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RESEARCH ARTICLE

NATURAL ADSORBENTS FOR REMOVAL OF HEXAVALENT CHROMIUM FROM WASTEWATER: A REVIEW

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ABSTRACT

The existence of Heavy metals in water is the sole issue these days. Environmental and Ecological imbalance can be utilised. The high range collection of heavy metals in water and polluted water have negative results on living organisms and the environment. In all the heavy metals like Pb^2+, Zn^2+, Cr^6+etc. Chromium has the most damaging effects on living organisms including plants or animals. It is produced from electroplating and tannery industries. Chromium pollutes the earth and groundwater. The contact of mankind to an extreme quantity of chromium straightly cause respiratory disorders and injures the lungs. Cause of industrialization the chromium pollution in the aqueous solution and wastewater is crossing the tolerance limits of forbearance. Different techniques are utilised for the removal of chromium from the water. Adsorption is a very economical method largely utilised to get rid of heavy metals from commercial and industrial wastewater. It has been examined that this technique is the most functional and commercially workable technique for eliminating heavy metals, specifically chromium. The existing article explains numerous minds of natural waste adsorbents that are observed to be productive in eliminating hexavalent chromium (Cr^6+) from factories elimination.

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INTRODUCTION

Heavy metals are the category of metals in addition to metalloids it's increased concentration in the surroundings is caused by anthropogenic schemes. Wastewater only cause is the development of the anthropogenic situation. Essential heavy metals content of boron, arsenic, nickel, iron, zinc, mercury, copper, iron, chromium, silver. These entire metals are very harmful to human beings even in footprints. Such heavy metals are in charge of numerous disorders in mankind such as cancer, osteoporosis, a disorder linked to liver, kidney etc. Apart from mankind such metals further limit the metabolic rate in vegetation and their growth and development. Wastewater treatment is the requirement of the time so we are aiming at the workability of surroundings, reuse, energy conservation and recycling. Such metals are unable to eliminate effortlessly yet need modern techniques for their elimination.

Chromium is a typically known dangerous pollutant that is the consequence of numerous industrial outgrowth. The topmost concentration of chromium in water as claimed by WHO is 0.05mg/l. Chromium metal is a breakable solid substance. It is greyish silver in colour and unusually clean in the environment. This chromium metal is extracted from the ore chromites ($FeCr_2O_4$) metals obtained below the earth's high point. It has more stiffness value and decomposition interference, primarily used for the gathering of examined steels. The usual organisation of chromium on the globe is approximately 100 ppm (1). At the place when the metal chromium is heated, it produces corrosive green colour chromic and it is not constant. The quantity of chromium in the atmosphere and water is accurately low in contrast with the waste contaminated water. Chromium occurs in two oxidation states-Hexavalent Chromium (Cr^6+), Trivalent Chromium (Cr^3+). 3. Cr(0). Trivalent Chromium (Cr^3+) is usually present in organic products, meat, and vegetables. It is one of the essential additives for people. Regular exposure to trivalent chromium can cause skin rashes and other infections. In both the chromium, the hexavalent is very risky, and has significant

impacts (Headache, cancer and so on,) on mankind wellness. In the decreased pH range, the Cr^{6}+compounds are good oxidants. The oxidation reaction by Cr^{6}+ is shown in Equation1.

$$2(CrO_4)^{2-} + 2H^{+} = (Cr_2O_7)^{2-} + H_2O \quad \text{Equation 1}$$

The chromium harmfulness ranges between 50-150 µg/kg (2). Cr (IV) is existing in nature and is most lethal in the environment because it can freely pass through in human physique through cells. Cr(III) is similarly rarely toxic and is nearly insoluble about pH=7. Discharge of a deadly amount of chromium per cent from the water and contaminated water is an amazing cycle and the charge of this interconnection is very high. A vast range of treatment technique is available such as the Adsorption method, Ion exchange, synthetic precipitation and so forth within reach to decrease the heavy metal amount from the waste water(3). Adsorption, Precipitation and Ion exchange are considered to be the very productive plan of action used to rid of the considerable metals from the contaminated water (4). Adsorption is the method at point particles are adsorbed on the exterior of the adsorbent. This method consists of film known as an adsorbent surface is built. The adsorption is of two types:

