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Adsorption of Heavy Metals: A Review

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ABSTRACT: Environmental pollution particularly from heavy metals and minerals in the wastewater is the most serious problem in India. Due to extensive anthropogenic activities such as industrial operations particularly mining, agricultural processes and disposal of industrial waste materials; their concentration has increased to dangerous levels. Heavy metals in industrial effluent include nickel, chromium, lead, arsenic and cadmium. So far, a number of efficient methods have been reviewed for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electro-dialysis, ultra-filtration, nano-filtration, coagulation, flocculation, floatation, etc. However, these methods have several disadvantages such as high reagent requirement, unpredictable metal ion removal, generation of toxic sludge etc. Adsorption process being very simple, economical, effective and versatile has become the most preferred methods for removal of toxic contaminants from wastewater. This paper reviews the use of various readily available natural materials as adsorbents of heavy metals from industrial wastewater. Various adsorbents reviewed include activated carbon, activated alumina, iron acetate activated alumina, silica gel, hydrogels, magnetic graphene oxide. And also Various low cost adsorbents reviewed includes sand, used tea leaves, eggshell, rice husk, activated carbon, olive stones, wood sawdust etc.

KEYWORDS: Heavy metals, Adsorption, Activated carbon, Activated alumina, Silica gel, Magnetic graphene oxide, Hydrogels, Low cost adsorbents.

I. INTRODUCTION

The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Environmental pollution particularly from heavy metals and minerals in the waste water is the most serious problem in India. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal.

Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause a serious threat to the human health. (Srivastava *et al.*, 2006). The release of large quantities of hazardous materials into the natural environment has resulted in a number of environmental problems and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health.

II HEAVY METAL TOXICITY

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ahalya *et al.*, 2003). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic.

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These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the world health organisation(WHO). Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers.

Table 1: SOURCES AND TOXIOLOGICAL EFFECTED OF SOME HEAVY METALS: (Alluri *et al.*, 2007).

Heavy Metal	Sources	Effects
Copper	<ul style="list-style-type: none"> Water pipes; Copper water heaters;; Frozen greens and canned greens using copper to produce an ultragreen color, Alcoholic beverages from copper brewery equipment. Instant gas hot water heaters; Hormone pills; Pesticides. insecticides; fungicides; Copper jewelry; Copper cooking pots 	<ul style="list-style-type: none"> Mental disorders, Anaemia; Arthritis/rheumatoid arthritis; Hypertension, Nausea/vomiting, Hyperactivity, Schizophrenia. Insomnia, Autism, Stuttering, Postpartum psychosis, Inflammation and enlargement of liver, heart problem, Cystic fibrosis.
Arsenic	<ul style="list-style-type: none"> Arsenic occur in rocks, soil, water, air and biota found in environment. In natural water, it is mostly found as trivalent arsenite, or pentavalent arsenate. Combustion of fossil fuel is a major source of arsenic in the environment through atmospheric deposition. 	<ul style="list-style-type: none"> Pollution of water affects both plants and organisms living in water. Heavy metals can cause great harm to humans, animals and the aquatic ecosystem. Polluted water exposure causes skin, lung, bladder and kidney cancer as well as pigmentation changes, neurological disorders, muscular weakness in humans.
Cadmium	<ul style="list-style-type: none"> Cadmium is produced as a by-product mainly from mining, smelting and refining of sulphide ores of zinc. Cadmium occurs naturally in the environment process of erosion and abrasion of rocks and soils, forest fires and volcanic eruptions. 	<ul style="list-style-type: none"> Cadmium is highly toxic to humans, plants and animals. Harmful effects of cadmium in humans include a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and testicular atrophy etc.
Lead	<ul style="list-style-type: none"> It is found in storage batteries, television tube, paint, printing, pigments, photographic materials, fuels, matches and explosives. One of the largest consumer of lead is batteries storage industry and petroleum industry in producing gasoline additives. 	<ul style="list-style-type: none"> Lead is toxic to most living things. Lead is known to damage the kidney, liver, reproductive system, basic cellular processes and brain function.
Fluoride	<ul style="list-style-type: none"> In Unnao, the content of fluoride in ground water increases because of chemical and leather industries. Industries such s mining steel, automobile, batteries and paints. Pollutants arising from increasing industrialization. 	<ul style="list-style-type: none"> Fluoride adversely affects the foetal cerebral function and neurotransmitters. Many people are affected with dental , skeletal and non-skeletal fluorosis. People with cardio-vascular and kidney problems. It affects every organ, tissue and

