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A Synoptic Review on Composite Adsorbents to Remove Heavy Metals from Industrial Wastewater

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Abstract – *In the present article, technical feasibility and economic viability of non-conventional adsorbents for heavy metal removal from industrial wastewater has been reviewed and studied. The treatment of industrial wastewater is critical concern, particularly removal of heavy metals because they are intractable and persistence in the environment. Many industries are generating large quantity of wastewater with high concentration of heavy metals like Ni, Cd, Cu, Zn, Pb, Cr and CN due to metal based substances used while manufacturing. Even low concentration of heavy metals in water causes many adverse effect and severe diseases to human. Removal of contaminates from industrial wastewater is done by different conventional adsorbents like activated alumina, bauxite zeolite & activated charcoal but they are costly and not readily available nearby places. In last 30 years, few researchers successfully developed non-conventional and composite adsorbents from waste and naturally available material. Adsorption equilibrium models like Langmuir, Freundlich, Ridlich Peterson and other Isotherm are also used to understand the mechanism to develop new efficient adsorbent. Adsorbents are also characterized by X-ray Diffraction, Scanning Electron Microscope, Fourier Transform Infrared Spectroscopy, X-ray Fluorescence and Brunauer Emmette Teller Device to correlate the adsorption capacity. However, still there is scope to carry out research to achieve more heavy metal removal efficiency at low cost by modifying and developing composite adsorbent and to use it practically at large scale.*

Keywords- *Adsorption, Heavy Metal, Industrial Wastewater, Isotherm, Low Cost Adsorbents.*

INTRODUCTION

In last few decades, concentration of heavy metals in industrial wastewater while manufacturing are enormously increased due to more metallic items or metal based substances have been used by various industries like leather, tannery, textile, pigment, dyes, paint, wood processing, petroleum refining, photographic film production, fertilizer, paper, pesticides, metallurgical, galvanizing, metal finishing, power generation, electronic device manufacturing, mining, etc. Water contamination by toxic heavy metals such as Cr, Cd, Cu, Ni, Hg, Zn, Pb, As, Se, etc. is a big concern, which needs significant attention [1]. Heavy metals are well known for their toxicity and persistency. Mostly heavy metals are non-biodegradable, they find their way into water bodies and their presence in water may pose serious threats to all forms of life by accumulation in biota. When accepted levels of heavy metals are exceeded, it damages vital organs of the body such as kidney, liver, brain, reproductive and nervous system [2]. Heavy metals removal from aquatic effluent can be achieved using various conventional methods like chemical precipitation, ion exchange, electro dialysis, reverse osmosis, coagulation, membrane separation, etc. These methods are not very effective, are costly and require high energy input. They are also associated with generation of toxic sludge, disposal of which renders it expensive and non-ecofriendly in nature [3]. Heavy metals are generally considered to be those elements having an atomic weight between 63.5 and 200.6 and density 5 gm/cm^3. A large number of elements fall into those category, but a few of the highly toxic heavy metals are listed in Table 1.1. Various agencies and regulatory body have recommended safe levels for heavy metals for the protection of drinking water and aquatic life, which are given in Table 1.1. Although, awareness of metal poisoning has been rising in recent years, removal of metals ions from wastewater in an effective manner has become an important issue today. Owing to strict regulation and increased concern about heavy metals, this research focus is on the development of efficient and economical technologies for industrial wastewater purification.

Table 1 Source, Permissible Limits and Health Effects of Various Toxic Heavy Metals [1]

Heavy Metals	Sources	WHO Permissible Limit for Portable Water, mg/L	Potential Health Effects
As	Electronics, Metallurgical	0.01	Vascular Disease
Cd	Agricultural, fertilizers, Electronics, Metallurgical	0.003	Kidney Damages, Human Carcinogen
Cr	Metal Finishing, Electroplating	0.05	Headache, Diarrhoea, nausea, Vomiting,
Cu	Metal Finishing, Electroplating	2	Liver Damage, Insomnia
Ni	Metal Finishing, Electroplating, Metallurgical	0.02	Asthma, Nausea, Human Carcinogen
Zn	Fertilizers, Mining Operations	3.0	Depression, Neurological Signs
Pb	Electronics, Metallurgical, Waste Disposal	0.01	Damage to Brain, Kidney, Nervous System
Hg	Electronics, waste disposal	0.001	Damage to Kidney, Nervous System

