agricultur waste	2-8	2 – 9	1.5 – 5(mg/L)	100	100-200µm	97-45	[59-78]
Neem Leaves	4.1 -6	2-10 mg/mL	30mg/ 100mL	80	ND	98-67.7	[79-83]
Banana Peels	3 - 8	1 – 5	0.5-3.5gm/10gm	60-120	ND	96-60	[84-86]
Grape Leaves	1.5-9	0.2 - 3	25-200	10-120	Powder		[87-88]
Groundnut Hull	1-8	5 - 40	8.3 - 25	30-80	200-300 µm	82-96	89

Table (2): Various natural absorbents versus absorption efficiency:

3.Bio-treatment

While reviewing there are some reports on the removal of heavy metals in effluent by complexation of dry biomass [90-91]. Unfortunately, these methods were not employed on large scale. Many researchers have reported the methods of biosorption on chemical modified solid surface [92], it takes some time for the adsorption of heavy metals in water bodies, especially, at ppm level. Among the most promising types of biosorbents studied is the algal biomass [40-44], [93-94]. 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 [95]. Anabaena Bory ex Bornet & Flahault (Cyanobacteria), a blue green alga, is among a number of cyanobacteria that present gas vacuoles (aerotope) and form dense populations on the surface of lakes and reservoirs, the so-called blooms. Anabaena being structurally similar might also possesses the capabilities of heavy metal removal from effluents as this alga contain lipopolysaccaride envelop, that is proven to be helpful in ionic exchange properties/intracellular accumulation/adsorption onto cell surface. Adsorption of Cr(VI) by activated Vetivera roots and Blue green algae Anabaena supports that it is an effective low cost adsorbent for the removal of

Cr(VI) from plating effluent. Langmuir and Freundlich adsorption isotherm correlate the equilibrium adsorption data. In batch experiments both Vetiveria and Anabaena species were found to be cost effective biosorbent 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 [96]. Vetiveria zizanioides, 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 [97-98]. It is excellent for the removal of heavy metals from contaminated soil [99-100] and rehabilitating landfills [101]. Even though it is not an aquatic plant, vetiver can be established and survive under hydroponic conditions [102]. It can purify eutrophic water [103], gar- bage leachates [104] and wastewater from pig farms [105]. Therefore, vetiver has high potential to be used for industrial wastewater treatment.

4Nano-treatment

Using nanoparticles as adsorbents for the removal of (CrVI) from industrial effluents is recently investigated. Nanomaterials possess certain properties which make them an ideal adsorbent. These include a suitable particle size, large surface area, accessible pores and high stability [106]. 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 [107]. These nanoparticles can be synthesised by various physical, chemical and biological processes, and the adsorptive capacity of the particle varies according to the method of production. Below are some of nano-treatment processes:

- According to [108], 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. This was achieved by the synthesis of a magnetic zeolite/polypyrrole composite, which consisted of magnetic zeolite (embedded with magnetic Fe_3O_4 nanoparticles) mixed with the organic polymer polypyr- role. This adsorbent showed a removal efficiency of 99.99% when the pH was 2 and the initial Cr(VI) concentration was 300 mg/l.

- Zero-valent iron nanoparticles (nZVI) have become one of the most used metal nanoparticles for environmental remediation of Cr(VI). Since the redox potential of (CrVI) is much more positive than that of Fe⁰, it reduces the form of (CrVI) to its trivalent form (itself getting oxidised to Fe^{?3}), which then precipitates along with Fe²³ on the surface of the nanoparticles [109–111].
- Ion-exchange resins can be used as supporting material for the nZVI particles. While conventional ion-exchange resins can remove either a cation or an anion, resin-supported nZVI can eliminate both forms. Such resin-supported nZVI have been reported to remove Cr(VI) with an efficiency of 84.4% at optimal conditions [112].
- Using carboxymethyl cellulose (CMC) as a stabiliser for nZVI, 100% of Cr(VI) was reduced to Cr(III) from a solution containing 10 mg of Cr(VI)/l [113]. A major problem of using nZVI particles is the formation of a Fe(III)–Cr(III) (oxy)hydroxide film on the surface of the nanoparticles, rendering the surface passive, as it does not allow the Fe⁰ particles at the core to react with the Cr(VI) particles on the surface. This problem is usually overcome by cementing a second metal (preferably inert, such as Ag, Cu, Ni, Pd, Co) on to the surface of the transition metal, thus preventing the formation of the self-inhibiting film [114-115]. Such bimetallic combinations, for example nZVI/Cu, demon-