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Nickel	<ul style="list-style-type: none"> Effluents of silver refineries, electroplating, zinc base casting and storage battery industries. 	<ul style="list-style-type: none"> cell in the body. Dermatitis, Myocarditis, Encephalopathy, pulmonary fibrosis, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration.
Chromium	<ul style="list-style-type: none"> Steel and textile industry 	<ul style="list-style-type: none"> Skin rashes, respiratory problems, haemolysis, acute renal failure, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, Pulmonary fibrosis.

Non-biodegradable contaminants pose a serious health and environmental hazard and removal of these wastes cannot be achieved using secondary methods. Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption_ can be used to remove these recalcitrant wastes. So far, a number of efficient methods have been developed for heavy metal removal. Fenglian *et al.* (2011) and Rao *et al.* (2011) reviewed various methods for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation, etc. Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. However, chemical processes produce a large amount of metallic sludge, making metal recovery difficult. The sludge also needs further disposal. In addition, effluent after such treatment usually has unacceptably high total dissolved solids. When applied to dilute metal waste or lower concentrations of metal ions, these processes are either ineffective or not cost-effective and require high level of expertise; hence they are not applied by many end-users. However, most of these methods are costly and require high level of expertise; hence they are not applied by many end-users. For these reasons, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and robustness. Low cost adsorbents derived from agricultural by-products and industrial solid wastes could be used to remove recalcitrant wastes from synthetic wastewater. Conversion of these materials into adsorbents for wastewater treatment would help to reduce the cost of waste disposal. The adsorption of toxic waste from industrial wastewater using agricultural waste and industrial by-products has been massively investigated (Basu *et al.*, 2006; Srivastava *et al.*, 2006). The technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed (Babel *et al.*, 2003). Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as chitosan, zeolites, and other adsorbents, which have high adsorption capacity and are locally available. There are many sources of activated carbon from organic waste.

Table 2: THE MAXIMUM CONTAMINATION LIMIT STANDARDS(MCLS)

Heavy Metal	Atomic Number	MCLS(mg/l)
Copper	29	0.25
Arsenic	33	0.050
Cadmium	48	0.01
Lead	82	0.006
Nickel	28	0.20
Chromium	24	0.05
Fluoride	09	1.5

III NEED FOR THE REMOVAL OF HEAVY METALS

Discharge of industrial, domestic and agriculture waste in rivers and lakes cause deposit of pollutants in sediments. Such pollutants include heavy metals, which danger for human health after being incorporated in food chain. Heavy metals cannot be destroyed through biological degradation, as is the case with most organic pollutants. Incidence of

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 2, February 2016

heavy metals accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the world. Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which in the metal can become easily detached or introduced into the cell. Exposure to different metals may occur in common circumstances, particularly in industrial setting. Accidents in some environments can result in acute, high level exposure. Some of the heavy metals are toxic to aquatic organisms even at low concentration. The problem of metal pollution in water and aquatic organisms including fish, needs continuous monitoring and surveillance as these elements do not degrade and tend to biomagnified in man through food chain. Hence there is a need to remove the heavy metals from then aquatic ecosystems. Research and development, therefore focSuses on sector-specific methods and technologies to remove colour and heavy metals.

I.III TOXIC EFFECT ON AQUATIC ORGANISMS

Aquatic organisms are more affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system. The metals are mineralized by micro-organisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals by now, several times biomagnified is taken up by man when he consumes fish from the contaminated water.

- Slightly elevated metal levels in natural waters may cause the following sub-lethal effects in aquatic organisms: histological or morphological change in tissues;
- Changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation;
- Change in biochemistry, such as enzyme activity and blood chemistry;
- Change in behaviour; and
- Change in reproduction.

