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Removal of Chromium (VI) and Fluoride by Various Treatment Methods from Industrial Effluent

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Abstract

Fresh water is vital to human life and economic well-being, and societies extract vast quantities of water from rivers, lakes, wetlands, and underground aquifers but most of these freshwater sources are polluted by different chemicals discharged from industries. Our need for fresh water has long caused us to overlook equally vital benefits of water that remains in streams to sustain healthy freshwater habitats. Wastewater treatment for heavy metal treatment is gaining importance because of the increase in pollution and scarcity of water. Chromium may be person such substantial metal emitted from electroplating, lather, iron and steel commercial enterprises. In the available review, the examination conveyed out to chromium evacuation will be summarized. Those investigation might have been conveyed out on the viewpoints for example, such that Rate removal, effectiveness what's more economy. The second phase of the current review is described about fluoride removal by different methods and removal efficiency. Around a few treatment advances connected to fluoride removal, adsorption transform need been investigated generally what's more offers palatable effects particularly with mineral-based or surface changed adsorbents. In this review, an far reaching rundown from claiming different adsorbents starting with written works need been aggregated what's more their adsorption capacities under different states (pH, introductory fluoride concentration, temperature, contact time, adsorbent surface charge, and so forth.) to fluoride evacuation Similarly as accessible in the written works need aid introduced alongside highlighting and examining those key headway on the preparation of novel adsorbents tried in this way for fluoride evacuation. It will be apparent starting with those writing review that different adsorbents bring indicated great possibility to those evacuations of fluoride. However, even now there is a requirement to figure out those useful utility for such produced adsorbents once a business scale, prompting those change for contamination control.

Keywords: Chromium; Fluoride; Adsorption; Coagulation; Industrial wastewater; Bio-adsorbents; Low cost treatment methods

Introduction

Water and its importance

Water is a chemical compound with the chemical formula H_2O. A water molecule contains one oxygen and two hydrogen atoms connected by covalent bonds. Water is a liquid at standard ambient temperature and pressure but it often co-

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exists on earth with its solid-state ice and gaseous state. Water also exists in a liquid crystal state near hydrophilic surfaces. Water is used for drinking, agriculture practices, and power generation and for industrial activities. 90 % of water is used for irrigation and 10 % is used for drinking and industrial activities. It is used as solvent, solute and catalyst [1].

Water is an important natural resource and without water cannot survive for few hours. Depending on quality of water for consumption, they are classified into two types i.e. potable type and non-potable water. Non potable waters are further classified into two types i.e. grey water and black water. Grey water can be treated and it can be reused by simple techniques. Black water contains sewage and can be made usage by only certain particular techniques and testing for drinking water quality

An increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high level of heavy metals, thereby creating serious environmental disposal problems [1]. Also exponential growth of the world's population over the past 25 years has resulted in environmental buildup of waste products, of which heavy metals are of particular concern. The pollution from industrial and urban waste, effluents and from agrochemicals in some water bodies and rivers had reached alarming level [2]. There are numerous ill effects of pollution, each type of pollutant having different effects, on human and animal health and ecology.

Keeping the water free from any pollutant is very important. Water is said to be "polluted" when it is changed in its chemical, physical or biological quality and composition, directly or indirectly by anthropogenic activities so that, it becomes unsuitable for drinking, domestic, agricultural or other purposes. Polluted water transmits a large number of diseases such as cholera, typhoid, dysentery, jaundice and bacterial or viral disease.

Water Pollution

Water is polluted by four kinds of substances like, traditional organic waste, waste generated from industrial process, Chemical agents for fertilizers and pesticides for crop protections and silt form degraded carbon attachments, while it is estimated, that ¾ of the wastewater generated is from municipal and industrial sources. Water pollution problems in many parts of the world are for worse. Most urban centers in Asia and Africa have no sewage system at all, including many cities with population over 1 million people. The result is tragic rate of morbidity and mortality in the less developed parts of the world. Water borne diseases such as cholera and typhoid; cause more than 1.5 billion episodes of diarrhea each year resulting in 4 million deaths annually [3].

Status of Water Pollution in India and it Impacts on Water Resources

Drinking water for more Indian cities come from rivers, lakes, wells and bore wells. There are fourteen major rivers in India and all of them are subjected to severe contamination and pollution. City sewage, industrial wastes and effluents are major contaminants that pollute the Indian rivers and lakes, due to lack of sewage treatment plants in most of the urban areas of India. Hence only a very small percentage of total Indian population is covered by sewerage facilities including sewage treatment plants. Aquatic life is being destroyed on large scale owing to deleted oxygen levels in river and lake water. Sugar mills, surgical industries, tanneries, paper and pulp mills, power stations, chemical and cement factories, distilleries and other metal working industries are some of the sources which contribute to the pollution of almost all rivers in a big way. These polluted rivers carry water borne disease producing organisms and are responsible for the ill health of the population. Nearly 60 % of all cases of diseases are caused by these water borne organisms.

To minimize the aspects of pollutions and improve environment thereby, Government of India has enacted the water Act 1974 (Prevention and Control of Pollution), and formed the central board for prevention and control of water pollution. The Government is trying to introduce more sewage facilities and sewage treatment plants wherever needed. The above act has regulations and provisions for taking penal action against those who are responsible for water pollution of rivers, estuaries etc.

The Central Ground Water Board (CGWB) assists in monitoring the industrial effluents for pollution load. There is problem of well water pollution by heavy metals and other toxicants in Delhi, Ahmadabad, Rajasthan and other states. All along the course, the river Ganga is polluted at several points. The main problem arises from domestic and industrial wastes. A rough estimate indicates that 27 major cities on the bank of the river alone dump about 1,200 million liters of wastewater into the river every day. There are over 300 industrial units located near the river. At Varanasi, about 6 million devotees take bath every year, besides these, 60 million liters of untreated sewage is dumped by 6 major and 61 small drains of the city daily. The ashes of about 40,000 human bodies and about 10,000 half-burnt bodies are thrown into river every year. About 60,000 car cases of cows, buffaloes and dogs etc, are dumped within the river at Varanasi annually.