1. Physisorption and 2. Chemisorption. The Physical Adsorption works best at the low-temperature range from 20-40 KJ/Mol, While chemisorptions are studied at a high temperature ranging from 40-400 KJ/Mol. Contrasted with the actual adsorption procedure, the chemical adsorption method needs to differentiate initiation energy for moving the particles into the adsorption surface. The Adsorption isotherm obtained is the detailed picture, and it is used to measure adsorbate and adsorbent at a compatible temperature (5). This paper aims todiscuss different methods and various types of natural as well as chemical adsorbents to decrease the contamination effect of the hexavalent chromium (Cr6+). Here, different natural adsorbents (a substance that adsorbs another) (6-10) have been utilized to get the metal particles from the water and wastewater. This review paper focuses on different types of adsorbents and factors which affect adsorption efficiency.

Adsorption: Different Techniques: Different Techniques which are usually adopted for the removal of heavy metal from wastewater are Adsorption, ion-exchange, chemical precipitation, Filtration, photocatalysis, coagulation/flocculation, electrodialysis, filtration, and electrochemical treatment.

Different types of Adsorbents

I Adsorbents: Natural

Sawdust: This effort utilized the watery ordering to get rid of the hexavalent chromium by utilising sawdust-like adsorbent. The reaction was achieved by melting the potassium dichromate (99.9%) using 1000 mL of purified water and the pH level was kept by using a solvent of acid and base (such as 0.5 N of HCL and 0.5 N of NaOH Solvent) (10). collected adsorption plan was operated and the drive out the capacity of Cr6+ had been examined in the following way.

Time of Contact: When the capability has arrived at the high range of nearly pH=1, the basic quantity of Cr6+ was adjusted to a level of 100-400mg/L. The capacity slowly become low from 86% to 66% for the time of contact 250 minutes.

pH level: The Adsorption of Cr6+ was achieved by differing the pH level from 1-11. The strength of removal of Cr6+ was detected with an increase of pH level nearly 6.9. The highest clearance capacity was reached at the pH=1.

Adsorbent part: The removal ability of hexavalent chromium was higher in the level 98.3% to 99.8%. The consideration of adsorbent was expanded in the level of 4 gm/L to 24 gm/L. Also, it is examined that the adsorption control lowered from 12.20 mg/g to 2.06 gm/g. In this state, the complete consequences were examined at 8.7 mg/g for nearly99% of the adsorption capability of hexavalent Chromium.

Aim of the beginning: The infatuation was adjusted in the level of 50-500 mg/g as stated in the operation and because of this idea, the removal capacity lowered from 99.9% to 89% and besides, it come about at the very largely adsorption restricts level from 4.98 to 41.45 mg/g.

Molecular measurement: In this analysis, the calculation of the size of the molecule was not done. But it was examined that when the size of the molecule was higher the adsorption, productiveness lowered. Industrial and Electroplating emanating was utilised to eliminate Cr6+ by utilising the natural adsorbent coconut shell charcoal. The adsorption of chromium was done by using 0.7071gm of $K_2Cr_2O_7$in half litre of deionized water. The technique used for adsorption of Chromium is Collection technique (15-20).

pH level: The productiveness of the hexavalent chromium metal was studied with changing pH is the range of 2 to 9. In the current activity, the ability was expanded from 75% to 86% at the pH level from 2 to 6. And at the end along, the capability constantly become lower with 85% to 33% at the pH level from 6.5 to 9.

Time of contact: Increment in removal capability from 60% to 87% for the time of contact from 30 to 180 minutes the productiveness achieved in accordance value.

Adsorbent section: The adsorbent quantity was developed from1.5gm/L to 25.5 gm/L and numerous situations (like Time of contact, pH etc) were reserved instability. Currently, the abundance of the chromium discharge enlarged 20mg/L, at this concentration from there on the productiveness remain consistent.

Aim of the beginning: The centre of chromium was altered from 5 mg/L to 25 mg/L. The very ultimate adsorption efficiency is regularly decreased by the decrease in the aim.
Size of the Adsorbent: The particles size of adsorbent was in the range of 0.42 mm to 1.70 mm. This technique uses different adsorbent with different particles size were used together.

Shell of Coconut: Various scientist have also used coconut shell as an adsorbent to remove metal specially hexavalent Chromium. Adsorption interaction occurs in assemblage and part considered after the part was adsorbed in the company different categories of various characteristics at the atmospheric temperature (11-14).

