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Efficacy of Agricultural Wastes in the Removal of Hexavalent Chromium-A Review.

N Muthulakshmi Andal* and S Charulatha

Department of Chemistry, PSGR Krishnammal College for Women, Affiliated to Bharathiar University, Coimbatore-641 004, Tamil Nadu, India.

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***For Correspondence**

Department of Chemistry, PSGR Krishnammal College for Women, Affiliated to Bharathiar University, Coimbatore- 641 004, Tamil Nadu, India.

Email Id: andaldr@gmail.com

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ABSTRACT

Hexavalent Chromium is a major pollutant released during several industrial operations. It is also reported as one of the metals known to be carcinogenic and has an adverse potential to modify the DNA transcription process. The removal of hexavalent chromium has been studied by various authors employing adsorbents developed from waste agro by-products to assess their adsorption characteristics. This paper focuses on the comparison of some agro based products in the removal of Cr(VI) ions. An extensive list of agricultural based products such as Coconut Coir, *Prunus amygdalus*, *Cissus quadrangularis,* Soapnut Acacia, *Justicia adhatoda,* Bhringraj*, Aerva lanata, Trianthema portulacastrum, Tephrosia purpurea, Solanum nigrum, Datura metel, Cleome viscose, Asparagus racemosus* for the removal of Cr(VI) from aqueous solutions and the discharged effluents from industries are reviewed in this work. As chemically modified adsorbents exhibit higher adsorption capacity, a number of chemicals have been utilized for the required modifications of the adsorbent materials in the research articles. The results declared by the authors have been compared and summarized for further probe into the extensive utilization of the employed materials.

INTRODUCTION

Metal- rich mine tailings, metal smelting, electroplating, gas exhausts, energy and fuel production, down wash from power lines, intensive agriculture and sludge dumping are the most important human activities that contaminate soils with large quantities of toxic metals [1,2].An increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of effluent's discharges that contain high levels of heavy metals, thereby creating serious environmental disposal problems [3,4].

Water pollution due to chromium salts is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries and chromate precipitation [5]. Among the toxic metal ions, chromium is one of the common contaminant which gains importance due to its high toxic nature even at very low concentrations [6]. In the environment, it exists in two stable forms which are + III and the + VI states. While Cr(III) is known to be an essential trace element in plants and animal metabolism, the Cr(VI) is toxic, carcinogenic and mutagenic [7]. Hexavalent chromium is a cancer- causing agent and can pose health risks such as liver damage, dermatitis and gastrointestinal ulcers [8].

According to the Indian standards (1974), the permissible limit of Cr(VI) for industrial effluent discharge into inland surface water is 0.10 mg/L and into public sewage is 2.00mg/L. According to USEPA(1990), the tolerance limit to discharge, chromium(VI) into inland surface water is 0.10 mg/L and in drinking water is 0.05 mg/L [9]. But the industrial and mining effluents contain much higher concentrations compared to the permissible limit [10].

Some of the techniques which have been used in the removal of metals from effluents include ion-exchange, chemical precipitation, electro dialysis, electrolytic extraction, reverse osmosis and cementation. These methods are expensive and have the inability to remove metals at low concentrations [11, 12]. Abatement of pollution due to Cr (VI) consists of two main processes, one is reduction of Cr (VI) as such and the other is the reduction followed by precipitation technique, the latter being widely used for the treatment of wastewater containing Cr(VI) [13].

Due to magnitude of the problem of heavy metal pollution, research into a new dimension and economic methods of removal has been on the hype recently. Several researchers have reported on the potential use of agricultural by-products as good substrates for the removal of heavy metal ions from aqueous solutions and wastewaters [14]. So the efforts are being directed towards the use of natural low cost adsorbents for the removal of heavy metals. Use of natural materials which are available in large quantities [15] or certain waste products from industrial or agricultural background possess reasonably good potential as inexpensive adsorbents. Some of the low cost materials have been tested as adsorbents for heavy metal removal. Conversion of this waste into useful adsorbent has contributed not only to the treatment of heavy metal contaminated environment but also to minimize the solid wastes. These research activities indicate promising results but further efforts are still required in order to maximize metal removal efficiency and minimize the preparation costs [16].

