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Removal of Hexavalent Chromium Ion (Cr^{6+}) From Industrial Effluents Using Low Cost Bio-Adsorbents: A Review

Radharani Das[1*], Subhadeep saha[2], Gourisankar Roy Mahapatra[3]

[*]*Corresponding Email- radhadas6@gmail.com*
[1,2]*Department of Chemical Engineering, Haldia Institute of Technology, Haldia 721657, India*
[3]School of Applied Sciences and Humanities

Abstract:

Effluents from various industries like electroplating, leather tanning, cement, petrochemicals, dye etc, contains significant amount of toxic hexavalent chromium, Cr(VI) with concentration of 10^{th} to 100^{th} ppm level. The toxic and carcinogenic effects of heavy metals present in industrial damages kidney function and lungs activity, also leads to respiratory problem in the aquatic life and human beings. Industrial effluents containing hazardous metals pollutes the soil and surface water . To avoid the health hazard from long term exposure of Cr(VI) , there is high demand of feasible cost effective, clean technologies which would save environment . Many technologies are used to eliminate the Cr(VI) from the industrial wastes are precipitation, coagulation, membrane separation and ion exchange. Adsorption is one of the low cost , environment friendly methods widely used for the elimination of toxic metals from industrial effluents mostly Cr(VI) .

This review presents about the use of different types of waste materials as natural adsorbents for the removal of Cr(VI) from waste effluents. Results obtained from the experiments were fitted to the various isotherms and kinetic models. The effect of various factors on toxic heavy metals reduction have been studied thoroughly . The literature show that the effective removal of Cr(VI) from industrial effluent is strongly dependent on adsorbent amount , adsorbent type, time of contact , pH of the media, concentration of Cr(VI) ions and operating temperature. It was suggested by the researchers that the activated leaves and agricultural wastes may be applied as low coast alternative bio-sorbents as replacements of different chemicals for removal of metals from water . However, gaps have been recognized for the development of methodologies, regeneration od adsorbents, reuse of treated water and harmless disposal of the sorbents, optimization and industrialization of the appropriate agricultural adsorbents.

Keywords: Agricultural wastes .Chromium,. Adsorption models . Bio-sorbent . Heavy metals

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Introduction:

Hexavalent chromium, $Cr^{6+,}$ is a highly toxic metal that has detrimental effects on the environment and human health. such as stomach pain, organ failure, nervous disorder, cancer, and nervous disorders. In a recent study of an extensive review on the adsorption performances of various adsorbents for eradication of carcinogenic Cr^{6+} was reported by Jonas Bayuo[1]. The element chromium is not biodegradable. Chromium's toxicity level ranges from 50 to 150 m/kg [2]. Chromium contamination in water and wastewater must be removed, which is a labor-intensive and expensive process. Tetravalent and hexavalent chromium are the two main types of chromium that can be found in the environment. However, the highly oxidizing hexavalent ion can release free radicals. Hexavalent ions of chromium are more toxic than tetravalent ions. As an illustration, the tannery industry uses only about 60–70% of the total chromium used in tanning, and 30–40% of that is removed and released into the environment as tannery effluent. Industrial and manufacturing activities result in the annual environmental discharge of more than 1,70,000 metric tons of chromium waste. The Indian Standards allow for a maximum of 0.05 mg/l of Cr^{6+} in potable drinking water. Public sewage discharge into land surface waters is 2.00 mg/l, while industrial effluent discharge is 0.10 mg/l. [3]. Chromium is primarily used in heavy industries like steel, textiles, and electroplating. The earth's crust contains 100 ppm of chromium on average[4, 5].When chromium is heated, chromic acid, a green substance that is unstable, is produced. Chromium levels in air and water are extremely low when compared to water that has been contaminated. Through FTIR characterization, we were able to demonstrate how adsorption caused changes in the adsorbent's structure both before and after the reaction. Other methods include polymer nanoparticles, activated carbon, reverse osmosis, electrodialysis, membrane separation, and reverse osmosis. The most effective of these techniques, adsorption appears to be quick, easy to use, inexpensive, and effective at lower concentrations. Other approaches are extremely costly and non-regenerative, making separation a very expensive process that is ineffective. Plant-based bio-adsorbents are a viable option for wastewater treatment because they are affordable, abundant, renewable, and primarily made of cellulose and lignin. Plant material contains cellulosic material that is effective at adsorbing heavy ions. Common bio-adsorbents used in studies on biosorption using plant material to remove chromium includeneem leaves, green tea leaves, grape leaves banana peels, coconut shell, sawdust, agricultural waste, bamboo waste, activated carbon, groundnut hull, rice husk, and potato peeling powder etc. The main objective of this paper is to thorough review on the various bio-adsorbents that have been employed recently in studies to remove Cr^{6+} from industrial waste water.