Industrial Development & Its Impact on Environment

Industrialization increased the capacity of production of goods and enhances the standards of life. Many chemicals like phenyl, DDT, cleaning lotions, acids are used in day to day life. These chemicals have brought potential dangers due to toxic waste generated during the production and usage. Long term or indiscriminate usage of certain materials may cause cancer, delayed nervous system, malformation and mutagenic changes. Once they enter into water bodies, they disperse and spread from local to global regions causing various problems.

Indian chemical industry is one of the largest and most advanced among the ones in the developing countries. Indian chemical industry produce include, paints, petroleum products, polymers, fertilizers, dyes and dye intermediates, drugs and pharmaceuticals, pesticides, edible and industrial oils, synthetic paints, inks and numerous specially organic and inorganic chemicals [4-7]. Much of the industrial effluents are discharged without treatment to open watercourses, reducing the quality of larger volumes of water and sometimes in filtrating aquifers and contaminating ground water resources. Worldwide, it is estimated that industry is responsible for dumping 300-400 million tons of heavy metals, solvents, toxic sludge and other waste into water each year [8].

During the process of civilization and development, our country (India) has given permission to many pharmaceutical, pesticide, paint, steel, polymer, fertilizer industries to start their production. These industries causing significant change in the water quality due to various activities like discharging untreated waste in the immediate neighborhood or in some nearby low laying areas, mostly in open channels, which join various surface water bodies such as large ponds, streams, rivers etc.

Chromium

Chromium is an odorless and tasteless metallic element with an atomic number of 24 and atomic weight of 51.996. Chromium can exist in nine different oxidation states from -II to +VI. Oxidation states of II, III and VI are the most common with Chromium-III being most stable. Compound with chromium oxidation state of II, are strongly reducing while Chromium-VI compounds are strongly oxidizing state. While -II, -I, 0 and IV compounds, are rare in nature. Chromium-VI is principal species found in surface water and aerobic soils while chromium-III dominates in mildly reducing environments such as sediments and wetlands [9]. Trivalent chromium is an acid that forms strong complexes with various O-N-, and S-containing ligands and many organic compounds. The principal species of trivalent chromium are Cr^{3+}, $Cr\ (OH)^{2+}$, $Cr\ (OH)_3$ and $Cr\ (OH)^4$. The solubility of Chromium-III is limited by the formation of highly insoluble oxides, hydroxides and phosphates and its strong tendency to adsorb to surfaces [10]. There are demonstrated instances of chromium being released to the environment, by leakage, poor storage, or inadequate industrial disposal practices [11].

Uses of Chromium

Metallic chromium is used mainly for making steel and other alloys. Chromium compounds in either the chromium-III or Chromium-VI forms are used for chrome plating dye and pigments, leather and wood preservation.

Health effects of Chromium

The heavy metal chromium toxicity results in damage or reduces mental and nervous functions in human beings. It may reduce the energy levels and damage the blood composition, lungs, kidney, liver and other vital organs [12]. The long term exposure of chromium may results in Alzeimer’s disease, Parkinson’s disease, muscular dystrophy and multiple sclerosis. Cancer may also be cause by contact with continuous exposure of chromium metal or metal containing compounds. Hence, it is essential to learn about exposure of heavy metals like chromium and take protective measures against excessive exposure [13].

Heavy metal Chromium -III has low toxicity and is reported as a nutritionally essential element for human and it is added to vitamins as a dietary supplement. Chromium-VI is more toxic and causes health risks, which causes allergic reactions. The continuous exposure of such chromium states may enter into body through inhalation at work places, neighborhoods or through consumption of food, particularly seed foods and causes several health disorders [14].

Fluoride

Fluoride is the simplest unary fluorine anion, the other being the tentatively investigated difluoridofluorate (F^-) anion. Its salts are important chemical reagents and industrial chemicals, mainly used in the production of hydrogen fluoride for fluorocarbons. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxide ion. Fluoride ions occur on earth in several minerals, particularly fluorite, but are only present in trace quantities in water. Fluorine is considered as an essential element for human beings. In potable waters, a fluoride concentration of 20µg/ml is necessary to prevent tooth decay [15]. However, at higher concentration (>20µg/ml), it has adverse effects such as causing fluorosis. Fluoride toxicity is prevalent in various parts of Andhra Pradesh, Telangana, Madhya Pradesh, Rajasthan and Gujarat [16]. Due to natural as well as anthropogenic causes, the levels of fluoride in ground waters can exceed the permissible levels.

In states like Andhra Pradesh, Telangana, Gujarat, Maharashtra and Rajasthan, the majority of districts contain high levels of fluoride in their routine food and water. In India 19 out of 35 states and union territories, the ground water is highly contaminated with fluoride due to industrial and anthropogenic activities. The fluoride levels in those 19 states are range from 1.0 mg/L to 48 mg/L. The state where fluoride is prevalent is shown in **FIG.1**. The long term use of dental products, anti-depressant and anti-cholesterol is an important source of excess amount of fluoride in human body [17-19].