strate pseudo-first-order kinetics or Langmuir-Hinshel- wood first-order kinetics [114, 116]. The second metal acts as an electron shuttle between the two metal systems, thus forming a catalyst. It also protects the surface of nZVIs from corrosion [115]. Another drawback of using nZVI particles is that their removal from treated water is tedious. This can be overcome by using magnetised nZVI nanoparticles, i.e. nZVI nanoparticles coated with magnetic Fe₃O₄ nanoparticle which could be removed easily with the help of an external magnetic field [117]. Such ZVI-Fe₃O₄ nanocomposites form a heterogeneous Fenton-like system, which showed an increase in Cr(VI) removal efficiency from 48.8% (using bare nFe₃O₄) to 96.4% (using nZVI-Fe₃O₄) nanocomposites) in 2 h [18-119]. nZVI has also been assembled on magnetic $Fe_{2}O_{4}$ /graphene nanocom- posites to tackle both the drawbacks mentioned above, and it shows a Cr(VI) removal efficiency of 83.8%, following pseudo-second-order kinetics [120]. Use of ultrasound technology contributes to an increase in the available surface area and induces new reactive sites for the reduction reaction of Cr(VI) [121].

- Metallic heterogeneous nano-supported catalyst is applied when using formic acid is an organic and non-toxic reducing agent that reduces Cr(VI) to Cr(III), while itself getting converted to CO_2 and H_2 , which can be recycled for industrial purposes. Different nano-supported metallic heterogeneous catalysts were investigated, namely graphene oxide-supported Ni nanoparticles [122], TiO₂-supported Pd nanoparticles [123], Pd nanoparticles supported on amine-functionalised SiO₂ [124], among others.
- More recently, 3D urchin- shaped monometallic palladium was used as a nanocatalyst for the detoxification process of Cr(VI)-contaminated industrial effluents using formic acid. It was found that the rate of detoxification process could be en-

Reviewing Remediation methods for efficient removal of Hexavalent Chromium (Cr6+) from Industrial Effluent

hanced by exposure to light of appropriate intensity. Further, this nanocatalyst exhibited stable catalytic activity even after six cycles of reaction [125].

- Magnetite (Fe_3O_4) nanoparticles can also be used individually for removal of Cr(VI) from wastewater [125]. Maghemite (c- Fe_2O_3) coated with polydopamine (a cate- cholamine) showed a Cr(VI) removal efficiency of 97% at pH of 3 [126-127].
- In the presence of solar radiation ZnO nanoparticles were used as photocatalysts for the reduction of Cr(VI) to Cr(III) [128-129]. Such photocatalytic reduction experiments have also been carried out on TiO₂ [130-131] and WO₃ [132]. The mechanism of photocatalysis is based on the principle of semiconductor solid catalysis, wherein electrons move from valence band to conduction band on being stimulated by light of appropriate wavelength. The charge carriers on the surface of the catalysts (such as O₂) take up the electron promoted to the conduction band, and the O₂⁻ thus formed engages in redox reactions with the adsorbed pollutants. H₂O is used to fill the lack valence band [133].
- Cerium oxide nanoparticles stabilised with hexamethylenetetramine were able to remove Cr(VI) with 96.5% efficiency, and after the treatment process, the nanoparticles could be centrifuged out of the water, while (CrVI) could be desorbed using NaOH [134]. The ability of hydrous cerium oxide nanoparticles to adsorb Cr(VI) was also investigated, which yielded positive results [135]. The potential of $CoFe_2O_4$ nanoparticles (synthesised in a cost- effective manner) for remediation of Cr(VI) from wastewater released from a printing press was quantified to be 67%, with no major loss of adsorption capacity up to three reaction cycles [134].
- Manganese dioxide/iron oxide/acid oxidised multi-walled

carbon nanotube magnetic nanocomposites $(MnO_2/Fe_3O_4/o-MWCNTs)$ were used for Cr(VI) removal from wastewater. Apart from being highly efficient in this purpose, Cr(VI) can be desorbed and the adsorbent may be regenerated by using an alkali. However, the efficiency of Cr(VI) adsorption efficiency reduces to 85% after five cycles of reuse of these nanotubes [136].