II. METHODS OF HEAVY METAL REMOVAL

II.I CHEMICAL PRECIPITATION

Chemical precipitation processes are the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. Gopalratnam *et al.* (1988) found 80% removal of Zn, Cu, and Pb, and up to 96.2% removal of oil from industrial wastewaters by using a joint hydroxide precipitation and air floatation system.

II.II ION EXCHANGE

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus an acquired an electrical charge) from solution is exchanged for similarly charged ion attached to an immobile solid particle. These solid ion exchanged particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. An organic ion exchange resin is composed of high-molecular-weight polyelectrolyte that can exchange their mobile ions for of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchange per unit of resin. Most of the resins used are synthetic because their characteristics can be tailored to specific application. Synthatic resin made by polymerization of organic compounds in a porous threedimensional structure. Ion exchange resins are classified as cation exchangers, whom it has positively charged mobile ions available for exchange, and anion exchanger. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 2, February 2016

II.III ELECTRODIALYSIS

Electro Dialysis (ED) is a membrane process, by which ions are transported through semi permeable membrane, under the influence of an electric potential. The membranes are cation- or anion-selective, which basically means that either positive ions or negative ions will flow through. Cation-selective membranes are polyelectrolytes with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through. Nataraj et al. (2007) performed a new working system to investigate the removal of hexavalent chromium ions using a built electro dialysis (ED) pilot plant comprising a set of ion-exchange membranes.

II.IV COAGULATION/ FLOCCULATION

Coagulation and flocculation are an essential part of drinking water treatment as well as wastewater treatment. Coagulation is the chemical reaction which occurs when a chemical or coagulant is added to the water. The coagulant encourages the colloidal material in the water to join together into small aggregates called “flocs”. Suspended matter is then attracted to these flocs. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out. Randtke *et al.* (1997) reviews the basic mechanisms involved in the removal of organic contaminants by coagulation. Kuo *et al.* (2001) studied the effects of initial pH and turbidity, alum and pre ozonation doses, and flocculation time on the removal of dissolved organic matter during alum coagulation.

II.V ULTRAFILTRATION

Ultrafiltration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. It is a pressure-driven purification process in which water and low molecular weight substances permeate a membrane while particles, colloids, and macromolecules are retained. The primary removal mechanism is size exclusion, although the electrical charge and surface chemistry of the particles or membrane may affect the purification efficiency. Landaburu-Aguirre et al. (2009) investigated the removal of zinc from synthetic wastewater.

II.VI MEMBRANE FILTRATION

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultra filtration, nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater. Unique specialties enable UF to allow the passage of water and low-molecular weight solute, while retaining the macromolecules, which have a size larger than the pore size of the membrane. The only disadvantage of this process is the generation of sludge.

II.VII REVERSE OSMOSIS

Reverse osmosis (RO) process cellophane-like membranes separate purified water from contaminated water. RO is when a pressure is applied to the concentrated side of the membrane forcing purified water into the dilute side, the rejected impurities from the concentrated side being washed away in the reject water. Applications that have been reported for RO processes include the treatment of organic containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive wastewater, municipal wastewater, and contaminated groundwater (Slater *et al.*, 1983; Cartwright, 1985; Ghabris *et al.*, 1989; Williams *et al.*, 1990).

II.VIII ADSORPTION

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical,

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 2, February 2016

biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness (Yadanaparthi *et al.* 2009, Kwon *et al.*, 2010,). Adsorption is commonly used technique for the removal of metal ions from various industrial effluents (Gottipati *et al.*, 2012). In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the surface experience a bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption and chemisorption.

II.IX TYPES OF ADSORPTION

At molecular level, adsorption is due to attractive interactions between a surface and a species being adsorbed.