Agricultural Wastes as Low Cost Adsorbents

The idea of using various agricultural wastes and their by-products for the removal of heavy metals from aqueous solutions has been investigated by many authors. Friedman and Waiss, (1972), Randall et al. (1974) and Henderson et al (1977) have investigated the efficiency of number of different organic waste materials as sorbents for heavy metals. The obvious advantages of this method compared to other are the lower cost involved when organic waste materials are used [17].

Coconut Coir- Activated Carbon

Coconut coir is a residue in the processing of coconut and is available at minimal cost.Coconut coir activated carbon is a suitable substitute for commercial activated carbon in the adsorptive removal of Cr(VI) from water. It is rich in lignin (16–45%), hemicellulose (24–47%) and pectin (2%) content [18]. The carboxylate and phenolic groups of lignin, hemicellulose and pectin are known as the main sites of metal binding [19]. Dichromate anion, $Cr_2O_7^{2-}$of potassium dichromate was the source of Cr (VI) of the aqueous solution. In aqueous solutions, chromate, (CrO_4^{2-}), and dichromate, ($Cr_2O_7^{2-}$), exist in a chemical equilibrium $2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$.The dichromate anion can become the predominant ion in acidic solution and the chromate ion is the predominant ion in alkaline solutions. Malay Chaudhuri [20] et al had employed this coconut coir activated carbon for adsorption of Cr (VI).The extent of Cr(VI) adsorption increased with decrease in its concentration and increase in contact time.Maximum adsorption of the metal by the activated carbon was observed at low pH 1–2 which may be attributed to the presence of large amount of hydrogen ions (H^+) neutralizing the negatively charged adsorbent surface reducing hindrance to the diffusion of $HCrO_4^-$ anion. Adsorption increased with carbon dose and attained maximum adsorption (100%) at 8 g/L carbon dose of coconut coir. The characteristics of Coconut coir activated carbon are presented in table 1.

Table 1: Characteristics of Coconut coir activated carbon

Parameters	Coconut coir activated carbon
Surface area (m^2/g)	826
Micropore area (m^2/g)	551
Micropore volume (mL/g)	0.025
Average pore diameter (Å)	24
Ash content (%)	14
Bulk density (g/mL)	0.31
pH	4.8

Nut Shell Carbon

Mosleh M. Manfe et al [21] reported that the *Prunus amygdalus*(Almond nutshell) which belongs to Roaceae family is adsorbent can be used efficiently to treat Cr(VI) contaminated wastewaters. The maximum uptake capacity of the adsorbent was observed at pH 1.8. The percentage adsorption as well as uptake capacity of the adsorbent increased with decrease in pH. The percentage adsorption was found to be increased with adsorbent dose whereas decreased with adsorbate concentration. The percentage adsorption increased from 55.1 to 90.2 when the adsorbent dose increased from 0.8 to 2.4 g/L. The percentage removal of Cr (VI) by this adsorbent is found to be 60%.

Plant Leaf Powders

The sorption characteristics of bio-adsorbents derived from leaves of *Justicia adhatoda, Cissus quadrangularis,* Soapnut Acacia for the removal of Cr (VI) had been studied by K. P.C. Sekhar [22].

*Justicia adhatoda*isa herbal plant hat blossoms in cold season and is called Vaidyamata Singhee in Sanskrit. It belongs Acanthaceae family and grows wild in abundance all over India. It is reported to have many medicinal values especially related to heart ailments. *Cissus quadrangularis*is a perennial plant of the grape family and is commonly known as Veldt Grape or Devil's Backbone. It is native to India and grows to a height of 1.5 m. It belongs to Vitaceae family. Soapnut Acacia is an herb which belongs to Mirnosaceae family and is well grown in coastal plains of south India. Its plant material are used as astringentand cleanser and also in the preparation some traditional tribal formulations. It is endowed with medicinal values in curing skin diseases, renal calculi, vesicle calculi, hemorrhoid, leprosy, abscesses, eczema and biliousness.