Applicability of Various Natural Adsorbents for Removal of Cr^{6+}:

Coconut Shell :

The effect of adsorbent doses , solution Ph, time of contact , particle size of coconut shell and concentration of Cr^{6+} on removal performance was studied by Alam et. all, Smita et. all[6-9] . It was noted that the rate of removal of Cr^{6+} improved from 10 to 95.64 % in the first 12 hr and the optimum elimination was obtained as 99.75% after 36 hr. at pH 2 and at 30^o C using 20 gm/l adsorbent with particle size range of 75 – 600 micro meter. However, at higher pH, degradation decreases due to lower concentration of H^+ . They also reported that the Cr (VI) removal rate diminished from 99.71% to 44.72% if the concentration of Cr^{6+}changed from 100 to 1000 mg/L,

Ayub et all, [10] used charcoal powder prepared from Coconut shell as an adsorbent to eliminate the Cr^{6+} from the electroplating industrial waste using the batch adsorption technique at various pH, contact ime and adsorbent doses. It was found that the performance was reduced from 85% to 33% for increase of pH value from 6.5 to 9 and removal percentage increased from 61% to 87% for increasing time of contact from 30 min to 3 hrs with adsorbent dose of 20 mg/L.

Saw dust:

ZainulAkmarZakaria et.al [11] studied the adsorption characteristics of untreated rubber wood sawdust (RWS) for removal of Cr(VI) and found the optimum removal about 100% at pH less than 2.

Suresh Gupta et al [12] studied on synthetically prepared electroplating and tannery waste water using biodegradable modified saw dust. They achieved more than 95% removal efficiency have optimum adsorption capacity of 41.5 mg/gm at pH of 1. They also agreed that the Langmuir isotherm model and second order reaction kinetics was suitable for this sawdust -Cr(VI) adsorption process. They also succeed to get 95% solute from the adsorbent during desorption studies.

An extensive review was done by A. Sukla et all.[13] about the applicability of sawdust for removal of hazardous contaminants present in the waste waterusing adsorption process. They focused on impact of various parameters on the adsorption mechanism, found satisfactory conditions for optimum elimination of hazardous unwanted contaminants.

Agricultural wastes:

Effect of various operating parameter like pH, particle size, contact time and adsorbent doses on Cr^{+6} removal was observed by S. Dhanakumar et .al. [14] using treated cooked tea dust . They obtained 90% removal at optimum pH of 2. Bio-sorptive behaviour of spent tea leaves for adsorption of Cr^{+6} from tannery waste water and the influence of independent parameters like contact time, adsorbent amount ,contact time and pH was also studied by Alam et al. [7]. They found 95.4% removal of solute using 14.0 g/L adsorbent dose and achieved optimum sorption capacity of 10.6 mg/g at pH of 10.0.

Anand .S . A [15] et.al achieved 90 % reduction of Cr^{+6} using rice husk ash as an adsorbent from the synthetic solution. Maize bran, an agricultural waste was taken by S.H. Hasan et.al [16] for removal of $Cr^{+6}$from aqueous solutions and reported that this adsorption is mono layer in nature and effective at higher temperature and lower pH range .

R. Gayathri et.al [17] observed the capacity of tamarind seeds , a cheap adsorbent and achieved 80% elimination of Cr^{+6} . They reported that the maximum monolayer adsorption of Cr(VI) on tamarind seeds was obtained as 29.41 mg/g at pH 2 in equilibrium time of 240 min .