- **Physical Adsorption:** It is a result of intermolecular forces of attraction between molecules of the adsorbent and adsorbate. Physical adsorption occurs when the intermolecular attractive forces between molecules of a solid and the gas are greater than those between molecules of the gas itself. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substances.
- **Chemical Adsorption:** It is a result of chemical interaction between the solid and the adsorbed surface. It is also called activated adsorption. It is irreversible. It is particularly important in catalysis. Therefore, the energy of chemisorptions considered like chemical reaction. It may be exothermic or endothermic processes ranging from very small to very magnitudes. The elementary step in chemisorption often involves large activation energy (Activated adsorption)

II.X .ADSORPTION DYNAMIC

It is generally accepted that adsorption dynamic consists of the following consecutive steps:

- Transportation of adsorbate from the bulk solution to external surface of the adsorbent by diffusion through the liquid boundary layer.
- Internal (interphase) mass transfer the by pore diffusion from the outer surface of the adsorbent to the inner surface the porous structure.
- Surface diffusion along the porous surface.
- Adsorption of the adsorbate on the active sites on the internal surface of the pores.

The last step, adsorption, is usually very rapid in comparison to the remaining steps. Therefore, the overall rate of adsorption is controlled by either film or intra particle diffusion, or a combination of both.

II.XI ADSORBENT PROPERTIES

To be suitable for commercial applications, a sorbent should have high selectivity to enable sharp separations, high capacity to minimize the amount of sorbent needed, favorable kinetic and transport properties for rapid sorption, chemical and thermal stability, including extremely low solubility in the contacting fluid, to preserve the amount of sorbent and its properties, hardness and mechanical strength for long life, no tendency to promote undesirable chemical reactions, the capability of being regenerated when used with commercial feed stocks.

III. VARIOUS ADSORBENTS ARE USED IN ADSORPTION PROCESSES

III.I ACTIVATED CARBON

Activated carbon is the most widely used adsorbent. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It can remove a wide variety of toxic metals. Some widely used adsorbents for adsorption of metal ions include activated carbon (Pollard *et al.*, 1992, Satapathy *et al.*, 2006), clay minerals (Wilson *et al.* 2006), biomaterials, industrial solid wastes and zeolites (Wang *et*

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

al, 2008). Natural material or certain waste from industrial or agricultural operation is one of the resources for low cost adsorbents. Generally, these materials are locally and easily available in large quantities. Therefore, they are inexpensive and have little economic value (Mohana *et al.*, 2007) Scattered research has already been conducted on a wide variety of sorbents. Some of the reported low-cost sorbents include bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginates, xanthate, zeolite, clay, ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool modified cotton.

III.II IRON COATED ACTIVATED CARBON

Activated carbon was impregnated with iron using ferrous chloride solution for the impregnation process for removing arsenic, cadmium and lead from the synthetic waste water. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis demonstrated that the impregnated iron was distributed on the internal surface of the activated carbon. Iron impregnated activated carbon was treated with sodium hydroxide to stabilize iron in activated carbon. The impact of the amount of impregnated iron in activated carbon on arsenic, cadmium and lead adsorption capacities and kinetics were investigated in this study. Freundlich and Langmuir models were also studied for the reaction kinetics. Gu *et al.* (2005) developed iron containing granular activated carbon for arsenic removal from water.

III.III ACTIVATED ALUMINA

Activated alumina is a filter media made by aluminum ore so that it becomes porous and highly adsorptive. It can also be described as a granulated form of aluminum oxide. Activated alumina removes a variety of contaminants that often co-exist with fluoride such as excessive arsenic. The medium requires periodic cleaning with an appropriate regenerator such as alum or acid in order to remain effective. Activated alumina has been used as an effective adsorbent especially for point of use applications. The main disadvantage of activated alumina is that the adsorption efficiency is highest only at low pH and contaminants like arsenates must be peroxidized to arsenites before adsorption in addition, the use of other treatment methods would be necessary to reduce levels of other contaminants of health concern. M. Ghaedi *et al.* (2013) work on the adsorption by activated alumina.

III.IV IRON ACETATE COATED ACTIVATED ALUMINA

The adsorption potential of iron acetate coated activated alumina (IACAA) for removal of arsenic [As (III)] as arsenite by batch sorption technique is good. IACAA was characterized by XRD, FTIR, EDAX and SEM instruments. Percentage adsorption on IACAA was determined as a function of pH, contact time and adsorbent dose. The study revealed that the removal of As (III) was best achieved at pH = 7.4. The initial As (III) concentration (0.45 mg/L) came down to less than 0.01 mg/L at contact time 90 min with adsorbent dose of 1 g/100 mL. The sorption was reasonably explained with Langmuir and Freundlich isotherms.

