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# A Review on Chromium (VI) Removal Using Low Cost Biowaste Materials

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**ABSTRACT**
Industrial effluents contain heavy metal ions like cadmium(II), chromium(VI), mercury(II), lead(II)  etc leads to detrimental effects. Besides polluting the water, they affect the aquatic ecosystem and cause disorders in humans. Treatment of polluted water is imminent since water is a finite resource. Adsorption technique is a widely used treatment process in which activated carbon is used as the adsorbent. The necessity for efficient and economical methods for the elimination of these discharged toxic metal ions   has directed studies towards the production of low cost alternatives to commercial activated carbons. Agro waste materials which are discarded could be considered as the alternatives. This paper presents a review of the available literature using biowastes for the removal of chromium(VI) heavy metal ion  from aqueous solution.
*Keywords*- **Heavy metal ions, Cr(VI),  activated carbon, biowastes, batch studies**

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## I.   INTRODUCTION

Water resources are used for various purposes including direct consumption, domestic use, irrigation, fisheries, recreation, navigation, livestock, mining, hydropower and other industries. Water is highly abundant in the natural hydrological cycle. The sources of water are  surface water and ground water.  Accumulation of heavy metal ions in the water due to industrialization which has become a global concern due to their adverse effects. Chromium is a transition element of atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. Chromium was discovered in 1797 by the French chemist Louis Vauquelin. It was named chromium (Greek Chroma, 'color') because of many different colors found in its compounds. Chromium is the Earth's 21st most abundant element (about 122 ppm) and the sixth most abundant transition metal. The principal chromium is ferric chromite, $FeCr_2O_4$ , found mainly in South Africa (with 96% of the world's reserves), Russia, and the Philippines. Less common sources include crocoite, $PbCrO_4$ and chrome ochre, $Cr_2O_3$. The gem stones emerald and ruby owe their colors to traces of chromium[1]. Chromium is present in the environment in several different forms. The most common forms are chromium(0), chromium(III), and chromium(VI). Chromium(III) occurs naturally in the environment and is an essential nutrient. Chromium(VI) and chromium(0) are generally produced by industrial processes. The metal chromium, which is the chromium(0) form, is used for making steel. Chromium(VI) and chromium(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. Cr(VI) is mobile in the environment and is highly toxic. Cr(VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases.  At short-term exposure levels above the maximum contaminant level, Cr(VI) causes skin and stomach irritation or ulceration. Long-term exposure at levels above maximum contaminant can cause dermatitis, damage to liver, kidney circulation, nerve tissue damage, and death in large doses[2]. In the industrialized world, the use of chromium in industries like electroplating, textile, leather tanning, metallurgical metal finishing, photography, dye manufacturing, ink and pigments, power generation, and chemical manufacturing etc., is extensive and hence it is not uncommon for the aqueous effluents from such industrial plants to have high amounts of chromium[3]. Hence it is highly imperative to remove Cr(VI) from the aqueous solution.

There are many conventional techniques currently in use for remediation of Cr(VI) from industrial effluents. These processes mainly involve immobilisation of Cr(VI) and/or reduction of toxic Cr(VI) to the less-toxic Cr(III). The latter can be achieved chemically by means of a variety of sulphur or iron-based compounds, such as Fe(II) , amorphous $FeS_2$, calcium polysulphide, sodium

thiosulphate and many more. The major disadvantage of chemical reduction is the generation of a huge amount of toxic sludge. 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]

Adsorption is one of the most widely used treatment strategy, highly useful for the removal of both organics and inorganics from water and wastewater. It is a process by which the concentration of solute is enriched at the surface of the adsorbent. Adsorption using activated carbon includes a broad range of carbonaceous materials that exhibit a high degree of porosity and large surface area and find widespread use for the removal of toxic biodegradable and non-biodegradable substances from wastewater. It can treat wastewater to acceptable quality suitable for reuse. Despite the prolific use of the commercial activated carbon for water and wastewater treatment, carbon adsorption remained an expensive treatment process. This has prompted the researchers for a growing interest for the production of low cost activated carbon from other carbonaceous precursors. Much emphasis has been placed on the last two decades on agricultural wastes as source of carbon with a view to bringing about a significant cost reduction in the treatment of water and wastewater. Both industrial and agricultural wastes have been examined as sources for the preparation of low cost activated carbons.