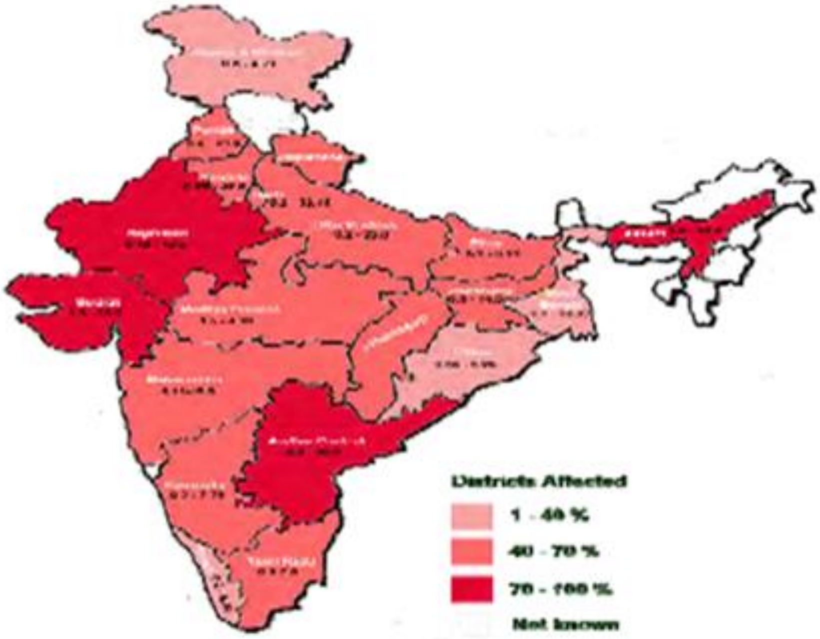

FIG. 1. **Fluoride prevalent states India.**

Health effects of Fluoride

Many of the environmental researchers reported that fluoride is toxic than heavy metal like lead and arsenic. The increase in level of fluoride in ground and surface water due to various industrial activities leads several health disorders. Especially the problem of excess fluoride in drinking water is increasing day by day and excess amount of fluoride shows its effect on Teeth, Bones, Thyroid and Brain and leads to several diseases which called Skeletal Fluorosis and Dental Fluorosis **FIG. 2**. A Significant relationship between fluoride intake by water and prevalence of dental fluorosis has been reported by several researchers [20-24].

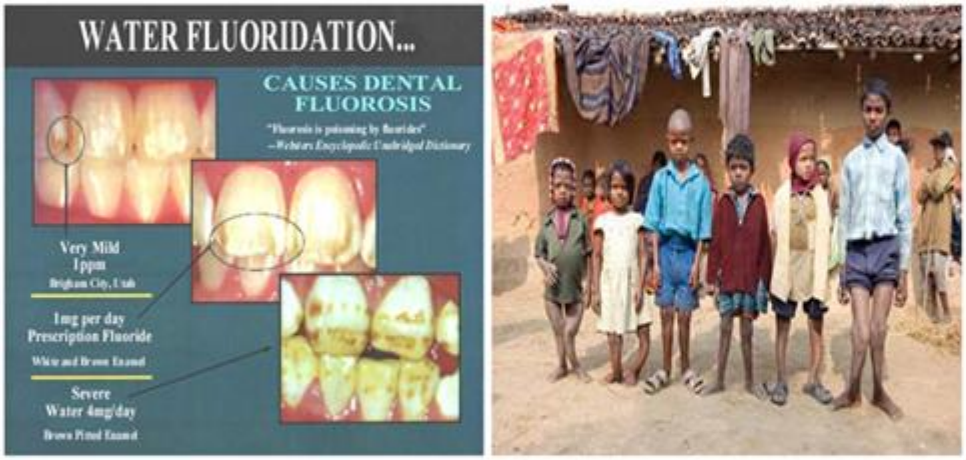

FIG. 2. **Effect of excess amount of fluoride intake on human health.**

Treatment Methods of Wastewater

The various low cost and commercial treatment technologies of wastewater were shown in **FIG. 3**. From the figure and extensive literature survey it came to know that adsorption and coagulation techniques are low cost and eco-friendly technique to treat the wastewaters [25].

An increased use of various chemicals in the process industries has resulted in the releasing of large quantities of aqueous effluents that contain high levels of impurities, thereby creating serious environmental disposal problems [26]. Also exponential growth of the world's population over the past 10 years has resulted in environmental buildup of waste products, of which heavy metals are of particular concern [27]. Heavy metal like chromium, not biodegradable [28] are therefore of great concern because they are being added to soil, water and air in increasing amounts.

Increased knowledge about toxicological effects of pollutants like chromium and fluoride on human and other ecological parameters as well as increased legal requirements for reduction in industrial emissions necessitates research and development in the area of wastewater treatment. Since these pollutants (chromium & fluoride) accumulate in the food chain and because of their persistent nature, it is necessary to remove them from wastewater [29-30].

The need for economical and effective methods for removing chromium and fluoride from wastewater has therefore resulted in the search for other materials that may be useful in reducing the levels of chromium and fluoride in the environment [31]. Existing technologies for these two pollutant removal from wastewaters are costly. They include ion exchange resin, solvent extraction, electrolytic and precipitation processes, electro dialysis and membrane technology [32]. Other conventional technologies which have also been used ranged from granular activated carbon to reverse osmosis. These processes are however, not economically feasible for small scale industries prevalent in developing economies due to large capital investment [33]. Precipitation processes which are the most widely used techniques for treating wastewater with high metal concentrations often results in the production of large volumes of sludge containing high levels of heavy metals. Thus, additional treatment such as coagulation, phytoremediation and adsorption processes are required in order to purify the effluent prior to discharge [34].

