



## The Removal of Chromium from Waste Water Using Agricultural wastes as Adsorbents -A Review

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### ABSTRACT

The hexavalent chromium present in waste water has adverse affect on aquatic life and humans. Various methods are available for the removal of hexavalent chromium includes chemical precipitation, ion exchange, reduction, electrochemical precipitation, solvent extraction, membrane separation, evaporation, foam separation and biosorption. Among these, biosorption is one of the low cost separation technique for the removal of chromium using agricultural waste as adsorbents which are cheap and readily available and also has the advantage of practical replacement to conventional processes. The kinetic models and adsorption isotherms for the efficient removal of hexavalent chromium are presented from various sources. The present review elaborate the findings of hexavalent chromium removal with the maximum metal uptake, adsorption parameters using agricultural wastes as adsorbents.

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### 1. Introduction

Effluent released from process industries such as petroleum refining, steel industries, paint industries, leather tanning, electroplating, textile industries, etc, causes water contamination with heavy metals in all over world [1-3]. Several millions of tons of chromite ore are produced in a year, all over world. Direct reduction of the chromite ore is the source for production of ferrochromite. The chemical reduction (the aluminothermic process) or by electrolysis of either  $\text{CrO}_3$  or chrome alum solutions is the source for production of chromium metal. The chromium prevails in aqueous phase in two oxidation states, i.e. trivalent chromium ( $\text{Cr}^{+3}$  and  $\text{Cr}(\text{OH})^{2+}$ ) and hexavalent chromium ( $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$ , etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic to humans. [4-6]. Chrome plating, the result of which is often referred to simply as chrome is a technique of electroplating a thin layer of chromium on to a metal [7].

Cr (VI) has 100 times more toxicity than Cr (III) because of it has the nature of water solubility, mobility and easy reduction [8]. The toxic effect of Cr (VI) is due to oxidizing nature and the formation of free radicals, resulting from the reduction of Cr (VI) to Cr (III) occurring inside the cell [9-10]. According to World Health Organization (WHO), it is recommended that the toxic limits of chromium (VI) in waste water is at the level of 0.05mg/l [8].

Hexavalent chromium has adverse effect on growth parameters of plants by accumulation on it[11-14]; it may transfer to the living organisms through food chain. Various experiments revealed that the toxicity of chromium picolinate in renal impairment, skin blisters and pustules, anemia, hemolysis, tissue edema, liver dysfunction, neural cell injury, impaired cognitive, perceptual and motor activity, enhanced production of hydroxyl radicals, chromosomal aberration,

depletion of antioxidant enzymes and DNA damage in mice [15].

Several methods used for the removal chromium from the wastewater includes reduction followed by chemical precipitation [16], ion exchange [17], reduction [18], electrochemical precipitation [19], solvent extraction [20], membrane separation [21], evaporation [22] and foam separation [23]. The two steps present in chemical precipitation method includes the reduction of Cr (VI) under acidic conditions, followed by the precipitation of Cr (III) hydroxide. the sulfur dioxide, sodium sulfite, sodium bisulfate and ferrous sulfate are generally used as reducing agents. An ion exchange works on the basic principle of exchanging either cations or anions from the surrounding materials. The removal efficacy of electrochemical precipitation method is greater than 99% but the major drawback is the consumption of electrical power. In solvent extraction of chromium, several ion-association systems were employed such as triphenylsulfonium, ammonium, triphenylphosphonium, tetraphenylstibonium and triphenylselenium cations [24]. Foam separation is a process in which solute substances adsorb at the gas-liquid interface between a dispersed phase and a liquid phase[25].

Above cited conventional chromium elimination processes are ineffective for diluted solutions. In recent years, much focus is given on biosorption using readily available biomass for the removal of heavy metals. This process can be used in economic way for purifying the industrial waste water whereby drinking water quality can be improved and impact on animals, aquatic species and humans may be reduced. A considerable research was carried out by various researchers using bio-adsorbent materials for the removal of heavy metals from industrial effluents. Since this noble approach is effective and cheap, many researchers have been investigating the

various kinds of biomaterials that effectively remove Cr (VI) from aqueous solutions. These materials are identified as adsorbents and the binding of metals by biomass is referred to as biosorption.