Smita M, et.al [18] studied the efficiency of the activated sugarcane bagasse at various agitation time, solute concentration, and pH and reported 96.1% removal of Cr^{+6} . Ravi K. Et al [19] and Davoud B[20] et al , Prasant K.S et[12] all used various agricultural waste and activated carbon to remove the Cr^{6+} from the aqueous solution having concentration range from 1.5 to 5 mg/L. They found that maximum adsorption of rice straw was 96. 72% at Ph 8.0 They also found thatthe reduction of Cr^{6+} increases from 45% to 97.12%with the increase of adsorbent amount from 2 gm/L to 9 gm/L. They also suggest that elimination efficiency decreased from 76% to 46% with the change of concentration of Cr^{6+} from 1.5 mg/L to 5 mg/.

Wheat straw and Eupatorium adenophorum were selected by Song et al. [22] for reduction of Cr(VI) from synthetic wastes. They reported that about 99.9% of Cr^{+6} may be reduced with an maximum adsorption capacity of 89.21 mg/g at 278 K and pH of 1.0. The amount of Cr(VI) adsorption was increased at higher temperature representing that this sorption process wasendothermic. They also found that theLangmuir adsorption isotherm and pseudo second- order kinetic model were fitted well in this sorption process .

Immobilized biomass from corn cob was selected by Manzoor et al. [23] to eliminate Cr(VI) and Cr(III) from waste stream. They were able to remove 277.60 mg/g and 208.6 mg/gm of Cr(VI) and Cr(III) in this adsorption process . They also agreed that the Langmuir and pseudo second- order models were followed the experimental results very satisfactorily

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Neem leaves and spent tea leaves powder:

B.V. Babuet. al [13], Parmeeta et all [24]and P.Venksataswara et.al [25]studied the potentiality of the neem leaf powder for elimination of Cr^{+6} from dilute solution . Maximum adsorption capacity of the NLP was found as 62.97 mg/gm by Babu et al .They achieved 90% removal of hexavalent chromium. Theyalso suggested that the adsorption process fitted the pseudo second order kinetics suitably.

R .Das et all [26]The results show that about 95-99 % reduction of Cr(VI) may be achieved successfully depending on nature of adsorbents. An attempt has been made to find out the rate constants of this sorption process using first order reversible, pseudo first order and pseudo second order kinetic model. Applicability of Freundlich Isotherm and rearranged Langmuir model have been explored. The maximum adsorption of Cr(VI) was obtained as 102.04 mg/gm using NLP using 0.5 g/l adsorbent at pH-1.29, and temperature 302 K **.**

Sharma et all [27]] conducted adsorption of Cr(VI) on Neem leaf powder. They found

that Langmuir model follow the sorption process with the uptake capacity of 0.1 mg/g. It was found that 87. 0% and (6.3 mg/L) of Cr(VI) was removed from the the aqueous media by 1.6 g neem leaf powder for a contact time of 5 hr at 27.0 °C at pH ranged from 4.5–7.5. Jeyaseelan et all [28] selected Green Tea Leaves as anadsorbent for the elimination of Cr(VI) from the synthetic solution and observed that the maximum capability for reduction of Cr(VI) was up to 99%. The values of thermodynamic parameters like ∆G, ∆H, and ∆S proved that the process was exothermic and spontaneous in nature. The results of kinetic studies show that the adsorption process is suitable for pseudo-second-order kinetics.
Alam et al. [29] used spent tea leaves to conduct a study for elimination of Cr(VI) from tannery wastewater. Effects of various operating parameters including adsorbent amount , Cr(VI) concentration, contact time, pH and temperature on removal of Cr(VI) were determined using the batch process. They found thatoptimum reduction of Cr(VI) from the industrial wastes was 95.4% using spent tea leaves at a pH of 10.0 and an adsorbent amount of 14.0 gm/L, with optimum adsorption capacity of 10.6 mg/g.