Powdered leaves of *Justicia adhatoda*, *Cissus quadrangularis*, Soapnut Acacia are found to have strong affinity towards Cr(VI) ions at low pH values. Percentage removal of dichromate is pH sensitive and also depends on sorption concentrations and time of equilibration. The conditions for the maximum extraction of Cr(VI) at minimum sorbent concentration and equilibration time have been optimized. Tenfold excess of common cations present in natural waters, viz., Ca^{2+}, Mg^{2+},Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}, have synergistic effect in increasing the % removal of Cr(VI). SO_4^{2-}, PO_4^{3-} and CO_3^{2-} are found to be interfering with the extractability of Cr(VI) in the order: $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$. The other anions: NO_3^-,Cl^- and F^- are found to have marginal interference. The percentage removal of Cr(VI) from synthetic waters with the powdered leaves are 88.0%, 88.0%, and 84.0% for *Justicia adhatoda*, *Cissus quadrangularis*, Soapnut Acacia respectively at pH 2 and at optimum equilibration time and sorbent concentrations. The sorbent dosage needed for the maximum extraction of dichromate at an optimum equilibration time is reported to be 2.5 gram/500 ml for the powdered leaves of *Justicia adhatoda* 2.5 gm/500 ml for powdered leaves of *Cissus quadrangulari*s 2.0 gm/ 500 ml for powdered leaves of Soapnut Acacia.

K. P.C. Sekhar and R. V. Vishnu Babu [23] have employed powdered leaves of Bhringraj, *Aerva lanata, Trianthema portulacastrum*L for extracting Cr(VI) from polluted waters. Bhringraj is one of the distinguished medicinal herbs and it belongs to Asteraceae family and it grows all over the worldcommonly in moist places as a weeds. *Aervalanata*is a woody prostrate or perennial herb which belongs to Amaranthaceace family. *Trianthema portulacastrum*L. belongs to Aizoaceae family, creeps up to 800 m in sandy and muddy coastal zones of Southeast Asia, tropical America and Africa. The percentage of maximum extractability of Cr(VI) at optimum conditions of pH and equilibration time are found to be 96.0%, 92.0% and 84.0% Bhringraj *, Aerva lanata, Trianthema portulacastrum L*. respectively. The dosage of the sorbent materials were found to be 1.5 gram/500 ml for the powdered leaves of Bhringraj 2.0 gm/500 ml for powderedleaves of *Aervalanata* 2.5 gm/500 ml for powdered leaves of *Trianthema portulacastrum L.*

R.H. Krishna Reddy [24] employedthe plant leaves and their ashes of *Tephrosia purpurea* and *Solanum nigrum* for the removal of Cr(VI) from industrial effluents and polluted lakes. The sorption abilities of these plant materials have been studied with respect to various physicochemical parameters such as pH, equilibration time and sorbent concentration in controlling the Cr(VI) pollution in wastewaters adopting batch system of extractions. Conditions for maximum extraction have been optimized. With synthetic waters, percentage of extractions of Cr(VI) were found to be 84.0% and 88.0% with powdered leaves and their ashes of *Tephrosia purpurea* respectively and 100.0% in the case of both the powdered leaves and their ashes of *Solanum nigrum*. The common cations present in natural waters, viz., Ca^{2+}, Mg^{2+} , Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} are found to have synergistic effect in increasing the % removal of the studied metal ion while anions like PO_4^{3-}, SO_4^{2-} and CO_3^{2-} are interfering but monovalent ions NO_3^-,Cl^- and F^- have marginal interference. Sorption increased with dosages. The maximum % removal was observed at parameters factors of1.5 gram/500 ml and 2.5 gm/ 500 ml for the powdered leaves and ashes of *Tephrosia purpurea* and *Solanum nigrum* respectively.