In this article, there are two approaches regarding the nature of adsorbents. One is conventional adsorbents and another is non-conventional adsorbents. The major advantages of non-conventional adsorbents over the conventional adsorbents include easy available source, low cost, high effectiveness, ecofriendly, minimum waste disposal, etc. On this basis it is reviewed the literature of collection and analysis of data on hexavalent chromium (VI).

## 2. Biosorbent materials

A large number of materials have been investigated as biosorbent for hexavalent chromium removal. A fundamentally important characteristic of good adsorbents [26, 27] is their high porosity and consequent larger surface area with more specific adsorption sites. Most adsorbents which have been used in pollution control have porous structure. The porous structure not only increases surface area and consecutively adsorption but also the kinetics of the adsorption. Some of the important adsorbents used in pollution control and various industrial operations are discussed herein.

### 2.1 Naturally occurring materials/Agricultural materials as adsorbents

Various naturally occurring materials used as adsorbents are available in large quantities. The abundance of these materials in most continents of the world and their low cost make them suitable as adsorbents for the removal of chromium from wastewaters. Wood is the most widely spread natural material and its use as adsorbent for the removal of chromium. The drawback of this adsorbent was the long equilibration time required for adsorption and low adsorption capacity.

Timber industry generates bark a by-product that is effective because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate [28]. The adsorption capacities of various adsorbents such as sawdust, redwood bark, walnut hull, groundnut hull etc is shown in Table 1.

## 3. Modeling of adsorption

Mathematical models can describe the behavior of the biosorption processes operating under different experimental conditions. They are very useful for scale up studies or process optimization. A number of models with varying degrees of complexity have been developed to describe the metal biosorption systems. These are of two types: kinetic models and equilibrium models.

### 3.1. Kinetic models

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ( $r^2$  values close or equal to one). A relatively high  $r^2$  value indicates that the model successfully describes the kinetic of Cr (VI) adsorption.

#### 3.1.1 Pseudo-first order or lagrange kinetic model

It is the first equation for sorption [53, 54] of liquid/solid system based on solid capacity. The pseudo first order equation is generally expressed as

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

Here  $q_e$  and  $q_t$  are the adsorption capacities at equilibrium and at time  $t$ , respectively (mg/g) and  $k_1$  is the rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ). Eq (1) can be arranged to obtain the more useful form

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (2)$$

The values of  $\log(q_e - q_t)$  were linearly correlated with  $t$ . The plot of  $\log(q_e - q_t)$  vs  $t$  should give a linear relationship from which  $k_1$  can be for determined from the slope. Eq (2) differs from a true first order equation in two ways: (i) the parameter  $k_1(q_e - q_t)$  does not represent the number of available sites, and (ii) the parameter  $\log q_e$  is the adjustable parameter and often it is found not equal to the intercept of the plot of  $\log(q_e - q_t)$  vs  $t$  where as in a true first order  $\log q_e$  should be equal to the intercept.

**Table 1. Reported adsorption capacities (mg/g) for agriculture products as adsorbents.**

Material used	Metal uptake, mg/g	Isotherms it follows	Kinetics it follows	References
Almond shell	3.40	Langmuir, Freundlich	----	[29]
Wall nut	8.01	Langmuir, Freundlich	----	[29]
Activated tamarind seeds	29.7	Langmuir, Freundlich, Tempkin, D-R-Model, R-P-Model	2 <sup>nd</sup> order	[30]
Hazel nut	8.28	Langmuir, Freundlich	----	[29]
Brazilian pine fruit wastes	240	Sips model	Elovich, 2 <sup>nd</sup> order	[31]
Bael fruit shell	17.27	Langmuir, Freundlich	2 <sup>nd</sup> order	[32]
Coir pith	317.65	Langmuir	----	[33]
Groundnut husk carbon	7.0	Freundlich	---	[34]
Hazelnut shell	17.7	Langmuir, Freundlich	---	[35]
Coconut coir pith	76.3	Langmuir,	2 <sup>nd</sup> order,	[36]

