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Review Article

# Natural Products and By-Products as a Cost-Effective Adsorbent for Cr (VI) Removal from Water Sources: A Review

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**Abstract**

Management of wastewater in a suitable way is the dire need of today. Wastewater contains varieties of contaminants, which make water toxic and unfit for re-usable. Heavy metals contribute to a large part of water contamination and Chromium (VI) is a major toxic heavy metal which usually found in wastewater. Many synthetic adsorbents such as metal oxides, chelating agents are reported having high adsorption capacity and high removal efficiency, but disposal of such synthetic adsorbents is a problem due to their non-biodegradable nature. This limitation of synthetic adsorbents results in the use of natural products and by products as the adsorbents for removal of Chromium (VI) from wastewater. In past decades a lot of work has been done for water purification especially for the removal of Chromium (VI) metals by utilizing natural products. But all these information is scattered. Herein, an attempt is made to present the scattered information into a systematic way in the form of review article. In this review, hexavalent form of chromium removal by low-cost natural products and by products is summarized.

**Keywords:** Wastewater; Chromium; Metal oxides

## Introduction

Water is very precious component for day today life. Life without water is not possible. No one even think of life without water. It is need of every living creature on earth whatever it is humans, animals or plants. But only water is not sufficient, it should be pure and non-toxic for consumption. Pure water resources are very limited on earth and due to rapid urbanization and industrializations these water resources are getting contaminated at a very fast phase. The main cause of contamination of water bodies are the toxic chemical waste [1]. These chemicals are gotten mixed into water bodies from the municipal and industrial waste. Municipal waste consists of toxic chemicals from beauty products such as face cream, sunscreen, shaving cream, perfumes, hair dyes, etc. Waste from textile, mining, metal plating, fertilizer, steek and battery industries, etc. are main cause for water bodies contamination by industries [2].

Disposal of industrial effluents is the major problem now days [3]. These effluents contaminants the water bodies and make water unfit for use. The industrial waste contains toxic organic and inorganic pollutants [4]. Organic pollutants include dyes, pesticides, antibiotics, phenol, etc [5]. While inorganic pollutants include heavy metals such as chromium (VI) and cadmium (II) [6]. These contaminants are toxic for human health and are carcinogenic in nature. Theses contaminants also affect the physical- biological functional of human and animal body [7].

Chromium is a heavy metal and is a toxic contaminant found in water sources. It exists in two forms trivalent chromium and hexavalent chromium [8]. Both these forms of chromium are found in water and are toxic [4]. However hexavalent form of chromium is more toxic as compare to the trivalent form. Hexavalent form of chromium is very toxic for humans as it causes lungs cancer, nasal perforation etc [9]. Some other significant effects of hexavalent form of chromium on human health are dermatitis, bronchial carcinomas, ulcerations of the skin and mucous membranes, nasal septum perforation, allergic asthmatic responses, gastro-enteritis, hepatocellular deficit, allergic and eczematous skin reactions, and renal oligoanuric deficiency [3].

Sources of chromium in water:

- **Natural sources:** Various iron and aluminum minerals and chromium ores such as crocoites ($PbCrO_4$), chromite ($FeCr_2O_4$) and eskolaite ($Cr_2O_3$)10.

- **Anthropogenic:** Leather and textile industries, Electro paint industries, Chemical industries, metallurgical industries etc [11].

World Health Organization (WHO) sets norms for the potable pure and safe drinking water. WHO sets certain permissible limits for every contaminant in water? These limits are for human health safety. Initially in 1958, WHO sets permissible limits for hexavalent chromium only but later on modified the guidelines for total chromium ion concentration. According to WHO, the permissible limit of chromium for drinking water are 0.05mg/L [12]. Because of its highly toxic nature of chromium, even a very little concentration is very harmful for soil profile, aquatic and animal life and lethal for human health.

### Toxic effects of chromium

Chromium is one of the major hazardous and toxic pollutants




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found in wastewater. Chromium is found in two forms i.e., Cr (III), trivalent form and Cr (VI), hexavalent form. Out of these two forms, Cr (III) is considered as less toxic while Cr (VI) is considered as highly toxic for all living beings. It is due to the high oxidation potential and high solubility of hexavalent chromium ion. Naturally, Cr (VI) is found as chromites in rocks and other natural complexes. Other sources of Chromium (VI) are industries such as tanning industries, electroplating industries, textile industries, pulp and paper processing industries, etc [13].