The overall study reveals that the adsorption of arsenic onto IACAA is found to be dependent on pH, adsorbent dose and contact time. Best removal of As (III) is achieved at pH = 7.4. The initial As (III) concentration (0.45 mg/L) comes down to less than 0.01 mg/L with the minimal adsorbent dose (1 g/100 mL) at contact time 90 minutes. The thermodynamic studies of sorption of arsenic on IACAA show that the reaction is spontaneous and endothermic process. The equilibrium data are fitted to both Langmuir and Freundlich adsorption isotherm. But it is found that Langmuir isotherm model fitted well followed by Freundlich. The pseudo second order kinetic model is found to be the best correlation of the data for sorption of arsenic on IACAA. The kinetic of the reaction follows intraparticle diffusion model. Bhdaditya Das *et al.* works on the arsenic (III) adsorption on iron acetate coated activated alumina.

III.V SILICA GEL

Silica gel is a non-toxic, inert and efficient support and is generated by decreasing the pH value of the alkali silicate solution to less than ten. The solubility of silica is then reduced to form the gel and as the silica begins to gel, cells in silica are trapped in a porous gel, which is a three-dimensional SiO₂ network. Porous silica gel is an inorganic synthetic

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

polymeric matrix often used to entrap cells and its use for entrapment is called the sol-gel technique. Reactive sites of silica gel exist in large numbers, and therefore, the number of immobilized organic molecules is high, which result in good sorption capacity for metal ions.

III.VI MAGNETIC GRAPHENE OXIDE

Jin Hur, Jeawon Shin, Jeseung Yoo et.al (2015) proposed their work on Competitive Adsorption of Metals onto Magnetic Graphene Oxide: Comparison with Other Carbonaceous Adsorbents. In this work, competitive adsorption isotherms of Cu(II), Pb(II), and Cd(II) were examined on magnetic graphene oxide(GO), multiwalled carbon nanotubes(MWCNTs), and powered activated carbon(PAC). A series of analyses confirmed the successful synthesis of the magnetic graphene oxide based on a simple ultrafiltration method. Irrespective of the adsorbents, the adsorption was highly dependent on pH. The maximum adsorption capacities of the adsorbents were generally higher in the order of Pb(II)> Cu(II)> Cd(II). The antagonistic effects were influenced by solution by solution pH as well as the type of metals, and they were higher in the order of the magnetic GO> MWCNT> PAC.

III.VII HYDROGELS

M. Mohsen, N. A. Maziad E. Gomaa et.al (2015) prosed their work on “Characterization of Some Hydrogels Used in Water Purification: Correlation of Swelling and Free-Volume Properties”. In this study, the main objective is to develop a good chelation and ion exchange hydrogel. This hydrogel is obtained by polymerization of dimethyl amino ethyl methacrylate (DMAEMA) and acrylic acid (AAc) by gamma irradiation, for the purpose of separation of some heavy and toxic metals like Ni, Cu and Co from water. The adsorption affinity of DMAEMA/AAc hydrogel at different treatment times is in the following order Ni> Cu> Co. However, the order becomes Co> Ni> Cu by the variation of the pH of the metal ion solution; the variation of its concentration leads to a different order of Cu> Co> Ni.

IV. LOW COST ADSORBENT

IV.I DEFINITION

In general, an adsorbent can be assumed as “low-cost” if it requires a little bit processing, is abundant in nature, or is a by-product or a waste from an industry. Natural material or certain waste from industrial or agricultural operation is one of the resources for low cost adsorbents. Generally, these materials are locally and easily available in large quantities. Therefore, they are inexpensive and have little economic value.

IV.II CHITOSAN

Chitosan and its derivatives are examples of value-added materials. They are produced from chitin, which is a natural carbohydrate polymer found in the skeleton of crustaceans, such as crab, shrimp. Chitosan is a polymer obtained from deacetylation of chitin.