		Freundlich D.R.Model	Elovich	
Maize bran	312.52	Langmuir	2 <sup>nd</sup> order	[37]
Rice bran	312.5	Langmuir, Freundlich	1 <sup>st</sup> order	[38]
Rice husk	10.4	Freundlich, D-R-Model	----	[39]
Saw dust	41.5	Langmuir	2 <sup>nd</sup> order	[40]
Borassus flabellifer coir powder	3.7473	Freundlich	2 <sup>nd</sup> order	[41]
Carrot residue	45.09(Cr(III))	Langmuir, Freundlich	---	[42]
walnut hull	98.13	Langmuir, Freundlich	1 <sup>st</sup> order	[43]
Ground nut hull	30.95(a)	Langmuir, Freundlich	2 <sup>nd</sup> order	[44]
Pistachio hull powder	116.3	Langmuir	2 <sup>nd</sup> order	[45]
Indian gooseberry seed powder	38.46	Langmuir, Freundlich	2 <sup>nd</sup> order	[46]
Limonia acidissima hull powder	20.408	Langmuir . Freundlich	1 <sup>st</sup> order 2 <sup>nd</sup> order	[47]
Ragi husk powder	43.478	Langmuir . Freundlich	1 <sup>st</sup> order 2 <sup>nd</sup> order	[48]
Custard apple peel powder	7.874	Langmuir Freundlich	2 <sup>nd</sup> order	[49]
Mangrove leaves	5.724	Langmuir, Freundlich	2n order	[50]
Reed mat	1.662	Langmuir, Freundlich	2n order	[50]
Green taro	1.418	Langmuir, Freundlich	2n order	[50]
Alligator weed	82.57	Langmuir , Freundlich, Tempkin	2 <sup>nd</sup> order Elovich	[51]
Saw dust	20.70	Langmuir , Freundlich	2 <sup>nd</sup> order I-P-Diffusion model	[52]
Neem bark	19.60	Langmuir , Freundlich	2 <sup>nd</sup> order I-P-Diffusion model	[52]

### 3.1.2. Pseudo-second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (3)$$

Where  $k_2$  is the rate constant of pseudo second order adsorption ( $\text{g}^{-1}\text{min}^{-1}$ ). Eq (3) can be rearranged to obtain more useful form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (4)$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

And  $k_2$  is obtained from plot of  $t/q_t$  vs  $t$ . The model is best fit for hexavalent chromium removal by many agents.

### 3.1.3. Intra-particle diffusion model

The adsorption of hexavalent chromium on a porous adsorbent is the combination of four consecutive steps [55]; diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles [55]. According to Weber and Moris [56] if the rate limiting step is the intra-particle diffusion, then amount of adsorbed at any time should be directly proportional to the square root of contact time  $t$  and shall pass through the origin which is defined mathematically in Eq (6)

$$q_t = k_{id} t^{0.5} \quad (6)$$

A linearised form is Eq (7) where  $q_t$  is the amount of Cr (VI) adsorbed.  $t$  is the contact time.  $K_{id}$  is the intra-particle diffusion coefficient.

$$\log q_t = \log k_{id} + 0.5 \log t \quad (7)$$

A plot of  $\log q_t$  against  $0.5 \log t$  should give a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The value of  $k_{id}$  can be calculated from intercept of such plot. Higher values of  $k_{id}$  illustrate an enhancement in the rate of adsorption. Intra particle diffusion coefficient values have been calculated by various workers to bring a better understanding of the process.