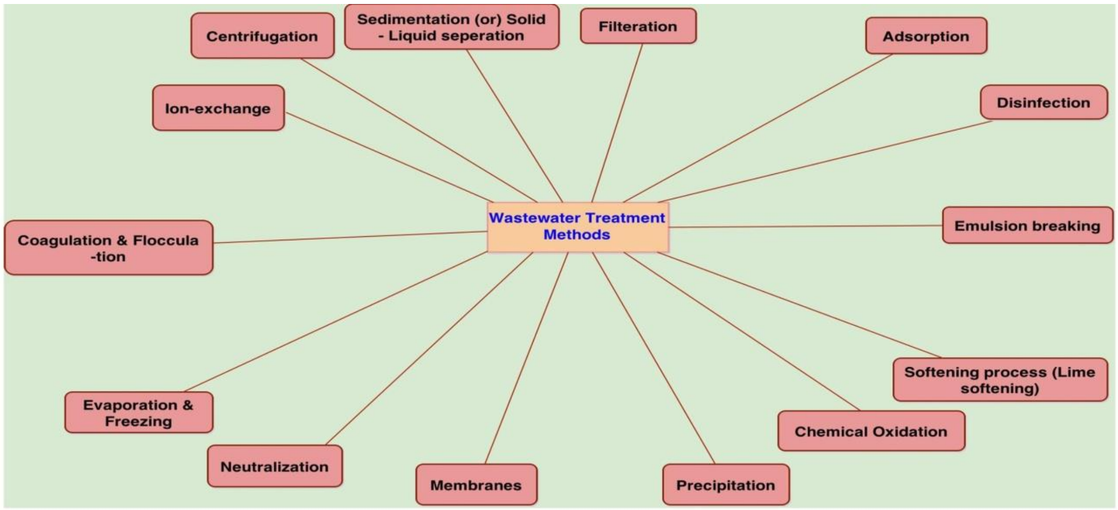

Fig-2.1: various treatment technologies for wastewater treatment

FIG. 3. **Various treatment technologies for wastewater treatment.**

Bio-removal is the accumulation and concentration of heavy metals from aqueous solutions using biological materials [35]. Metals removal has been achieved by adsorption on different materials such as activated carbon, agricultural waste, moss peat, minerals, amongst others [36].

Adsorption

Adsorption is procuring more interest as one of the most effective processes for treatment of industrial effluent containing toxic materials like chromium and fluoride. The occurrence of non-biodegradable wastes in streams and lakes threatens the use of water resources and various treatment methods have been used for the removal of these wastes. Among these methods, adsorption using commercial activated carbon has proven to be efficient, however it is highly expensive. Hence in recent years there has been a continuous search for locally available and cheaper adsorbent [37].

The adsorption phenomenon is impact by the nature of solution in which the contaminant is dispersed, molecular size and polarity of the contaminant and the type of adsorbent. Coagulation and Flocculation are important unit processes for water treatment. For water and wastewater treatment, coagulation and flocculation phenomena are conventional and extremely important. Therefore, it is necessary to do a comprehensive literature review on different sources and characteristics of industrial wastewater. Furthermore, a complete assessment of various treatment methods for wastewater treatment used to remove recalcitrant wastes from industrial wastewater is also important. The present literature review clearly establishes that wastewater treatment using low cost adsorbents prepared from waste from brick, classroom, timber and agricultural fields.

Surface characteristics and pore structures of adsorbents are the main properties in determining adsorption equilibrium and rate properties which are needed for plant design. New adsorbents are continuously being developed, introducing new applications for adsorption technology. Adsorption equilibrium is the fundamental factor in designing adsorption operations.

When adsorption takes place with suspended adsorbent particles in a vessel, adsorbate is transported from the bulk fluid phase to the adsorption sites in the adsorbent particle. In this type of situation, changes in the amount adsorbed or concentration in the fluid phase can be predicted by solving the set of differential equations describing the mass balances in the particle, at the outer surface and between the particle and the fluid phase. Determination of diffusion parameters should be done with a simple kinetic system. These discussions are also applicable to the analysis and design of adsorption operation in a vessel or differential reactor.

Advantages of Adsorption

- Metals at low concentration can be selectively removed.
- Effluent discharge concentration meets the govt. regulation.
- System operates over the broad pH ranges (2-9).
- System is effective over temperature ranges of 4-90ºC.
- System offers low capital investment and low operation cost.
- Convert metal pollutant to metal product.
- System offers simple design, easy operation

Adsorption is a good weapon in the fight against toxic metals threatening our environment.

Types of Adsorption

There are two types of adsorption phenomena, physical adsorption and chemical adsorption [38].

Physical adsorption (Vander Waals adsorption)

Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed. It is a readily reversible phenomenon. In industrial adsorption operations this reversibility is used for the recovery of adsorbent for reuse, for recovery of adsorbed substance or for the fractionation of the mixtures.

Physical adsorption mechanism involves Van der waals' forces of attraction between the pollutant and the cell surface, which is not dependent on the cell metabolism. Tsezos and Volesky [39] verified that thorium and uranium biosorption by fungal biomass of *Rhizopus arrhizus* is based on physical adsorption in the cell- wall chitin structure. Kuyucak and Volesky [40] hypothesized that uranium, cadmium, zinc,copper and cobalt biosorption by dead biomass of algae, fungi and yeast takes place through electrostatic interaction between ions in solution and cells walls. Physical adsorption is furthermore responsible for copper, nickel, cadmium, zinc and lead biosorption by *Rhizopus arrhizus* [41].

Chemisorption

Chemisorption is the result of chemical interaction between the solid adsorbent and the adsorbed substance. The adhesive force and the heat liberated are much greater those that found in physical adsorption. The process is frequently irreversible. Some substances under condition of low temperature undergo only physical adsorption substantially. But they exhibit chemisorption at high temperatures and sometimes both the phenomena may occur at the same time. Chemisorption is of particular importance in catalysis.

Adsorption Mechanisms

The complexity of the adsorbent structure implies that there are many ways for the metal to be captured by the cell. Adsorption mechanisms are therefore various and in some cases they are still not very well understood. Metal adsorption and biosorption onto agricultural wastes is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption [42-43]. They may be classified by the following different criteria.