Fruit peels and Seed Powder :

Ashraf et all [30] used by acrylonitrile treated banana peels for eradication of Cr(VI) from aqueous solutions using adsorption. The alkaline hydrolysis was done using 10% NaOH followed by treatment of Banana peels with 10 % HCl. The optimum adsorption of 96% Cr(VI) were found at pH 3, adsorbent amount of 4 g/L, concentration of Cr(VI) 400 mg/L and contact time of 2 hr. They suggested that the sorption process fitted with Freundlich isotherm as well as Langmuir model . Experimental results were suitable to fit the Pseudo-second order kinetic model . Thermodynamic results indicate that the adsorption process is spontaneous and exothermic in nature . Because of its significant adsorptivity and negligible cost, grafted banana peels may be considered as an active adsorbent for reduction of Cr(VI) from effluent water.
The impact of various parameters like adsorbent mount , Cr(VI) ion concentration, pH, particle size of adsorbent and agitation time, has been was investigated by Hema Krishna R et al [31]. Adsorption performance of powder Papaya Seeds (PPS) for reduction of Cr^{+6} and Kinetic studies confirmed the suitability of the pseudo first order model fir this adsorption process.
FaraiMutongo [32]studied on the impacts of the initial Cr(VI) ion concentration, dose ofpotato peel powder on removal kinetics of the metal ions . They explored that 4 gm/l adsorbent was capable for fully reduction of Cr(VI) ion, at pH 2.5, and contact time of 48 mins only with maximum adsorption capacity of 3.28 mg/g . The kinetic model forCr(VI) removal using potato peel powderadsorption process found the fitness of pseudo-first-order as well as pseudo-second-order models. The experimental findings show that potato peels have high potential to as bio-sorbent for elimination of Cr(VI) ion from waste water.

Ekpete et al. [33]found performance of the orange peel (Citrus sinensis) powder for elimination of Cr(VI) and Zn(II) from aquatic solution at pH of 3.0 and temperature of 30.0 °C. The effect of various operating parameters like time ofcontact, Cr(VI) concentration, adsorbent amount , temperature and pH on the adsorption process was studied. . They found the maximum capacities of 8.1 mg/g and 1.1 mg/g for Cr(VI) and Zn(II) ions respectively. They suggested that the Langmuir isotherm was suitable to correlate with the equilibrium data obtained in this sorption process efficiently.

Nut shell :

Sunil et al.[34] selected groundnut shell powder, activated charcoal and activated neem leaf powder, for removal of Cr^{+6} from the waste water .They reported elimination of 79.4–87.4 % forneem powder and 81.9–95.7% for activated neem leaf powder. For activated charcoal, the removal range was 89.0–97.65 %. They found that the optimum reduction of Cr(VI) significantly depends on acidic medium , solute concentration and temperature

Raw macadamia nutshell powder and chemicallyactivated macadamia nutshell were selected as adsorbent of Cr^{+6} by Pakade et al. [35]. They suggested the optimum adsorption conditions are pH 2.0, adsorbent dose of 0.2 g and initial solute concentration of 100 mg/l . The maximum elimination of Cr^{+6} from wastewater was found as 99.0 % using Almond green hull powder by Nasseh et al. [36]

.Rai et al. [37]eliminated Cr(VI) from wastewater using activated carbon prepared from almond shell powder in a batch adsorption process . They also studied the impact of various parameters like adsorbent amount , Cr(VI) concentration, pH of the solution, time of contact, and operating temperature on the adsorption of Cr(VI). They declared that about 100.0% reduction was possible at pH of 2.0. Theyalso reported the Langmuir isotherm and pseudo-second-order kinetic models are suitable to fit the experimental results. .

Bamboo waste

Dula et.al. [38] achieved 98.3% Cr^{+6} removal and 59.23 mg/g adsorption capacity at 27 ^{o}C and pH 2.0 using activated carbon produced from bamboo waste treating with KOH and heating at 1073 K using Batch adsorption process. They found that the process is spontaneous, exothermic in nature and better fitted with Freundlich isotherm model.

Adsorption efficiency of activated carbon of Nigerian bamboo, sintered at 8000^{o} C was studied by Ademiluyi[39] et all (2016) for elimination of various metal ions like Cr, Ni, Cu, Pb, Cd etc from aqueous solution. They found that the order of adsorption capacity using this activated carbon was lead > Cadmium > Copper > Zinc > Nickel >Chromium in the order if ionic radius of the various metal ions. Results of their study implies that the activated bamboo can work as a good alternative for reduction of multiple metal ions from the industrial waste water.