Heavy metals are toxic to human beings and animals. The metals get bio-accumulated and tend to biomagnified along the food chain. Thus, the organisms at higher trophic level are more susceptible to be affected by their toxicity. The high concentration of heavy metals found in drinking water source has raised concern in many parts of the world. Treating the industrial effluents contaminated with heavy metals within the industrial premises before being discharged is efficient way to remove heavy metals rather than treating high volume of wastewater or water in a general treatment plant [2]. Various conventional processes for removing heavy metals from wastewater, such as chemical precipitation, coagulation-flocculation, adsorption, ions exchange, membrane separation and electrochemical deposition have been developed in recent years. The adsorption process implies the presence of a solid adsorbent that binds molecules/ions by physical attractive forces, ion exchange and chemical binding. There are different types of adsorbent such as mineral, organic or biological origin, zeolites, industrial by products, agricultural waste and polymers materials.

TOXICITY AND SOURCES

Heavy metals are a natural constituent on earth commonly known with properties such as having persistence, high toxicity and also serving as non-biodegradable pollutants when they accumulate in the ecosystem. Source of heavy metals that penetrate into the water system can derive from both natural and anthropogenic sources. The main source of heavy metals contamination or generation involves urban industrial wastewater. The presence of heavy metals in the heavy metals in the environment leads to a growing number of environmental problems such as deterioration of several ecosystems due to its persistence accumulation. Heavy metals are toxic and carcinogenic elements, which causes serious lung and kidney problem, aside from gastrointestinal distress, pulmonary diseases and many other serious diseases [9].

CONVENTIONAL PROCESS

Many treatment technologies are used for heavy metals removal form wastewater and these are classified into biological, chemical, and physical processes. But for the removal of heavy metals biological treatment are not used as they are less efficient. The conventional technologies for heavy metals removal are chemical precipitation, membrane filtration, reverse osmosis, electro dialysis, solvent extraction, evaporation, oxidation and adsorption. Chemical precipitations are widely used for heavy metals removal but disposal of large quantity of sludge creates more critical problem. The negative and positive points of the conventional methods are given in Table 2

Table 2 Technologies for Heavy Metal Removal [1]

Technology	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy cost and formation by-product
Ion Exchange	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
Membrane Filtration	Good removal of heavy metals	Expensive
Coagulation-flocculation	Economically feasible	High sludge production
Electrochemical Treatment	Rapid Process and effective for certain metals	High energy cost
Ozonation	Applied gaseous state	Short Life
Electrokinetic Coagulation	Economically feasible	High sludge production
Biological Treatment	Feasible in removing some metals	Technology yet to established
Adsorption	Flexibility and Simplicity of design, Ease in Operation and Insensitivity to toxic pollutants	Adsorbents requires regeneration

The problems faced while using conventional methods are high consumption of reagent, energy, low selectivity, high operational cost, generation of sludge, technical feasibility and less efficiency. It is need of hour to develop the alternative source to swap the conventional methods.

ADSORPTION PROCESS

It is a mass transfer process in which a substance is transferred from the liquid phase to the surface of a solid due to physical and chemical interaction. Due to simplicity, flexibility, economy and efficiency, adsorption process can be used as best option for removal of heavy metals form industrial wastewater. Few researchers also carried out research on new adsorbent successfully and proved that it can be used as alternative adsorbent. However efficiency and economy is concern it needs more research [9]. Interrelation between adsorbent and adsorbate are studied by many adsorption models like Langmuir isotherm model, Freundlich isotherm model, pseudo first order, pseudo second order kinetic models and other empirical equations.

ADSORPTION ISOTHERM

There are several isotherm is used to study the mechanism and interrelation between adsorbent and adosorbate, however the well-known and more suitable adsorption isotherm models are Langmuir and Freundlich isotherm.

Langmuir Isotherm: In this model, molecules are adsorbed at a fixed number of well-defined active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of mono molecular layers and there is no interaction between the adsorbed molecules [25].

$$Qe = \frac{Qmax(b * Ce)}{1 + b\ (Ce)}$$

Where Qe is the metal adsorption capacity of adsorbent and intensively depends on the physical and chemical properties of adsorbent and adsorbate.

Freundlich Isotherm: This model interprets the adsorption on homogeneous surface with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorption.

$$Qe = \frac{Kf\ (Ce)}{n}$$

Where Kf is the adsorption equilibrium constant while 1/n is the heterogeneity factor which is related to the capacity and intensity of the adsorption and Ce is the equilibrium concentration in mg/L. When the adsorbate concentration increases, the concentration of adsorbate surface also increase and correspondingly, the sorption energy exponentially decreases over the completion of the sorption center of the adsorbent [26].