### Techniques available for Cr removal

Wide numbers of advanced techniques are reported and available for the removal of Chromium from wastewater such as ion exchange, reverse osmosis, electrochemical processing, adsorption, membrane filtration, chemical precipitation, redox and photocatalysis process, etc [14]. Each of these techniques has some pros and cons. Some common limitations of these techniques are high cost, low removal rate, toxic to environment and high sludge production, etc [15]. Because of these limitations, these techniques are not fit for industrial use. Out of these techniques, because of its low cost and ecofriendly nature, adsorption best fitted to industries for the removal of Chromium from wastewater and taking natural products and by products are the most conventional adsorbents for industries to remove Chromium from wastewater [16].

## Natural Adsorbents

Natural products and by products are present on entire globe and can be used for adsorbents for the removal of hexavalent form of Chromium from the wastewater [17]. These products are in abundant in nature in the form of agricultural waste, products from different types of wild trees and plants, etc. Due to the vast availability of these products, they are cheap and also eco-friendly in nature [18]. So, these products and be employed as low-cost and eco-friendly adsorbents for the uptake of hexavalent form of Chromium from wastewater. These products are rich in cellulose, lignin and other various types of functional groups which help them to make interaction with hexavalent form of Chromium and hence show good adsorption potential.

### Corn cobs

Corn plant is also known as mass cane, is exceptionally easy to grow. It has a strong, woody stem with clusters of strappy dark green leaves with a lime-green stripe running down the middle [19]. The advantage of this natural product is its low cost and high efficiency for Cr (VI) adsorption as compare to other natural and synthetic adsorbents. S.M. Ali et al. have studied the removal of Cr (VI) by corn cobs. Different parameters like pH and contact time were studied and it is found that the maximum removal efficiency 95.05% of Cr (VI) is obtained at pH of 5.4 and contact time 4.18hrs. Further increase or decrease in pH result in the decrease in % removal of Cr (VI) by adsorbent.

### Leaves powder of herbal plants

Powders of leaves of some herbal plants like Mentha, *Achyranthes aspera*, *Hybiscus roja sinensis*, *Emblica officinalis*, *Azadirachta indica*, *Ocimum sanctum* etc. have great tendency to adsorb Cr (VI). V. Krishna Veni and K. Ravindhranath has studied the uptake of Cr (VI) from waste water by leaves powder of herbal plants [20]. The study contains different physiochemical parameters like pH, contact time and sorbent concentration and it is found that maximum removal of 97.1% with leaves powder of Achyranthes aspera at pH 2, contact time 4hrs and sorbent concentration of 2g/L. It is observed that with increase in pH of solution % Removal of Cr (VI) decreases.

### Custard apple peel powder

Custard apple is a fruit grows on the *Annona reticulata* tree. The peel of Custard apple is a potential adsorbent for Cr (VI) removal from contaminated water. It becomes an important adsorbent because of its low lost and easily availability [21]. The extensive study of removal of Cr (VI) from aqueous solution by custard apple peel powder is done by D. Krishnaa and R. Padma Sree [15]. The study contains the effect of pH, contact time and adsorbent concentration. The maximum 90.47% removal of Cr (VI) is obtained when pH of solution is maintained at 3 with 120min of contact time and adsorbent dosage of 0.4g for 10ppm solution of Cr (VI). Also % removal decrease with increase of pH. For these studies different isotherm studies are done and characterizations techniques are performed to validate the results.

### Neem leaf powder

Neem is a tree with scientific name Azadirachta indica. Leaves of neem acts as a good adsorbent with high efficiency for Cr (VI) removal. The main advantage of this adsorbent is that it is easily available as neem is a common tree which makes it very low-cost adsorbent [22]. Bisorption of Cr (VI) from waste water using neem leaf powder as an adsorbent is studied by S. Gopalakrishnan et al. There work describes various physiochemical parameters which effect the % removal of Cr (VI). These parameters are agitation time, temperature, adsorbent dosage and initial Cr (VI) concentration. After adsorption isotherm and other studies, it is found that 100% removal of Cr (VI) from 200ppm Cr (VI) solution by neem leaf occurs when adsorbent dose is 1gm at 29°C and equilibrium agitation time is 180min. and % removal decrease with increase in the temperature and initial concentration of Cr (VI) in solution.