IV.III PREPARATION OF CHITOSAN

Shrimp shell waste materials were collected from Khulna, Bangladesh. Shrimp shells were scraped free of loose tissue, washed with cold water and dried in sun for 2 days. Chitin was extracted from shrimp shell. The process mainly involved the following steps:

IV.IV DEMINERALIZATION OF SHELL

In this step, the shells were suspended in 4% HCl at room temperature in the ratio of 1 : 14 (w/v). After 36 hours, the shells were quite squashy and were rinsed with water to remove acid and calcium chloride.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

IV.V DEPROTEINIZATION OF SHELL

The demineralized shells were then treated with 5% NaOH at 90°C for 24 hours with a solvent to solid ratio of 12 : 1 (v/w). The residue was then collected and washed to neutrality in running tap water then it was dried in sun and the product is chitin. The preparation of Chitosan is simply deacetylation of chitin.

Removal of acetyl groups from the chitin was achieved by using 70% NaOH solution with a solid to solvent ratio of 1 : 14 (w/v) at room temperature for 72 hours. The mixture was stirred after some times for homogenous reaction. The resulting chitosans were washed to neutrality in running tap water and rinsed with distilled water. Then filtered and dried in sun.

IV.VI EGG SHELL

Egg shell is largely-crystalline calcium carbonate. The calcium comes partly from the hen's bones and when necessary the hen can mobilize 10 percent of her bone for the purpose.

IV.VII EGG SHELL PREPARATION

Natural and boiled hen and duck egg shells were washed with tap water several times then air-dried and incubated in hot air oven at 40°C for 30 minutes (because protein component in egg shell can denature at high temperature; > 40°C). Consequently, egg shells were ground to a powder in a grinder, and sieved to obtain between 60-100 mesh (0.25-0.104 mm) size particles.

IV.VIII LIGNIN

Lignin or lignen is a complex chemical compound most commonly derived from wood, and an integral part of secondary cell walls of plants and some algae. The term was introduced in 1819 by de Candolle and is derived from the Latin word lignum meaning wood. It is one of the most abundant organic polymers on Earth, exceeded only by cellulose, employing 30% of non-fossil organic carbon, and constituting from a quarter to a third of the dry mass of wood. As a biopolymer, lignin is unusual because of its heterogeneity of a defined primary structure. Its most commonly noted function is the support through strengthening of wood (xylem cells) in trees. In lignin structure there is an aromatic three-dimensional polymer structure containing a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups, making it potentially useful as an adsorbent material for removal of heavy metals from water. Guo et.al has studies adsorption of metals ions on lignin.

IV.IX CAST IRON FILINGS AND STEEL WOOL

Waste and low-cost materials like Cast-Iron Filings (wastes from mechanical workshops, lathes) and Steel Wool (commercially available, used for cleaning of wood surfaces prior to polishing) were investigated to assess their potential for removal of Arsenic from water by the process of adsorption by conducting different types of batch adsorption experiments, continuous flow column studies and candle filter studies. Batch sorption experiments brought forth the effectiveness of sorbent materials for removal of Arsenic from water achieving a removal of 90-95% at favorable pH conditions which lie in the normal range. Isothermal equilibrium data fitted well into the Langmuir model suggesting formation of unimolecular monolayer of sorbate over a homogenous surface of uniform energy. Both desorption studies and the shape of the saturation curves denote high affinity of the sorbent for the sorbate. Regeneration studies indicate repeated regeneration of the sorbents thus extending the usage of the sorbent following regenerations. While sulfates, Fluoride and chlorides have little influence on sorptive removal, phosphates and silicates exercise considerable influence by reducing removal. Fixed bed continuous down-flow column studies conducted using ground water spiked with 300ug/l Arsenic (V) at flow rates of 5.0 and 10.0 ml/min indicated the usefulness of the sorbents for engineering applications for removal of Arsenic from water. Candle filter studies conducted by filling the hollow portion of the candles used in the domestic filters filled with sorbent material further demonstrated the utility of the existing household filters for removal of Arsenic (V) to less than the permissible limits of BIS/WHO by simply

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

filling the hollow portion with the sorbent material. No leaching of Iron was found in the filtered water. Sridhar Rao.T* et.al has works on low cost adsorption.