ACTIIVATED ALUMINA AND BAUXITE

Activated alumina consists of hydroxylated alumina oxide, Al2O3. They are porous solid made by thermal treatment and effective to carry adsorption process. Bauxite consists of mainly alumina hydroxide minerals but also contains small and variable amounts of silica, iron oxides hematite oxide and alumina silicate clays. Its surface area is in range from 25 to 250 m^2/g and therefore widely used in place of alumina.

ZEOLITE AND ION EXCHANGE RESINS

There are more than 40 natural and 100 synthetic zeolites. They are also considered as selective adsorbents. Zeolite has surface area in the range of 1 to 20 m^2 /g. Ion exchange resin also used for removal of specific organic compounds.

ACTIVATED CARBON

Activated carbon is a typical, most famous and widely used adsorbent in wastewater treatment throughout the world. Activated carbon can be prepared from a variety of carbon containing materials such as pinewoods, rice husk, palm shell, sawdust, anthracites, coconut shell, etc. The activated carbon generally exists in two forms powdered and granular form. Moreover granular form is more used due to continuous contacting.

MODIFIED ACTIVATED CARBON

It has been observed that modification of activated carbon by different chemical treatment increases adsorption capacity. Surface area, structural, and chemical properties can be changed by various oxidizing agents such as H_2O_2, $HClO_4$, HNO_3, HCL, NaOH, KOH, etc.

LOW COST ALTERNATIVE ADSORBENTS

Activated carbon is widely used all over the world to remove wide variety of contaminates from wastewater as well as water. However, it has restrictions of availability at low cost and in sufficient quantity therefore researcher looking for new alternative adsorbents which is of low cost and easily available. Few efforts have been made to develop low cost adsorbents from easily available material and they are classified according to availability source as natural material, agricultural waste and industrial waste [27].

Naturally Occurring Materials: Some of materials investigated successfully and used as adsorbents are chitin, peat, natural coal, bentonite, clay, etc. It is found that particular natural material is effective to remove particular contaminates form wastewater.

Agricultural Waste as Adsorbents: Many agricultural wastes like peanut shell, rice husk, orange peels, banana peels, etc. are causing problem of disposal. All these waste are burnt, which causes a lot of problems of air pollution and all. However, better use of these wastes as adsorbent which is cheaply available is a good alternative. These agricultural wastes are effective after some modification for the removal of heavy metals of from industrial waste water.

Industrial Waste as Adsorbents: Rapidly growing industries are producing enormous quantities of secondary product and waste, which is again problem for management and disposal. Some them of them are being put to use while others find no proper utilization and are dumped elsewhere. If solid waste is used as adsorbent then it will give two fold advantages in reducing pollution. Some of the industrial wastes are used by researcher successfully as adsorbents are fly ash, blast furnace slag, dust and sludge, red muds from alumina industries, etc. The adsorbents developed by industrial waste are have shown a tendency to remove inorganic contaminates like metal ions more effectively than organic constituents [27].

METHODOLOGY

Selecting a proper material is very important from naturally available material, agricultural waste and industrial waste. Adsorbent can be done by pyrolysis technology from selected individual material or taking composite material by doing right combination with some modification by oxidizing agent, strong or weak acid or alkalis like Hydrogen Peroxide (H2O2), Phosphoric Acid (H3PO4), KOH, HCl, H2SO4, HNO3, etc. to increase adsorption efficiency. After preparation of composite adsorbents characterization of adsorbents are done by various devices like X Ray Diffraction, Scanning Electron Microscope & Brunauer Emmette Teller to analysis of crystallographic structure, chemical composition, surface topography, surface area, porosity & adsorption capacity. Spectrophotometer is used to carry out water and wastewater analysis to detect initial and final presence of heavy metals after conducting experimental work. Adsorption models are used to inter-relate the heavy metal removal by various composite and also results are compared.

CONCLUSION

Use of conventional adsorbent is restricted due to its higher cost and no availability. Many non-conventional adsorbents are investigated successfully used as alternative adsorbents, which is an effective and economic for removal of concentration of heavy metal from wastewater. The adsorption capacity is dependent on the type of the adsorbent used and the nature of the waste water used. More research is needed to analyze and understand the mechanism of greatest affinity towards heavy metal. The bonding between adsorbent and adsorbed metal can be derived and best fitted by Freundlich isotherm as compare to other adsorption models. Composite adsorbents & modified adsorbent can be an effective and economic method for removal of heavy metal from wastewater. Hence, there is need to developed composite adsorbent from different combination and modification.

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