Adsorbent section: The hexavalent chromium purging effectiveness obtained was around 88.28% with an adsorbent section of 15 gm/L. It was observed that the effectiveness was slowly increased from 53.3% to 84.1% when the section is expanded up to 10 gm/L. It can be concluded that the proficiency has been actively reliant upon the adsorbent section. At the point where the adsorbent section is enlarged, the expulsion productivity of substantial metal is found to be additionally enlarged.

pH level: The most intense adsorption of Hexavalent chromium (83%) was obtained at a pH of 1.5. The pH range was maintained between 1.5 to 7 pH range and because of this change; the capability of Hexavalent Chromium had slowly declined to 36%. It can be explained that at a low pH range the presence of H+ particles is drawn in by the unfavourably charged hydroxyl bunch (- OH) on the adsorbed surface.

Aim of the beginning: The infatuation altered from range 5-100 gm/L. Now, the very ultimate removal capability accompanied was up to 87% at the centre of 51 mg/L. At the place when the conjunction of chromium was enlarged the removal efficiency was successfully decreased.

Time of contact: The contact duration of the evacuation ability of hexavalent chromium depends on the size of the particles. The molecule size taken in this work was (75 um-600 um) in different quantities of basic adsorbate collection of 50 gm/L. The large removable efficiency was achieved at the range of 75 um size of the molecule and its time of contact was around 10 hours and from that place, it remained the same.

Size of the molecule: The molecular dimension is likewise one of the important characters for the adsorption of heavy metals. At a point when the dimension of the molecule was high, it is observed that the adsorption proficiency is decreased. In this research, the size of the molecule reaches around (75 um-600 um) and it is also seen that the greatest proficiency of 83 % was attained with the molecule size of 75 um and it was observed that the productiveness got reduced when the size of the molecule is declined.

Green tea leaves: Green tea leaves were also used for the removal of hexavalent chromium from the aqueous arrangements. Potassium dichromate was used as a reserved arrangement, collection adsorption observers were wholely and the removalcapability of hexavalent chromium portion needed to go through in the accompanying categories (51-56).

pH: Around 92% productiveness at pH=2, when pH was maintained in the range of 3.5 to 10 the capacity level is decreased. It was found that adsorption at pH was not at all observed. The very ultimate adsorption productiveness (92%) was achieved at pH2 and lately the capacity level was quietly decreased when the pH from 3 to 10 arrangement was altered. Lately, at pH 6 the adsorption of hexavalent chromium was not capable.

Time of contact: The experimental time was 30 minutes to 300 minutes. Although the very productive adsorption capability has arrived at 180 minutes and the place ahead, the productiveness was successfully decreased, and it accomplishes the consistent value.

Aim of the beginning: The conjunction of chromium was altered from 5 mg/L to 500 mg/L.

Groundnut hull: Groundnut structure was used for removal of Cr+6 as an adsorbent from the watery arrangement. The hull of the groundnut body was utilized in two different methods for the adsorption. The first one is MGS (Modified Groundnut Shell), and the second one is UGS (Unmodified Groundnut Shell). Potassium dichromate was used as a suitable answer for chromium adsorption and grouping adsorption steps had been used and the efficiency of chromium adsorption was discussed from the accompanying various categories of adsorption (64,65).

pH level: The adsorption of chromium using both the MGS and UGS was discussed at various ranges of pH i.e. (1to8). At around pH =2, two different adsorbents have provided excellent removal capability of chromium, although as compared with UGS (82%), The MGS has given that the very ultimate removal effectiveness (96%) of the hexavalent chromium. At the end, where the level of pH enlarged, the capability of chromium was successfully declined and it achieves harmony.

Time of contact: The current job observes that the largest adsorption capability was achieved at 30 minutes for all the adsorbents (UGS, MGS). Later that the productiveness gets in balance state. The adsorption gets the harmony state for all the adsorbents (UGS, MGS) at 1 hour and 80 minutes and from that end along, the productiveness was constantly decreased (66).

Aim of the beginning: The fixation was altered from 0 to 24 mg/L. The largest adsorption capability was examined at 18 mg/L collections of chromium and besides that, it goes to balance for MGS. Although, the removal capability of chromium was accomplished at the highest range when the aim was in 8.3 mg/L for UGS.