### 3.2. Equilibrium model

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbents. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

#### 3.2.1 Langmuir model

The Langmuir isotherm [57] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is represented as Eq (8).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (8)$$

Here  $q_e$  is the metal concentration adsorbed in solid (biomass),  $C_e$  is the metal residual concentration in the

solution.  $q_{\max}$  is the maximum specific uptake corresponding to sites saturation, and  $b$  is the ratio of adsorption/desorption rates. Two derivatives of the Langmuir equation are Eq.(9) & Eq.(10).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (9)$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \quad (10)$$

### 3.2.2 Freundlich model

The Freundlich isotherm, first proposed in 1906, is based on multilayer adsorption with interaction between adsorbed molecules [58]. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The application of the Freundlich Eq (13) suggests that adsorption energy exponentially decreases on completion of the adsorption centers of an adsorbent. For adsorption from solution, the Freundlich isotherm is represented by Eq (11).

$$q_e = K_f C_e^{\frac{1}{n}} \quad (11)$$

Here  $K_f$  is the Freundlich constant and is also known as Freundlich capacity and  $n$  stands for adsorption intensity.  $Q_e$  is the amount of chromium adsorbed at equilibrium and  $C_e$  is the residual concentration of Cr (VI) in solution. The Freundlich equation is expressed linearly as Eq (12).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (12)$$

The values of  $K_f$  and  $n$  can be obtained from slope and intercept of a plot of  $\log q_e$  versus  $\log C_e$ . Both the parameters  $K_f$  and  $n$  affect the adsorption isotherm.

### 3.2.3 Langmuir-Freundlich model

In this model [59], the surface of the sorbent is considered to be homogeneous and sorption is a cooperative process due to adsorbate-adsorbate interaction. The Langmuir-Freundlich model is represented in Eq (13).

$$q_e = \frac{q_{\max} b C_e^{1/n}}{1 + b C_e^{1/n}} \quad (13)$$

### 3.2.4 Tempkin model

The Tempkin isotherm model contains a factor that takes care of the adsorbent-adsorbate interactions [60]. Tempkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage. The nonlinear form of Tempkin equation is given by Eq (14) and the linear form in Eq (15).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (14)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (15)$$

Here  $B_T = (RT/b_T)$ .  $T$  is the absolute temperature.  $R$  is the universal gas constant. Constant  $b_T$  is related to the heat of adsorption.  $A_T$  is the equilibrium binding constant corresponding to the maximum binding energy. A plot of  $q_e$  versus  $\ln C_e$  at a fixed temperature will give Tempkin isotherm constants,  $A_T$  and  $b_T$ .

### 3.2.5 Redlich-Peterson model

The Redlich-Peterson isotherm contains three parameters which may be used to represent adsorption equilibrium over a wide concentration range, and can be applied either in

homogeneous or heterogeneous systems due to its versatility [61, 62]. It is described in Eq (16).

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{b_R}} \quad (16)$$

The linearised form is Eq (17)

$$\ln \frac{K_R C_e}{q_e - 1} = b_R \ln(C_e) + \ln(\alpha_R) \quad (17)$$

It has three isotherm constants  $K_R$ ,  $\alpha_R$ , and  $b_R$ . The Redlich-Peterson isotherm constants cannot be obtained using graphical methods because of the three unknown parameters. A professional graphics software package is ideal for this.

### 3.2.6 BET model

The Brunauer, Emmer and Teller (BET) model is an extension of the Langmuir model [63]. It assumes that the Langmuir equation is applicable to each layer and a given layer may not be completely formed before the next layer forms Eq (18).

$$q_e = \frac{q_{\max} B C_e}{C_s - C_e} \left[ 1 + (B - 1) \frac{C_e}{C_s} \right] \quad (18)$$

Where  $C_s$  is the saturation concentration of the solute.  $B$  is a constant relating to the energy of interaction with the surface and other symbols are as previously described.

## 4. Conclusions

Agricultural wastes as adsorbents are cheap for the removal chromium from waste water, those represents an efficient and potential and also a practical replacement to the conventional processes. In spite of vast use of activated carbon in wastewater treatment, its use is sometimes restricted because of its high cost. To replace the expensive activated carbon, a wide range of inexpensive agricultural wastes as adsorbents were investigated utilizing naturally occurring materials and waste products of different sources. Some of them were found to be quite satisfactory. However, it is utmost important to dispose of the spent adsorbents in an environment friendly. Only limited information is available in the literature about safe disposal of spent adsorbents. More efforts should be made in this direction.

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