Types of Adsorbents

Most of the adsorption researches have been concentrated on the use of bacteria and fungi for the removal of heavy metals. Both viable and inactive cells have been studied. This generally involves culturing of these microorganisms using chemicals. A potential economical alternative would be to use, naturally abundant materials such as waste biomass. These natural materials can be easily processed and used for metal removal, and hence can offer an economical solution to the problem of water pollution.

Adsorbents for Chromium Removal

Among various available technologies for water pollution control listed above **(FIG. 3)**, adsorption process is considered better as compared to other methods because of convenience, easy operation and simplicity of design. Further, this process can remove and minimize different types of pollutants and thus it has a wider applicability in water pollution control. The removal of chromium (VI) by algae **(TABLE 1)**, fungi **(TABLE 2)**, bacteria **(TABLE 3)**, conventional adsorbents **(TABLE 4)** and non-conventional adsorbents **(TABLE 5)** were confirming that adsorption process has a wider application and better removal efficiency.

As the biosorption process of Cr (VI), involves mainly cell surface sequestration, cell wall modification can greatly alter the binding of metal ions. A number of methods had been employed for cell wall modification of microbial and plant derived biomass in order to enhance the chromium binding capacity of biomass and elucidate the mechanism of biosorption. The chromium adsorption capacity by different microbial, plant based and other low cost adsorbents were tabulated in **TABLE 6**.

Adsorbents for Fluoride Removal

Many researchers reported successfully fluoride remediation using different, conventional and non- conventional methods. An adsorption process considered better as compared to other methods because, a wide variety of adsorbents and their modifications have been tested for the removal of fluoride from water with 80-99 % removal efficiency. These investigations concluding that suitability of adsorption process for the removal of fluoride. The adsorbents tested for removal of fluoride include activated carbons prepared from biological sources, conventional adsorbents i.e. resins, activated alumina, bauxite, hemalite, polymeric resins, non - conventional and low - cost adsorbents which represented in **TABLE 7**.

Adsorbent	Conditions	Initial Cr(VI) concentration	Maximum removal	Reference
*Sargassum*Sea weed (marine algae)	Batch reactor non-living cells, dose=2.5g/L, 22^0C, pH=3.5, 10-60mins	10-100 (mg/L)	60(mg/l,40mins) KF=0.365 n=1.23 R^2=0.99 Q_0=114, b=4.44 R^2=0.99	Barkhordar and Ghaiseddin,2004 [44]
Sargassum wightii (Greville)	Batch adsorption, living cells, 22^0C, pH=3.5, 10 min-24 hrs	50 - 400 mg/L	Maximum removal 55.39 % at 50 mg/L initial chromium concentration, optimum pH 4, optimum biomass 8 gm/L, optimum contact time 12 hrs.	Abirami et al., 2012 [45]
Chlorella vulgaris *Chlorella crispate*	Batch reactor non-living cells, 25-35^0C, pH=1.0-5.0, 30-60mins	0-200 (mg/L)	2.98(mg/g/min) (pH=1.0-2.0, 35ºC) KF=4.99, 2.236. 20mg/g/min (pH=1.0-2.0,25ºC) KF=3.86, n=2.02	Nourbakashet et. al., 1994 [46]
Azolla caroliniana (fresh mass)	Batch adsorption, living cells, 22^0C, dosage 0.1 - 1.1 gm, 10 min-24 hrs	50 - 400 mg/L	Optimum contact time 11 days with a optimum dosage of 1 gm.	Bennicelli et al., 2004 [47]
Sptrogyraspecies *(*greenfilamentou salgae)	Batch reactor non-living cells, 25-35^0C, pH=1.0-6.0, 180mins, dose=1-15g/L	1-25(mg/L)	90%, (pH=2.0,120mins,5g/L) Q0=14.70 b=0.2, R^2=0.99	Gupta et al.,2001[48]
Padina tetrastromatica Hauck (Brown algae), *Gracilaria edulis S.G Gmelin* (Red algae) and *Ulva* *reticulata Forsskal*(Green algae)	Batch adsorption, living cells, pH 2-4.5, dosage 1-12 g/L, contact time 1 - 12 hours	1-500 mg/L	An increase in pH increases the rate of Bio sorption and at pH-4, all the seaweeds obtained maximum biosorption efficiency. Maximum of 50.85% of chromium was removed by powdered biomass of *Padina tetrastromatica*	Abirami et al., 2013 [49]

TABLE 1. **Biosorption of Chromium (VI) from aqueous solution by various algal biomasses.**

Adsorbent	**Conditions**	**Initial Cr(VI) concentration**	**Maximum removal**	**Reference**
Aspergillus sp.(filamentous)	Batch reactors, non-living cells, pH=2.0-6.0, dose=4.5g/L 150 rpm, 8h, 30^{0}C	50-500(mg/L)	10-27.5mg/g (pH=2.0,2h) Q0=29.2, b=.03 R^2=0.954, KF=6.8, n=4.5 R^2=0.987	Sen et al.,2010 [50]
Fusarium sp.(filamentous)	Batch reactors, non-living cells, pH=1.0-6.0, dose=4g/L 150 rpm, 8h, 30ºC	50-500 (mg/L)	12.5-47.5 (mg/g) (pH=2.0,2h) Q0=50.25, b=0.03 R^2=0.975 KF=7.90, n=3.12 R^2=0.996	Sen et al., 2005 [51]
Candida utilis & different species of yeast	Batch reactor, resting dehydrated cells, 30ºC, 72 hours	150 mg/L	9.0 mg/g, dehydrated cells	Rapport & Muter 1994 [52]
R. arrhizus S.cerevisiae	Batch reactors, non-living cells, PH=1.0-5.0, 25-30ºC, 30-60 mins	0-100 (mg/L)	8.40(mg/g/min) (pH=1.0-2.0, 35ºC, 60mins) KF=4.53, n=1.784. 30(mg/g/min) (pH=1.0-2.0, 35ºC, 60mins) KF=1.59, n=1.82	Prakasham et al., 1998 [53]