### Coffee husk

Coffee plants are grown nearly in 70 countries and during the processing of coffee from plant a significant amount of agriculture waste is generated, called Coffee husk and this made coffee husk cheap and easily available. Coffee husk has the potential to adsorb the Cr (VI) from waste water and act as a good and efficient adsorbent. The uptake of Cr (VI) by coffee husk largely depends on the pH, contact time, initial concentration and adsorbent dosages [23]. Adsorption isotherm studies is performed to determine the effect of all physiochemical parameters and it was noticed that maximum % removal obtained is 99% at the optimum pH condition of 2 and % removal decreases as the pH of solution is increased. It is also observed that % removal increases with increase in the contact time and the adsorbent dosages. For 50ppm solution of Cr (VI) the maximum removal of Cr (VI) occurs at the contact time of 180min. and 3g of adsorbent dosages.

### Activated coconut shell

Coconut is fruit used for a varsity of purposes ranging from food to cosmetics. Coconut can be also used for the remediation of contaminated water as Coconut shell is a potential adsorbent for the

**Table 1:** Reported natural products and by products for removal of Cr (VI) ion.

| Adsorbent | % Removal of Cr (VI) | Optimum pH | Contact time | Adsorbent dosages | References |
|---|---|---|---|---|---|
| Corn cobs | 95.05% | 5.2 | 4.18hrs | - | [29] |
| Leaves powder of herbal plants | 97.10% | 2 | 4hrs | 2g for 500ppm solution | [32] |
| Custard apple peel | 90.47% | 3 | 2hrs | 0.4g for 10ppm solution | [33] |
| Neem leaf | 100% | - | 3hrs | 1g for 200ppm solution | [22] |
| Coffee husk | 99% | 2 | 3hrs | 3g for 50ppm solution | [23] |
| Activated coconut shell | 88% | 2 | 1hrs | - | [34] |
| Multani mitti | 98% | 3 | 0.33hrs | 0.8g for 85ppm solution | [3] |
| Dolochar | 100% | 2 | 1hr | 25g for 10ppm solution | [26] |
| Eucalyptus bark | 99% | 2 | 2hrs | - | [27] |
| Oat biomass | 100% | 1 | 8hrs | 1g for 100ppm solution | [35] |

removal of Cr (VI) from water sources [24]. Abundant availability of coconut waste makes it cheaper and conventional adsorbent as compare to activated carbon for public and private sector. Through the detail studies of different parameters, it is found that for 10ppm Cr (VI) solution 88% removal of Cr (VI) is observed after 60min. of contact time at optimum pH 2 and as pH is increased from 2 to 12 the % removal of Cr (VI) decreases [21]. Absorption efficiency of coconut shell is explained on the basis of adsorption isotherm studies. Also, coconut coir can be also used as a potential adsorbent for Cr (VI) removal.

### Multani mitti

Multani Mitti is a type of clay commonly known as Fuller's earth. It has ability to decolorize oil without any chemical reaction. It also has great efficiency to uptake hexavalent form of chromium from contaminated water. Uptake of Cr (VI) from water using Multani Mitti as an natural adsorbent is a very low-cost adsorption technique which can be used at both small and large scale [25]. The removal efficiency of Multani Mitti for Cr (VI) is very high which make it a significant adsorbent. For increasing the % removal of Cr (VI) different physiochemical parameters like pH, adsorbent dosages, contact time etc. are optimized and it is observed that for 85ppm solution, 98% removal can be attained by 0.8g of adsorbent dosages at the optimum pH of 3 after 20min. of contact time. Through the kinetic study is cleared that adsorption process follows the pseudo second order kinetic model.

### Dolochar

Dolochar is a coal waste produced in significant quantity during the production of sponge iron. This waste can be utilized in a better way in water treatment. Dolochar can be employed as a potential adsorbent for Cr (VI) uptake from water as it has high adsorption efficiency for Cr (VI) [26]. As it is a waste produced during sponge iron production, which makes it very economical adsorbent. Adsorption studies are done which shows that dolochar can show 100% Cr (VI) removal from 10ppm Cr (VI) solution when 25g of adsorbent dosage are used for contact time of 60min. at the optimum pH 2 at 30˚C. Further increase in pH results in the decrease of % removal and all these studies are supported by pseudo second order kinetic.