Adsorbent section: The adsorbent portion was changed from 5 to 40 mg. Because of these changes in portion levels, the effectiveness of adsorption of chromium was progressively increased gradually (UGS-88% MGS-98%).

Size of the molecules: Adsorbents used are MGS and UGS as powder. The size of the adsorbent was in the range of 200-300 µm. Due to Equal size and no crucial alteration in the adsorption capability of chromium (67).

Bamboo waste: Some researchers used the bamboo squander as an adsorbent to remove the chromium metal content from the fluid arrangement. The bamboo squanders reacted with a potassium hydroxide arrangement and then washed with an HCL arrangement. The process of adsorption was done utilizing a potassium dichromate ($K_2Cr_2O_7$) arrangement (46-50). The grouping adsorption process was used and the removal productiveness of the chromium was studied in the accompanying categories.

pH level: The largest chromium adsorption (98.28%) was achieved at 2 pH, and with an increase in the pH level, the productiveness of the adsorption constantly decreased.

Table 1. Summarises the details about all these technologies.

TECHNIQUE	TYPE OF METAL REMOVED	COST	REACTION CONDITION	END-PRODUCT	PRECISION	EFFICIENCY
ADSORPTION	Large range covered depends on type sorbent used	Low cost	Simple operating condition, Only difficulty arises in separation of sorbent	Small amount of sludge,	No direct effect but organic matter present can effect metalpresent	Sorbent properties effect the efficiency of metal
Flocculation	Heavy metal cannot be removed	Cost feasibility but chemical usage is very high	Very simple to operate	Sludge volume is high	High flocculant can show increased removal of heavy metal	It works well in the condition where metals are linked with colloids
Photocatalysis	Can work under traces (even less than ppm)	-	Retention time high	By-products are less toxic	Some scientist investigated	Removal of lead and cadmium using radiations
Electrochemical treatment	Very effective in removal of heavy metals	Economic feasibility is less as initial setup cost is very high. Electrodes replacement if required	Though it is easy to operate but there can be problem of corrosion of electrode	Sludge production occurs but in small quantity	Removalof metal is possible but not all as the process is selective in nature	This process seperates various heavy metal & Organic matter
Ion-Exchange	This consist of resin which can easily remove various heavy metals	Operational cost is high i.e expensive in nature	pH sensitive method	If resin is regenerated it may cause pollution	Can remove only those heavy metals which are carrying high ionic charge	Presence of organic matter can cause delay
Chemical Precipitation	Not successful for solution of low metal concentration	Low cost but disposal of sludge waste require	Setup is simple, but some colloidal precipitate are formed	Large quantity of sludge formed	Complexing agent interrupts ppt of hydroxide	Easy removal of COD facilitated

Aim of the beginning: The aim was altered from 25mg/L to 150 mg/L. Due to this, the adsorption capacity of hexavalent chromium enlarged from about 92.87% to 98.71% and the arrangement reached its stability of 100mg/L.

Time of contact: The largest removal capacity was achieved at around 3 minutes and this was kept for about 20 minutes in conjunction with 100mg/L. From this end along, the capacity decreased bit by bit slowly, and it reached the captivation level.

Adsorbent section: The adsorbent section was combined at different levels (0.1 gm to 0.30 gm) to a consistent arrangement level of about 100 gm/L. The removal capability was gradually increased when the section was enlarged. The very ultimate adsorption (98.45%) was accomplished at the part level of 0.25 gm, later the efficiency becomes constant.

Size of the molecule: In this work, the size of the Fine particles was evenly i.e. 150 µm. Cause of this even size there is no crucial alteration in the productiveness of chromium adsorption. Potassium dichromate was utilised as a stable arrangement, cluster adsorption aim was finished and the removal capacity of hexavalent chromium fraction must be discussed in the accompanying categories (51-56).

Neem Leaves

The aqueous arrangement was used for the removal of the Cr6+ by utilizing the powder of Neem leaves as an adsorbent. Solution of Chromium chloride was taken, and it is broken up in refined water. The grouping adsorption method was guided and the removal capability of Cr6+ is discussed in the accompanying categories (29-32).

pH level: The greatest evacuation effectiveness (67.5%) was achieved at pH=4, after that it gradually diminished.