- Ionically modified nanoparticles have also been studied for applications in the field of nanoremediation. Magnetic Fe_3O_4 nanoparticles were modified by phosphonium silane, which enhanced their adsorption capacity of Cr(VI) at optimum pH. However, desorption of (CrVI) from these modified nanoparticles using NaOH was poor [137].
- Aminosilicate-functionalised titanium dioxide nanotubes modified with gold nanoparticles supported on EDAS (EDAS/(TiO₂ NTs-Au)_{NCM}) photocatalytically reduce Cr(VI) to Cr(III) (using oxalic acid as electron donor) with 77% efficiency. Light induces interfacial charge transfer from the $(TiO_2 NTs)_{NCM}$ to Cr(VI) through the gold nanoparticles, which act as sinks for the photogenerated electrons [138].
- A similar study was conducted by using chitosan as the polymer instead of polypyrrole, and a removal efficiency of 98% was reported at pH 2 and initial Cr(VI) concentration of 200 mg/l. A cross-linked silica gel/chitosan-g-poly(butyl acrylate) nanocomposite showed a maximum Cr(VI) adsorption capacity of 55.71 mg/g [139]. While bulk iron sulphide (FeS) has been used as a chemical reductant in the remediation of Cr(VI), FeS nanoparticles show higher reactivity due to larger surface area. These nanoparticles can be stabilised using CMC, and biochar can be used as a mechanical support to disperse the nanoparticles. Such a composite adsorbent showed a Cr(VI) adsorption capacity of 130.5 mg/g at a pH of 5.5 [140].

- Nanoparticles can also be applied on membranes used to enhance removal of (CrVI) ions from an aqueous solution. For example, the polysulphone (Psf) membrane is widely used for this purpose. To increase the hydrophilicity of the membrane, it was doped with SiO₂ nanoparticles (PSf/SiO₂), thus enhancing the (CrVI) flux through the membrane [141].

5. Other methods:

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 (CrVI) concentration, pH and current density as well as power consumption were evaluated to determine optimum (CrVI) 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 (CrVI) removal was 100% at the optimum values of 13 mA/cm², 7 and 750 ppm for current density, pH and concentration, respectively [142].
- b. Chemical Coagulation: Ferric chloride produced better results than aluminium sulphate. The COD and (CrVI) 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 (CrVI) 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 [145].

2.Solvent Extraction : The results demonstrated that 99.67% (CrVI)

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% (CrVI) 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 (CrVI) recovery from the (CrVI) (VI) waste solution was 95.40% [8]. 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 [144-145].
- b. Evaporation: Spent (CrVI) liquor was concentrated by evaporation in a triple-effect evaporator. The concentrated liquor was blended with fresh make-up (CrVI) and re-used in tannage. Although the energy cost of the evaporator, the leather produced by this make-up (CrVI) has a normal properties and this is due to the strict control of pH, basicity and salt. [146].

DISCUSSION :

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 labour-intensive [71].

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.

Natural Adsorbent, according to this review, it is concluded that sawdust is the best adsorbent to remove the $(CrVI)(Cr^{6+})$ 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 $(CrVI)(Cr^{6+})$. 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 $(CrVI)(Cr^{6+})$ from the industrial effluent such as tanneries, electroplating industries etc.

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; adsorbent 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 adsorbent 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 maxi- mum efficiency for the desorption process. This result obtained with EDTA can be attributed to the strong complexing ability to Cr(VI). HCl was selected as an effective desorbing agent due to the similar result with EDTA, and low cost of HCl.

The mathematical calculations with reference to Langmuir and Freundlich adsorption isotherm, are the most widely used for adsorption efficiency.

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 (CrVI) 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 reveal to be the most efficient in removing the (CrVI), but still more researches are needed for the regeneration of the absorbents and reuse of the (CrVI).

Nano-technology: In today's society of unstable economy, industries are reluctant to spend adequate money on remediation processes. Industrialists should be made 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 reduces 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 nanoadsorbents.

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

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