Plant Parts

Powdered leaves, Stems/barks and their ashes of *Datura metel, Cleome viscosa* and *Asparagus racemosus* had been reported in trapping Cr(VI) ions [25]. *Datura metel* is a shrub-like perennial herb which belongs to Solanaceae family of plants and grows up to 3 feet high in all the temperate and tropical regions of the globe. *Cleome viscosa*is a shrub which belonging to Cleomaceae family, grows in tropic and warm temperate regions of the world and is attributedtraditionally to possess medicinal values. *Asparagus racemosus* (Shatavari) is herb of Liliaceae family, growing at low altitudes to a height of 1-2 meters. The conditionsfor the maximum extraction of chromate at minimum dosage and equilibration time had been optimized.Sorbent dosage and time needed for the maximum removal is less for ash form than for the raw biomaterials in all plants, but among the ash forms of the plant materials, they are found to almost register the same % removal. Cr(VI) was determined Spectrophotometrically by using “DiphenylCarbazide” method [26].A comparison between the above mentioned adsorbents in the removal of Cr(VI) are listed in table 2 as % value.

Table 2: Comparison of percentage removal of Cr (VI) amongst the adsorbents

S.No	Adsorbents	% Removal	Reviewed Authors
1	Coconut coir	100%	Malay Chaudhuri et al
2	Nut shell carbon	60%	Mosleh M. Manfe et al
3	*Cissus quadrangularis*	88%	K. P.C. Sekhar et al
4	Soapnut Acacia	84%	K. P.C. Sekhar et al
5	*Justicia adhatoda*	88%	K. P.C. Sekhar et al
6	Bhringraj	96%	K. P.C. Sekhar and R. V. Vishnu Babu
7	*Aerva lanata*	92%	K. P.C. Sekhar and R. V. Vishnu Babu
8	*Trianthema portulacastrum*	84%	K. P.C. Sekhar and R. V. Vishnu Babu
9	*Tephrosia purpurea*	84%	R.H. Krishna Reddy
10	*Solanum nigrum*	88%	R.H. Krishna Reddy
11	*Datura metel* leave powder	100%	O. SreeDevi et al
12	*Datura metel* stem powder	100%	O. SreeDevi et al
13	*Datura metel* leave ashes	100%	O. SreeDevi et al
14	*Datura metel* stem ashes	100%	O. SreeDevi et al
15	*Cleome viscose leaves powder*	97%	O. SreeDevi et al
16	*Cleome viscose stem powder*	99%	O. SreeDevi et al
17	*Cleome viscose leaves ashes*	99%	O. SreeDevi et al
18	*Cleome viscose stem ashes*	100%	O. SreeDevi et al
19	*Asparagus racemosus leaves powder*	99%	O. SreeDevi et al
20	*Asparagus racemosus stem powder*	97%	O. Sree Devi et al
21	*Asparagus racemosus leaves ashes*	95%	O. SreeDevi et al
22	*Asparagus racemosus stem ashes*	99%	O. SreeDevi et al

Concluding Remarks

From the table 2, it is obvious that the activated carbon of coconut coir & the stem/bark/leaves of *Datura metel* (both in powder and ash form) have registered 100% removal of Cr (VI) under acidic pH conditions. Coconut coir shows 100% removal because it's having metal binding active sites (ie) carboxylate and phenolic groups of lignin, hemicelluloses and peptin. *Datura metel* have some functional groups like –OH/-COOH where their dissociation is pH dependent. This may be due to weak anion exchange ability at low pH, so Cr(VI) being an anion in the pH range 2-6 is sorbed by the plant materials resulting in higher percentage removal at low pH values. Also, the ashes of the stems of *Cleome viscose* exhibits 100% efficiency in trapping Cr(VI) ions. It is evident from the table that, the plant parts of *Cleome viscose & Asparagus racemosus* and also Bhringraj, *Aerva lanata* leaves have enhanced sorption capacity for Cr(VI) removal (90-99%), whereas the other sorbent materials have registered comparatively a lower % removal of Cr(VI).

CONCLUSION

Many researchers have reported numerous naturally occurring materials for the trapping of heavy metal ions. From this review, the efficiency of biosorbents in the removal of heavy metal ions in a multiple fold is revealed. Thus, the comparative study on biosorbents proves that they possess high potential in full- scale for the removal of toxic metal ions.

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