Activated carbon derived from Leaves/ stems or waste material :

Tuama et al [40]] studied to find out the efficiency of Tobaco leaves for removal of Cr^{+6} from water solution . Influence of various sorption parameters for reduction of Cr^{+6} was studied by Ba et al.41]using carbon derived from olive oil wastes in a batch process. They showed that the maximum sorption capacity of the developed carbon for Cr^{+6} was 74.9 mg/ g at pH 2.0 and Cr^{+3} was 14.3 mg/ g at 9.0 . Their experimental finding and kinetic studies confirm that this sorption process follows pseudo-second-order kinetic ,

Duranoglu and Beker, [42]] used activated carbon derived from peach stone for eradication of hazardous Cr(VI) . They reportedthat Cr(VI) biosorptionprocess was highly pH dependent and the maximum elimination was achieved at lower pH values. They also found that Freundlichisotherm and pseudo-second-order kinetic modelsare in good agreement with the equilibrium data from the experimental findings.

Acid-treated adsorbentprepared from Phragmities stem was used by Regmi et al. [43] to eliminate Cr(VI), Al(III) and Fe(II) ion from waste stream . They reported the maximum

reductioncapacity of Cr(VI) onto H_2SO_4 treated Phragmities waste was 200.0 mg/gm , which is quite satisfactory than the previously reported results.However , optimum removal of Al(III) and Freundlich and pseudo-second-order.. Fe(II) from wastewater. At a pH 1.0 and 2.7,.was 90.9 mg/g, 166.7 mg/g. They also suggested that the both isotherms and kinetic models we well-fitted with the results .

Conclusions :

The review on the performances of the various adsorbents showed that the sorption method using natural adsorbents has many advantages for the eradication of carcinogenic and toxic Cr(VI) wastewaters. This method is economic, a reliable,safe, efficient for the elimination of Cr(VI) from industrial effluent water. It was found from through review that the removal of Cr(VI) from wastewater is strongly depend on the pH of the media, contact time, adsorbent amount , particle size, solute concentration and temperature. It was reported by the researchers that the optimum elimination capability of Cr(VI) on the different natural adsorbents are in the range of 65.0–99.50% within pH range of 1.0–4.0 and contact time of 60.0–240 min at room temperature (30.0 °C). It was also suggested by the researcher thatthe Langmuir isotherm model and the pseudo second- kinetics model are most applicable for this adsorption process . The thermodynamic analysissuggest that the bio-sorption of Cr^{+6} on the various adsorbents was spontaneous and increases with temperature within the range of 30.0–60.0 °C. Activated Neem leaf powder is most effective choice for removing Cr(VI) ions by 99.5% within 120 minutes of contact at pH of 1.0 and optimum capacity 102 mg/gm . Further research should be done to develop the adsorbents quality , to increase applicability, and to regenerate the adsorbent and to get optimum elimination of Cr(VI) from waste stream and to save the environment.

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Authors Detail

Prof. (Dr) Radharani Das, Dean (CHE, BT, FT) , Haldia Institute of Technology, West Bengal completed B.Tech, M.Tech, Ph.D in Chemical Engg. from University of Calcutta and Post Doc. from University of Torino, Italy . She published more than 80 papers in various national and international journals and conferences. Received Certificate of Merit award - 2008 & best paper award-2000 from Institute of Engineers India (IEI), Gold Medal from Calcutta University in 2010 and "**Teacher of the year Award**" from West Bengal University of Technology in 2017. She served as District Science Advisor (PurbaMidnapore) for Environment. She is associated with many international Journals as reviewer and contributed for two books on Environmental Science (WILEY-VCH) as co-author. She is actively engaged with various research work in the field of Ceramic Membranes, Environmental Science, Separation Process and Adsorption Process Technology

S :Subhodeep is a B. Tech , 3rd year student of Dept. of Chemical Engg., Haldia Institute of Technology. He is actively involved with various mini projects and research work in the Institute.

Dr. GourisankarRoymahapatra : Dr. GourisankarRoymahapatra, currently working as an Associate Professor of Chemistry at the School of Applied Science and Humanities, Haldia Institute of Technology . His area of research interest includes NHC complexes, organometallics, catalysis, antibiotics, anti-carcinogenic, gas adsorption, hydrogen fuel, super alkali, and computational chemistry. He has published more than 85 articles in severalinternational journals alomg with 11 book chapters. Dr. Roymahapatra is the editorial board member and reviewer of several national and international journals.