A number of studies on chromium(VI) removal using activated carbon have been reported. This review presents a study of biosorbents used, concentration of the adsorbate, the mode of study, instrument , effect of various parameters for the removal of Cr(VI) from aqueous solution. Table 1 presents a comparative study of the selected literature dealing with the removal of chromium(VI) by adsorption using biowastes.

## II. LITERATURE REVIEW

**Table 1. Comparative study of the selected literature dealing with the removal of chromium(VI) using a variety of biowastes**

| Reference | Wastewater | Adsorbent | Mode of study | Initial concentration of adsorbate Cr(VI) | PH range | Dosage | Temperature | Contact time | Adsorption capacity |
|---|---|---|---|---|---|---|---|---|---|
| Chitra K et al (2014) [5] | Synthetic wastewater solution of $K_2Cr_2O_7$ | Carica papaya seeds | Batch | 10-50 ppm | 2-10 Optimum pH 2 | 0.05–1 g/100 mL | 303, 313 and 323 K | 0–150 min | 5.85 mg/g |
| Maninder Singh et al (2020) [6] | Synthetic aqueous solution of $K_2Cr_2O_7$ | water chest nut (Trapa natans) peel | Batch | 20-100 mg/L | 2-12 Optimum pH 7 | 0.2 to 1.0 g | 20, 30, 40, 50, 60 and 70 °C | 60-300 min | 59.17 mg/g |
| Yilleng M. T et al(2013) [7] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Canaruim schweinfurthii Seed Shell | Batch | 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L | 4±2 Optimum pH 4 | 60mg | Room temperature | 1 hour | 0.792mg/g |
| Adeyinka S. Yusuff (2019) [8] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Leucaena leucocephala seed pod | Batch | 50–250 mg/L | 2-10 Optimum pH 6 | 0.2–1.0 g | 25–45 $^0$C | 20–100 min | 26.94 mg/g |
| M.K. Rai et al (2016) [9] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Mango kernel | Batch | 20 to 80 mg/L | 2–8 Optimum pH 2 | 0.25 to 1 g | 35 °C | upto 250 min | 7.8 mg/g |
| Samson O. Owalude (2016) [10] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Ground nut hull | Batch | $6.0 \times 10^{-5}$ M, $1.2 \times 10^{-4}$ M, $1.8 \times 10^{-4}$ M, $2.5 \times 10^{-4}$ M $3.20 \times 10^{-4}$ and | 1 -8 Optimum pH 2 | 10 to 50mg. | Between 30 and 70 °C | upto 300 min | 131 mg/g |

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| | | | | $4.5 \times 10^{-4}$M | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Tamirat Dula et al (2014)[11] | Synthetic aqueous solution of $K_2Cr_2O_7$ | bamboo (Oxytenanthera abyssinica) | Batch | 25 to 150 mg/L | 2-8 Optimum pH 2 | 0.1 to 0.3 g | 298 K, 300 K, 308 K, 318 K | 3–120 min | 59.23 mg/g |
| K. Kavitha et al (2014)[12] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Vitex Negundo Stem | Batch | 50, to 125 mg/L | 3–9 Optimum pH 6.5 | 0.1 to 0.25 g/50 mL | 303K to 333K | 10 to 60 min | 207.88 mg/g |
| Radia Labied et al (2018)[13] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Ziziphus jujuba cores | Batch | 50–500 mg/L | 1-6 Optimum pH 2 | 0.5–3 g/L | 20–40$^0$C | upto 400 min | 196.38mg/g |
| R. Gayathri et al(2013)[14] | Synthetic aqueous solution of $K_2Cr_2O_7$ | Tamarind seeds | Batch | 200 mg/L to 700 mg/L | 2-10 Optimum pH2 | 2g-10g/L | 30 to 50$^0$C | 30 min to 240 min | 29.41 mg/g |

## 2.1 GENERAL METHODS IN EXPERIMENTAL STUDY

The adsorbents taken were agro based locally available biowastes . They were washed several times with distilled water, heated to required temperature, dried, and ground to desired size. Activation was done with chemicals like con.$H_2SO_4$[6, 14] , $ZnCl_2$ and $H_3PO_4$ [7], NaOH [8] ] in order to remove volatile impurities and further activation with oxidising chemicals like $H_3PO_4$ [9], pyromellitic dianhydride [10], potassium hydroxide [11], rubidium carbonate [13]. After chemical activation or carbonization the adsorbents were washed well with distilled water, crushed, dried, sieved and stored and was used for adsorption study.