IV.X ZEOLITES

Zeolites are micro porous, aluminosilicate minerals. The term zeolite was originally coined in 1756 by Swedish mineralogist Axel fredrik cronstedt, who observed that upon rapidly heating the material stibite, it produced large amounts of steam from water that had been absorbed by the material. Based on this he called the material zeolite, from the Greek meaning "to boil" and (lithos), meaning "stone". Zeolites have a three dimensional structure constituted by (Si, Al) O₄ connected by all their oxygen vertices forming channels tetrahedral the negative charge generated from the isomorphism substitution. The advantage to zeolites over resins, apart from their much lower cost, is their ion selectivity. Owing to zeolite's structural characteristics and their adsorbent properties, they have been applied as low cost adsorbents. Ouki and Kavannagh studied the performance of natural zeolites on the treatment of mixed metal effluents (Pb²⁺, Cd²⁺, Cu²⁺).

IV.XI SAWDUST

Sawdust and wood dust is a byproduct of cutting grinding or otherwise pulverizing wood with a saw or other tool, it is composed of fine particles of wood. It is also the byproduct of certain animals, birds and insects which live in wood, such as the woodpecker and carpenter ant. It can present a hazard in manufacturing industries, especially in terms of its flammability. Sawdust is the main component of particleboard. It contains various organic compounds (lignin, cellulose and hemicelluloses) with polyphenolic groups that could bind heavy metal ions through different mechanisms. Bryan et.al showed adsorption of hexavalent chromium by red fire sawdust.

IV.XII CARBON ANODE DUST

Industrial waste is one of the best low-cost adsorbents for heavy metal and organic matter removal. Since these materials are locally available in large quantities, they are inexpensive. Many applications of carbon materials are strongly influenced by their surface chemistry. Thus their uses as adsorbents in aqueous solution, in catalysis or electrochemical process are three examples in which the surface chemistry, microporous structure, high adsorption capacity and high degree of surface reactivity can have an important relevance in the materials performance. The carbon anode dust (CAD) originates from the baking and transport of carbon electrodes anodes in aluminum production industry and it is not recycled. Strkalj et.al have studied comparative adsorption performance for Ni (II) ions of acetic acid-modified, KOH modified and unmodified carbon anode dust.

IV.XIII AGRICULTURAL WASTE

Hexavalent chromium is present in the effluents product during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and cause environmental and public health problems. A.Y. Talokar works on studies on removal of chromium from waste water by adsorption using agricultural biomass as adsorbents. Non- conventional low cost adsorbents such as Fly ash powder(FA), Bagasse, Waste Straw Dust(WSD), Saw Dust(SD) and Coconut coir as compared to the powder activated carbon(AC) for the removal of chromium from aqueous solution. The efficiency of the adsorbent for the removal of chromium was investigated. The efficiency of adsorbent used is found in the order of AC>Bagasse>FA>SD>WSD>Coconut coir. The effect of chromium solution pH, contact time, adsorbent dosage, initial chromium concentration and adsorbent mesh size on adsorption were studied in a batch experiment. Fly ash, Bagasse, WSD, SD, and Coconut coir were the most active at pH = 6, which is closer to pH of chromium bearing industrial waste as compared to the pH 2.0 of powder activated carbon(PAC). The equilibrium data for the adsorption of chromium were analysed in the light of Langmuir and Freundlich isotherm models. The ultimate adsorption capacity for the adsorbents PAC, Bagasse, FA, SD, WSD and Coconut coir found out are 4.97 mg/gm, 4.91 mg/gm, 4.90 mg/gm, 4.89 mg/gm, 4.77mg/gm and 4.56 mg/gm respectively by column studies.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

IV.XIV NEEM LEAVES & EUCALYPTUS TREE PARTS

In the present work, chemically treated leaves, bark of eucalyptus & neem leaves have been used to study the adsorption of hexavalent chromium. B.V. Babu et.al (2007) worked on the adsorbent prepared from neem leaves and used for hexavalent chromium removal from aqueous solution. Neem leaves are activated by giving heat treatment and with the use of concentrated hydrochloric acid (36.5 wt%). The activated neem leaves are further treated with 100 mol of copper solution. Batch adsorption studies demonstrate that the adsorbent prepared from neem leaves has significant capacity for adsorption of hexavalent chromium from the aqueous solution. The adsorption of hexavalent chromium is found to be (99%) at low value of pH in the range of 1-3. Application of the Langmuir isotherm to the system yielding maximum adsorption capacity of 62.97 mg/gm. Use of adsorbent prepared from neem leaves is capable and cost effective for the removal of hexavalent chromium from aqueous solution.