TABLE 2. **Biosorption of Chromium (VI) from aqueous solution by various fungal biomasses.**

Adsorbent	**Conditions**	**Initial Cr(VI) concentration**	**Maximum removal**	**Reference**
Bacillus circulans bio film	Batch adsorption non-living cells, pH=2.0-7.0, 30ºC, 24-96h, 120rpm	50-500 mg/L	48% removal at (pH=7.0, 96h)	Khanafari et al., 2008 [54]
Bacillus cereus, Bacillus pumilis, Pantoea agglomerans.	Batch adsorption living cells,	10-300 mg/L	62-68, 58-62, 65-69 % removal at pH 2 and 3 respectively (1-2 h)	Sikander sultan et al., 2012 [55]
Bacillus circulan, Bacillus megaterium, Bacllus coaglans	Batch reactors, resting cells, pH= 2.5, 150rpm, 24h, 28ºC.	0-100mg/L	34.5(mg/g), 32(mg/g) and 23.8(mg/g)	Srinath et al., 2002 [56]
Microbacterium liquuefaciens MP30	Batch bio reactor resting cells immobilised in (PVA) alginate beads, 100rpm, 30ºC, 4d Continues flow bioreactor, flow rate=0.95mL/h,20d	100μm 50μm	Complete removal (90%removal)	PattanapipitPaisal et al.,2001 [57]
Distillery sludge	Batch reactor non-living cells, dose,1-20g/L, pH=3.0-10.0, 30ºC, 150min	10-40mg/L	64% (pH=3.0, 5g/L, 105 mins) Q0=5.7, b=0.49 K$_f$=2.05,n=3.91	Selvaraj et al., 2003 [58]
*Zoogloearamiger*a	Batch bioreactor, non-living cells, pH=2.0,100rpm,25ºC, 60mins	0-75(mg/L)	3.40(mg/g/min)KF=2.02,n =2.0	Nourbaksh et al., 1994 [59]

TABLE 3. **Biosorption of Chromium (VI) from aqueous solution by various bacterial biomasses.**

Adsorbent	Conditions	Initial Cr(VI) concentration	Maximum removal	Reference
Activated carbon & Bentonite	Batch adsorption, pH 2-6, dose 0.5 - 4.0 gm, 0-2 hours contact time	2- 600 mg/L	69 % removal with activated carbon, 73 % with bentonite at pH 2, optimum dosage 4 gm/L.	Wanees et al., 2012 [60]
Activated carbon from agri waste	Batch adsorption, Cornelian cherry, apricot stone and almond shells, pH 1-4, 0-200 rpm	20- 30 mg/L	99.99 %, 90.90 % and 99.99 % removal observed at pH 4, 200 rpm with 70 hours contact time	Bahadur & Mishra 2014 [61]
Zeolite Nax	Batch adsorption, pH 4 -7, 0-2 hours, 292 - 308 K temperature	5 - 50 mg/L	Maximum % removal at pH 4 with 60 min, contact time. Qo = 60414 mg/g, b =0.0357 L/mg, Kf = 0.3866, n = 1.583,	Pandey et al., 2010 [62]
Anion exchange resin	Batch adsorption, pH 2-11, dosage 0.4 - 2 gm/L	20 - 300 mg/L	Maximum removal observed at 120 mints with 1 gm/L adsorbent dosage	Rashid et al., 2014 [63]
Spectra/gel ion exchange resin	Batch adsorption, pH 2-11, dosage 0.4 - 2 gm/L	20 - 300 mg/L	Maximum removal observed at 120 mints with 1 gm/L adsorbent dosage	Barakat et al., 2013 [64]
Amberlite IRA 743 resin	Batch adsorption, pH 3-11, 0-2 hours,	0 - 500 mg/L	Optimum pH 3, optimum contact time 30 min, and it fitted into Freundlich isotherm model	Rajiv Gandhi et al., 2010 [65]

TABLE 4. **Adsorption of Chromium (VI) from aqueous solution by various conventional adsorbents.**

Adsorbent	Conditions	Initial Cr(VI) concentration	Maximum removal	Reference
Plataneus orientalis leaves	Batch pH=3.0-9.0 Dose=2.0g/L,20-30^{0}C, 300rpm, 30-240mins	2.0-40	5.01(mg/g) (pH=7.0,24^{0}C,120mins) Q0=5.7,b=0.29, R^2=0.956 and K_f=2.02,n=2.0,R^2=0.646	Mahvi et.al., 2007 [66]
Terminalia catappa leaves	Batch, Particle size 90μm, pH 2-8	2.0-80	5 gm/100 ml, (pH =2, 25 hours at room temperature with 83% removal, K_f =7.5x10-3, 1/n = 0.97	Enemose & Osakw, 2012 [67]
Plant *ulmus* leaves	Batch, pH=3.0-9.0 Dose=2.0g/L20-30^{0}C 300rpm,30-240mins	2.0-40	0.9(mg/g), 5.0(mg/g), (pH=6.0,240C,60mins,)	Gholami et al., 2006 [68]
Pine needles powder	Batch, dose 0.1 - 1.1 gm, pH= 2-7, 50-200 rpm, 125 -500 μm particle size	50-400	0.5 mg/L, pH= 3, 170 rpm, 125 -180 μm, with 45 minutes optimum contact time	Reza et al., 2011[69]
Rice hulls	Batch pH=2.0-8.0 30^{0}C	20-200	99-38% removal at optimum (pH=2.0)	Cici & Keles,1990 [70]
Azadirachta indica leaves	Batch, pH 1-6, dosage 2-10 gm,	10- 40	8gm/100ml (98 % removal), 30 mg/100ml (85% removal), pH =4.1 with 67.5% removal	Parineeta & Shubhangi, 2013 [71]
Lignocellul-osic material peat	Batch pH=2.0-7.0 Dose=1.0g/L,30^{0}C	10-200	30.16(mg/g) (pH=6.0)	Dean & Tobin,1999 [72]
Orange peel powder	Batch, dose= 1-5 gm/250 ml, pH=1-3, 75-180 rpm, 30^{o}C	1-5 ppm	pH=1, 180 rpm, 180 mesh size at 30oC, with a 98-99 % removal	Nitin & sapkal 2014 [73]
Plant water hyacinth: (*Eichhorniacrassipes*)	pH=2.0-6.0 30^{0}C, 8h	10	6.0(mg/g) (pH=6.0)	Lytle et.al., 1998 [74]