The researchers used synthetic aqueous solution of $K_2Cr_2O_7$ to prepare adsorbate solution. The synthetic stock solutions of chromium(VI) were prepared by dissolving chromium compounds of analytical grade in distilled water and the dilution is done accordingly.

Most researchers analysed the effect of characteristics of activated carbon like bulk density, moisture, dry matter, ash content , % yield carbon. The textural characteristics of the prepared activated carbon including specific surface area, pore volume and pore diameter were determined by the Brunauer, Emmett, and Teller (BET) method. The morphological characteristics were investigated through scanning electron microscope (SEM). More information about the nature of the functional groups are obtained using FTIR analysis.

Batch studies were made at ambient temperature with the known amount of synthetic chromium(VI) solution. The reaction mixture was placed in stoppered flasks and agitated in rotary shakers. The effect of various parameters like initial concentration, pH, adsorbent dosage, temperature and contact time were studied. The effects were studied by keeping the other parameters constant.

The concentration of chromium ions in the solution was analyzed using UV-Visible spectrophotometer or Atomic Absorption Spectrophotometer The removal of hexavalent chromium solution was calculated in terms of percentage removal.

The percentage removal of hexavalent chromium solution was calculated by using the following equation:

$$\% \, \text{Adsorption} = (C_0 - C_e)/\, C_0 \times 100$$

(1)

where $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations of hexavalent chromium ion in solutions.

## 2.2 OBSERVATIONS IN BATCH STUDY

Promising results have been obtained by the researchers in the batch studies.

### 2.2.1 Effect of PH

Adsorption depends on the pH of the solution. The literature review has shown that pH of 2 is mostly used as the optimum pH. The other pH are 4, 6.5 and 7 and negligible over 8. The reason for the higher adsorption of Cr (VI) at low pH may be due to the presence of the dominant species like negatively charged [HCrO$_4$] $^-$, [Cr$_2$O$_7$] $^{2-}$, [Cr$_4$O$_{13}$] $^{2-}$ and [Cr$_3$O$_{10}$] $^{2-}$ ions under such conditions. The negatively charged ion species are thus adsorbed on the positively charged active sites on the sorbent. It was the HCrO$_4$ $^-$ form of Cr (VI), which was the predominant species at this pH that adsorbed preferentially upon the biosorbent [5]

Higher Percentage removal of Cr(VI) at pH value 7 may have happened because at low pH hydrogen ion competes with Cr(VI) ions and

occupied adsorption sites. But at neutral pH 7, there is negligible competition of hydrogen ions due to which availability of sites for binding with Cr(VI) ions to the adsorbent is more. Attraction between the adsorbate and the adsorbent is because of the electrostatic interaction which is the main driving force for the adsorption of the metal ions that is stronger the interaction higher the adsorption[6].

### 2.2.2 Effect of initial concentration

It has been observed that the adsorption decreases with the increase in the initial concentration of the adsorbate.. It was due to the presence of the same active centres on the surface despite the increase in the initial adsorbate concentration which leads to the saturation of the active centres on the adsorbent[8]

### 2.2.3 Effect of contact time

Adsorption of Cr(VI) ion increased with rise in contact time till equilibrium was reached. Further increase in contact time did not increase the Cr(VI) adsorption process. . In the beginning all the active sites on the adsorbent are vacant hence adsorption proceeds at a faster rate and desorption at a lower rate, the net effect is faster increase in the extent of adsorption. As the active sites get occupied, the rates of adsorption and desorption tend to be equal and extent of adsorption reduces and eventually becomes nearly constant at equilibrium. Any further adsorption beyond this is through intra-particle diffusion which is a much slower process[9]

### 2.2.4 Effect of adsorbent dose

The extent of adsorption increased with increase in adsorbent dosage and then remained constant. Removal percentage of Cr (VI) increases as the biosorbent amount increases and then becomes constant. This increase in the efficiency of removal of metal ions with an increase in the biosorbent dosage may be due to the increase in the number of adsorption sites and increased adsorbent surface area for complexation of metal ions resulting in higher removal of metal ions at higher concentration levels. At high sorbent dose no significant improvement in adsorption was seen, this may be due to the binding of all ions to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining unadsorbed in the solution[5].