Indu Sharma et.al(2011) investigated removal of chromium from industrial effluent. It was investigated using Eucalyptus tereticornis bark with various parameters including amount of biomass, pH of solution and contact time. Biomass(2%) was able to remove 88% and 91.5% of chromium at pH 4.0 and 5.0, respectively from solution amended with 50 mg of hexavalent chromium 1/L. Maximum chromium removal capacities of treated bark biomass were 70% and 94% from tannery effluent and chrome plating effluent, respectively in column mode. The adsorption parameters were determined using both Langmuir and Freundlich isotherm model. Calorific value of native bark biomass, tannery effluent and chrome plating effluent treated biomass were 2227, 3885 and 4003 kcal/kg, respectively with increase in chromium laden biomass. The results revealed that chromium loaded bark biomass can be disposed off by incineration or used in furnace as a fuel.

IV.XV RICE HUSK

Rice husk is agricultural waste mostly available in rural areas, collected and grinding in grinders then sieved and washed with distilled water repeatedly for dirt and other particulate matter removal, then dried in hot oven at 100°C for 24 hours, then either directly used as an adsorbent or treated with H₂SO₄ and then washed again with distilled water for removing acidity, washing upto totally acidity are removed and then dried at 100°C for 12 hours then collected in air tight plastic bags and then used as an adsorbent. Ajmal, M., Rao. R.A.K., et.al(2003) are worked on Adsorption Studies on Rice Husk.

IV.XVI TEA WASTE

Procedure to prepare the adsorbent, firstly teawaste washed and then rins with distilled water. After drying in 100°C, it was ground and screened(mesh size 10). Decolorized and cleaned tea waste was dried at room temperature for a few days by spreading on gauze. Black tea was used for the experiments, soluble and colored components were removed from tea by washing with boiling water. This was repeated until the water was virtually color less. The tea leaves were then washed with distilled water and were oven dried for 12 hour at 85°C. The dried tea waste was sieved and stored in sealed polythene bags. Amarasinghe BMWPK and Williams AR.2007, worked on tea waste adsorbent.

IV.XVII COCONUT HUSK

Coconut easily available in all temple and religious places, collected them dried in hot oven at 80°C for 4 hours and then grinds in grinder in the powder form then sieved 120 mm sizes then washing with distilled water for dirt and other particulate matter removing, then again dried at 100°C for 24 hours then used as an adsorbent. Abad M., P. Noguera, R. Puchades,(2002) worked on this topic.

IV.VIII SEAWEED

Biosorption process is a promising technology for the heavy metals from industrial wastes and effluents using low-cost and effective biosorbents. Seaweed is a effective adsorbent for removal of heavy metals ions. Md. Sayedur Rahman and

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

Kathiresan V. Sathasivam (2015) worked on Heavy Metal Adsorption onto Kappaphycus sp. (this is a type of seaweed found in Malaysia) from Aqueous Solutions. Adsorption of Pb^{2+} , Cu^{2+} , Fe^{2+} and Zn^{2+} onto dried biomass of red seaweed Kappaphycus sp. was investigated as a function of pH, contact time, initial metal ion concentration and temperature. The dried biomass of Kappaphycus sp. May be used as a low-cost biosorbent for removal of heavy metal ions from aqueous solutions.

V. CONCLUSION

A review of various processes and adsorbents for heavy metal removal shows that adsorption process has great potential for the elimination of heavy metals from Industrial wastewater using low cost adsorbents. More studies should be carried out for low-cost adsorption process to promote large scale use of non-conventional adsorbents. Low cost adsorbents should be used to minimize cost and maximize heavy metal removal efficiency. But imprigmentation process gives better result.

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Vol. 5, Issue 2, February 2016

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(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 2, February 2016

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