TABLE 5. **Adsorption of Chromium (VI) from aqueous solution by various non-conventional adsorbents.**

Microorganisms	**Adsorption capacity (mg/g)**	**Reference**
Fungi		
Arthrobacter viscous	12.6	Silva et al., 2009 [75]
Aspergillus awamori	-	Gochev et al., 2010 [76]
Aspergillus foetidus	-	Prasanjit and Sumathi, 2005 [77]
Aspergillus niger	-	Goyal et al., 2003 [78]; Ahluwalia and Goyal, 2010 [79]
Aspergillus niger	117.33	Khambhaty et al., 2009 [80]
Aspergillus parasiticus	0.587	Shugaba et al., 2012 [81]
Aspergillus sydowi	1.76	Kumar et al. 2008 [82]
Aspergillus terreus	96.5	Dias et al., 2002 [83]
Bacteria		
Staphylococcus xylosus	143	Ziagova et al., 2007 [84]
Thiobacillus ferrooxidans	-	Celaya et al., 2000 [85]
Ochrobactrum anthropi	-	Ozdemir et al., 2003 [86]
Pseudomonas sp.	95	Ziagova et al., 2007 [84]
Algae		
Chlorella vulgaris	3.5	Nourbakhsh et al., 1994 [59]
Cladophora crispate	3	Nourbakhsh et al., 1994 [59]
Kappaphycus alvarezii	0.86	Kang et al., 2011 [87]
Pachymeniopis sp.	225	Lee et al., 2000 [88]
Spirulina sp.	90.91	Rezaei , 2013 [89]
Non-Conventional adsorbents		
Calotropis procera	32.26	Overah, 2011 [90]
Palm tree Branches	-	Shouman et al., 2013[91]
Wheat bran	0.94	Nameni et al., 2008 [92]
Sunflower head waste	7.85	Jain et al., 2013 [93]
Raw rice bran	0.07	Oliveira et al., 2005 [94]
Litchi chinensis Sonn Peel	-	Acosta-Rodriguez et al., 2012 [95]
Eucalyptus bark	-	Sarin and Pant, 2006 [96]
Ecklonia	233	Park et al., 2005 [97]
Almond Green Hull	2.04	Sahrananvard et al., 2011 [98]
Banana Skin	249	Park et al., 2008 [99]
Cupressus Female Cone	119	Murugan and Subramanian, 2003 [100]

TABLE 6. **Adsorption of Chromium (VI) by various non-conventional bio adsorbents.**

Adsorbent	**Concentration range (mg/L)**	**pH range**	**Temperature range (°C)**	**Contact time (min)**	**Surface area (m^2/g)**	**Model used to calculate adsorption capacity**	**Maximum adsorption capacity (mg/g)**	**Reference**
Activated carbon (rice straw)	5-20	2-10	25-55	60-1440	122.9	Langmuir	18.9	Daifullah et al., 2007 [101]
Activated carbon (*Morringa Indica*)	2-10	2-12	30-50	5-40	-	Langmuir	0.2314	Karthikeyan et al., 2011 [102]
Activated carbon (*Acacia farnesiana*)	1.5-15	5-8	Ambient	5-70	720	Freundlich	2.622	Hanumantharao et al., 2011[103]
Activated carbon (*Pithacelobium dulce*)	1-8	6-9	Ambient	10-120	-	Freundlich	1.9333	Emmanuel et al., 2008 [104]
Activated carbon (*Arachis hypogia*)	2-10	3-12	30-60	60-120	2.12	Freundlich	14.79	Alagumuthu et al., 2010 [105]
Activated carbon (*Cynodon dactylon*)	2-10	Neutral	30-60	15-195	7.3	Langmuir	4.755	Alagumuthu et al., 2011 [106]
Activated carbon (*Anacardium occidentale*)	2-10	3-12	30-60	60-210	-	Langmuir	1.95	Alagumuthu and Rajan 2010 [107]
Activated carbon (pecan nut shells)	5-40	Neutral	30	2160	17	Langmuir	2.3	Hernandez et al., 2012 [108]
Alginate (*Ulva japonica*)	21-252	2-11	30	1140	-	Langmuir	39.9	Pandey et al., 2012 [109]
Aluminum modified zeolitic tuff	0.5-10	5.5-8	Ambient	50-4320	139.22	Langmuir-Freundlich	10.25	Teutli et al., 2014 [110]
Aluminum (hydr)oxide coated pumice	5	3-11	20	0-4800	1.5	Langmuir	7.87	Salifu et al., 2013 [111]
Alginate entrapped Fe(III)-Zr(IV) binary	10	2-12	10-50	5-300	74.61	Langmuir	0.981	Swain et al., 2013 [112]