### 2.2.5 Effect of temperature

It has been observed that at ambient temperature appreciable rate of removal can be achieved. Variation in rate of removal with increase or decrease has been reported. The rise of adsorption capacity with temperature was due to the increase in kinetic energy of adsorbent particles. Thus the collision frequency between adsorbent and adsorbate increases, which results in the enhanced adsorption onto the surface of the adsorbent. Secondly, at high temperature due to bond rupture of functional groups on adsorbent surface increases active adsorption sites, which may also lead to enhanced adsorption[11]. In some cases the adsorption capacity decreased with increase in temperature suggesting that the adsorption process was exothermic[10].

### 2.2.6 Adsorption isotherm studies

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. Two isotherm equations have been used in the studies mostly namely Langmuir and Freundlich. Langmuir adsorption isotherm fitted the data better in most studies. In addition some have studied Dubinin - Radushkevich and Temkin adsorption isotherms.

Freundlich equation is

$$x/m = kC_e^{1/n}$$

(2)

where x = amount of solute adsorbed in mg/L

m = the weight of the adsorbent in g/L

$C_e$ = equilibrium concentration of the solute in mg/L

k, 1/n = constants characteristics of the system and are the measures of adsorption capacity in mg/g and intensity of adsorption in L/mg.

Langmuir isotherm equation is

$$C_e/q_e = 1/Q_o b + C_e/Q_o$$

(3)

where $C_e$ = equilibrium concentration in mg/L

$q_e$ = the amount adsorbed at equilibrium in mg/g

$Q_o$ and b= Langmuir constants related to adsorption capacity in mg/g and energy of

adsorption in L/mg

The Temkin equation is

$$q_e = a_t + 2.3b_t \log C_e$$

(4)

where $q_e$ = the amount adsorbed at equilibrium in mg/g

$C_e$ = equilibrium concentration in mg/L

$a_t$ and $b_t$ = Temkin isotherm constants related to adsorption capacity in mg/g and intensity . of adsorption in L/mg respectively.

### 2.2.7 Kinetic studies

Adsorption kinetic parameters were determined following the pseudo-first-order, pseudo-second-order models. Close agreement between experimental and calculated kinetic constants and coefficient of correlation close to unity indicated that the pseudo second order model better represents the experimental data in most of the cases.

The pseudo first order rate equation of Lagergren is

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

(5)

where $q_e$ = the amount of metal ions adsorbed at equilibrium (mg/g)

$q_t$ = the amount of metal ions adsorbed at time t (mg/g)

t = time (min)

$k_1$ = pseudo first order equilibrium rate constant (1/min)

The pseudo-second-order model rate equation is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(6)

where $q_e$ = the amount of metal ions adsorbed at equilibrium (mg/g)

$q_t$ = the amount of metal ions adsorbed at time t (mg/g)

t = time (min)

$k_2$ = pseudo second order adsorption rate constant (g/mg/min)

### 2.2.8 Desorption studies

In order to assess the reusability of the adsorbents ,the desorption studies were conducted by some researchers. Experiments were done upto 3 cycles. NaOH was used for desorption

## III. CONCLUSION

From the above analysis the review has established that removal of chromium(VI) from bio wastes is easy process, cost effective, requires less time and provides satisfactory results. It also addresses the uses of local biowaste resources. So at various locations and scales worldwide the local biowastes could be used for the removal of chromium(VI) from aqueous solution. From the study it is implied that more application of regenerating agents as well as their desorption efficiency is necessary to ascertain the reusability of the adsorbents due to the prevailing world environmental needs.

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