### Eucalyptus bark

**Eucalyptus plant mainly found in Australia:** All Australian forests are mainly consisting of Eucalyptus plants. These plants shed their barks. Eucalyptus bark has great adsorption efficiency for Cr (VI). It can be used as an economical adsorbent because of its easily availability and low cost. Its adsorption studies tell that for 200ppm solution 99% uptake of Cr (VI) is observed at the optimum pH 2 and 2hrs. of contact time [27]. It is also noticed that on increasing the adsorbent dosages % removal increases and on increasing pH from 2 to 12 % removal decreases. The kinetics studies show that the adsorption follows the first order kinetics.

## Adsorption Parameters

There are several factors which affect the adsorption of Chromium from wastewater. Some of these parameters are initial Chromium concentration in wastewater, contact time, pH of wastewater, adsorbent dosages, kinetic and isotherm model etc [28]. These parameters tell us about the rate of adsorption; time taken for complete adsorption, at what pH maximum adsorption occurs, what should be the optimum amount of adsorbent should be taken for maximum adsorption and up to what concentration of Chromium can be removed significantly from the contaminated wastewater.

Isotherm parameters such as Langmuir [29] and Freundlich parameters talks about the mechanism of adsorption reaction, where adsorption occurs in single layer or multi-layered. Langmuir model suggest that single-layered adsorption of chromium on the adsorbent while Freundlich suggests that adsorption of chromium occurs in the multi-layered form. These isotherms also give the brief description about the interaction between chromium ions and adsorbent, whether adsorption is physisorption or chemisorption [30]. Physisorption is about the only physical interaction between Chromium ions with adsorbent while Chemisorption tells that there is a chemical interaction between Chromium ions and adsorbent.

Kinetic parameters such as Pseudo-first order and Pseudo-first order describe the rate of adsorption process i.e., whether adsorption rate is fast or slow [31].

## Limitation and Future Work

The effectiveness of the biosorption method for environmental remediation utilizing agricultural waste materials has been thoroughly examined. Despite the fact that there have been several studies on the issue, the practicality of employing natural waste is still confined to the laboratory scale. It summarizes some of the issues surrounding the application of natural products and their waste for the uptake of toxic pollutants, as well as future research opportunities. The kind, features (lignin, hemicellulose, cellulose, wax content), and chemical characteristics of natural waste derived adsorbents vary (porosity, water retention, rate of crystallinity, ability to mold, tensile strength, surface area, adsorption capacity, specific functional groups, etc.). Adsorbents produced from natural species have been discovered as possible water remediation agents. However, the use of these natural materials in particular, as well as their waste in general, will highly be influenced by factors such as climate, weather conditions, location, and so on. Hence, in future detailed and advanced studies are required to understand the adsorption behaviors of natural products and their waste for the removal of toxic contaminants from wastewater. The adsorption capacities of natural products can be enhanced by activating them with functional groups.

## Conclusion

Industrial waste from textile and tanneries contains a large amount of toxic chemicals which are of great concern for human and animal health. Cr (VI) form of Chromium is lethal form which is usually found in water. There are many reported processes for the removal of Cr (VI) form of Chromium but due to their certain limitations such as high cost and non-eco-friendly limits their use for the remediation of contaminated wastewater generated by the municipal and industries. To overcome these limitations, we have tried to review the adsorption process for the treatment of industrial wastewater. We have collected the previously reported information about the adsorption process for the treatment of wastewater and tried to present that information into a simpler and systematic way. Herein, we have reviewed natural products and by products as a low-cost eco-friendly adsorbent for the uptake of hexavalent form of Chromium from contaminated wastewater. The Cr (VI) can be removed conventionally and economically by adsorption techniques. 99%-100% removal of Cr (VI) can be achieved using low-cost, highly efficient Natural products and By-products based adsorbents. The maximum % removal depends upon certain parameters such as pH of the wastewater, time for which adsorbent is added to wastewater for treatment, adsorbent dosages added to wastewater, initial Cr (VI) concentration in solution etc. Generally, % removal increases with increasing adsorbent dosages and decreases with increasing initial Cr (VI) concentration in solution. Also, it has been observed that maximum removal of Cr (VI) occurs at lower pH.

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