mixed oxide								
Apatitic tricalcium phosphate	30-60	4-11	20-40	90	-	Langmuir	15.15	Mourabet et al., 2015 [113]
Cerium dispersed in carbon	2.8-8.3	5.5-9	25-65	5-60	685	Langmuir	209	Liu et al., 2012 [114]
Calcined Mg/Fe layered double hydroxide	5-50	2.5-11	25	0-600	145.3	Langmuir	50.91	Kang et al., 2013 [115]
Calcium chloride modified natural zeolite	25-100	4-9	25-45	5-1200	-	Langmuir	1.766	Zhang et al., 2011 [116]
Cellulose@ HAP nanocomposites	5-10	4-9	25	5-700	76.257	Freundlich	2.76	Yu et al., 2013[117]
CeO2-ZrO2 nanocages	5-40	2-8	25-55	0-1440	29.61	Langmuir	175	Wang et al., 2013 [118]
Fe-Al-Ce nano-adsorbent	42	6.5-7.5	Ambient	2160	-	Langmuir	2.77	Chen et al., 2011 [119]
Fe-Al-Ce hydroxide	10-250	7	25	1440	56.4	Langmuir	51.3	Zhao et al., 2012 [120]
Fe-Ti oxide nano-adsorbent	50	6.9	Ambient	720	-	Langmuir	47.0	Babaeivelni et al., 2013 [121]
Graphene	5-40	3.6-10.2	0-50	1-110	3.08	Langmuir	48.31	Li et al., 2011 [122]
Hydrogen peroxide modified pumice	5-20	2-10	10-50	0-210	53.11	Freundlich	11.765	Sepehr et al., 2013 [123]
Hydrous bismuth oxides	10-35	4-12	20-40	60-360	76.042	Langmuir	1.93	Chai et al., 2013 [124]
Hydrous zirconium oxide	2-120	3-10	25	5-700	134	Freundlich	124	Dou et al., 2012 [125]
HFO doped alginate beads	5-10	3.5-9	20-40	0-3600	25.80	Langmuir	8.90	Sujana et al., 2013 [126]
HAP nanoparticle	10-50	2-11	25-55	60-1440	-	Langmuir-Freundlich	40.818	Zhang et al., 2012 [127]

Mg-doped nano ferrihydrite	10-150	1-10	20-45	30-480	248.6	Langmuir	64	Wajima et al., 2009 [128]
Meixnerite (calcined)	12.4-248	-	20	30-1800	-	Langmuir	56.8	Guo and Reardon 2012. [129]
Nitrate containing ZnCr layered double hydroxides	0-100	3-10	Ambient	0-1440	12	Langmuir	31	Koilraj and Kannan 2013 [130]

TABLE 7. **Adsorption of Fluoride by various conventional and non- conventional adsorbents.**

Coagulation-Flocculation

Water pollution can be attributed to discharge of untreated waste, dumping of industrial effluent, and run-off from agricultural fields. Impurities lay in water are in the general colloids size and are negatively charged. To remove colloidal impurities from water, numbers of methods are used and among all the methods, Coagulation/Flocculation is an important unit processes for this purpose. In water and wastewater treatment, coagulation and flocculation phenomena has been practiced from earliest times, using a variety of substances. The process of withdrawing the forces those stabilizes colloidal particles and causing aggregation of colloidal particles is called *Coagulation*/*Flocculation*. Coagulation-Flocculation is a combination of the *Coagulation*, *Flocculation*, *Sedimentation* and *Filtration*.

Materials used in Coagulation-Flocculation

Aluminum [Al (III)] and Iron [Fe (III)] based coagulants and their composites, and synthetic organic coagulants are used for water and wastewater treatment. Among them Polyaluminum chloride (PACl), a polymerized inorganic coagulants is widely used for it. Moreover, the natural materials (coagulants) obtained from microorganisms, animals, plants, vegetables and derivatives of the mineral origins have also been used for water and wastewater treatment. Among plant materials that have been tested over the years, the seeds from *Moringa Oleifeira* (*MO*) have been shown to be one of the most effective primary coagulants for water treatment. Organic polymers have potential limitations and due to concern over human health, most of the countries are prohibiting the use of organic coagulants. Polymerized inorganic coagulants have been developed and used in water and wastewater treatment. Polymerized inorganic coagulants have been shown their superior performance in water and wastewater treatment. These coagulants have high content of polymeric species and showed better coagulant efficiency compared to traditional coagulants.

Coagulation-Flocculation is the most widely applied process for the production of potable water as well as for the treating the wastewaters [131-132]. The present research work is focused on *Coagulation-Flocculation* process. The factor that stabilizes colloidal particles must be overcome and individual colloids must aggregate and grow bigger if they are being separated from suspension during coagulation. The process of destroying the stabilizing forces and causing aggregation of colloidal particles is called *Coagulation* [133]. Coagulation and Flocculation are important *unit processes* for water treatment. For water and wastewater treatment, coagulation and flocculation phenomena are conventional and extremely important. In the area of potable water treatment, clarification of water with coagulating agents has been practiced from ancient times, using variety of chemicals. In modern water treatment plants the coagulation and flocculation are still essential components of the overall suite of treatment processes. The need for a profound understanding of coagulation-flocculation processes is important today as it had been in the past. The commonly used coagulants divided into two general categories are metal coagulants and polymerized metal coagulants based on *Al* and *Fe* [134].

Coagulants for Chromium Removal

The several studies concluded that the removal of chromium my shown high % removal with electro coagulation technique [135-138], very less data is available on plant based and eco - friendly coagulant for removal of chromium.

Coagulants for Fluoride Removal

Most of the researchers developed defluoridation methods among them coagulation method is wide accepted method with high % removal of fluoride from water and wastewaters. The literature review concluded that most of the work carried with inorganic coagulants, salts of Al, Mg, Fe and electro coagulation methods [139].

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