Aim of the beginning: The largest removal capability was accomplished at 98% of the basic collection of 30 mg/100 mL.

Adsorbent section: The removal capacity of chromium metal enlarged when the adsorbent section has been ranged from 2 gm/100 mL to 10 gm/100 mL. The largest removal capability (85%) was achieved at the measurements range of 8 gm/ml and remained constant after that.

Time of contact: The effect of time of contact was not justly discussed in this exploration work. Although, with regards to the diagram the largest removal capability (67.5%) was achieved at the time of 80min and later the efficiency remained constant. **size:** The molecular size was not studied for the adsorbent molecule in this work. But, it is assumed that the molecule size is the important portion in the adsorption capability from the wastewater of continual metals.

7.Rural waste

Used water solution for removal of the Cr6+ by using adsorbent of Activated Carbon Rice straw. In this method, the removal of chromium was achieved by the use of potassium dichromate in purified water with the infatuation from 1.5 to 5 mg/L. The grouping adsorption rate was accomplished and the efficiency of the expulsion of hexavalent chromium was observed in the accompanying pattern (21-24).

pH level: The capacity of removal of chromium metal was done with a pH level of about 2 to 8 with starting chromium gathering of 1.5 mg/L. In this event, the largest removal proficiency (96.72%) was achieved at about pH=8. It is examined that time when the pH was lower the adsorption proficiency also decreased.

Adsorbent section: The section was altered from 2 gm/L to 9 gm/L due to which the removal proficiency of hexavalent chromium was successfully enlarged from 45% to 97.12%.

Time of contact: The removal of chromium was increased at the basic phases and following 100 minutes the removal capability accompanied a constant value. At this place, the removal was certain over the aim.

Aim of the beginning: The centre of chromium was altered from 1.5 mg/L to 6 mg/L. Due to this clarification, the adsorption capability had been diminished from 76% to 46%.
Size of the molecule: The various molecular size of adsorbent are 100, 150 and 200µm. They all were taken for the expulsion of chromium metal and it has been observed that the proficiency slowly decreased from 79.2%to53.3% with the basic collection of Chromium (1.5mg/L)(26-28).

Adsorbent based on Carbon

Adsorbents formed on carbon are nanoporous in the environment, it involves activated carbon, Carbon nanotubes, and Graphene. These adsorbents are specifically used for the elimination of heavy metals having a huge surface area. To increase the efficiency of the elimination of heavy metal by carbon formed adsorbent the surface charges of the functional group are required to be developed. Different techniques can be used to develop the adsorption productivity of the functional group, but this completely rests on the substance of the adsorbent due to few materials are costly. So substance should be chosen remembering the commercial feasibility. It has been declared by different analysts that a high surface area high the adsorption capability.

Biosorbents: Current investigations have observed that biosorption is the most productive method in the elimination from wastewater of heavy metals. It has been studied that there is different functional group like thiol, carboxyl, phosphate, hydroxyl etc enhance the biosorption of wastewater. The reaction through the biosorbent and contamination is achieved by different methods like aggregation, complexation or micro precipitation ion exchange, redox process. pH performs the most vital role in biosorption, it affects the theionisation of functional groups present in biosorbent along with charge density.

CONCLUSION

Including all the chromium present Hexavalent chromium (Cr6+) is a very dangerous metal. It is known as a derivative by numerous factories such as Electroplating, Tanneries. (68). The quantity of hexavalent chromium discharge is mostly high. Hexavalent Chromium can be changed into trivalent chromium and that technique is most expensive and cannot be achieved cause of its commercial interest and as well it is the low moderate method.

According to data as above, it can be decided that sawdust is the only best effective natural adsorbent, it can get rid of 99.9% Chromium from wastewater (69,70). Sawdust has an increased amount of carbon content (approx. 48%) because it is naturally organic (66). hence, it can simply adsorb different heavy metals in both liquids in addition to the gaseous state. It has been examined that a high amount of Agricultural waste (98%) and Bamboo waste (98%) can also adsorb hexavalent chromium. Yet the only disadvantage is that their ability is analysed from the watery solutions, and not among the factories derivative. nevertheless, if these adsorbents are combined in different proportions they will manifest 100% productivity in removing Hexavalent Chromium (Cr6+) from the factories derivatives.

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