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Bioadsorbents and Filters for Removal of Heavy Metals in Different Environmental Samples-A Brief Review

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ABSTRACT

To eliminate the problem of heavy metals, there are naturally occurring materials that are locally and commonly found and are very much encouraged as low cost adsorbents such as industrial and agricultural wastes. Several agricultural and industrial wastes as potential adsorbents have been viewed, which includes wood ash and bone ash, cassava waste, chitosan-g-poly (butyl acrylate)/ bentonite nano composite, *Eucalyptus tereticornis* bark, sarooj clay, orange fruit peel, fly ash, potato peels, coconut shell charcoal, pecan shells, bagasse fly ash, waste sludge, pith and saw dust, maize cob and husk, hazelnut shell, soybean hull, jackfruit, crab shell, neem leaves, cooked tea dust, teak leaves, cashewnut shells, aerogel carbon, sewage sludge ash and lignite-based fly ash. The adsorption details of these adsorbents have been keenly viewed and judged in batch studies mostly. The judgment is on the basis of adsorption isotherms, thermodynamics and parameters like contact time, adsorbent dosage, pH, initial metal concentration and adsorption capacity. Hence, it is proved from the review of these adsorbents that they are highly selective in terms of separation, thermally and mechanically stable and do not foul, regenerative and less soluble in liquids. They are commonly available and are very less costly with removal efficiency up to 99%. The usage of these adsorbents is better applicable at low pH and oxidized or carbonized or activated before using them as adsorbents to remove heavy metal ions from agricultural, industrial and municipal wastes.

INTRODUCTION

Heavy metals are very poisonous to the soil condition as they are dangerous to human health and other components of the environment. The metals persist in soil, especially in clay and moist soil where they bind with the particles and remain there for longer time periods as metals. The metals only decompose and dissolve at low pH, therefore acidic environment is not good for soil health (Singh 2016). There are some metals that persist in the food chains and get accumulated in the body. Such metals are very chronic in nature and may disturb the metabolic activities. The metal toxicity depends on duration of exposure, route of exposure and adsorbed concentration of metal (Kisielowska 2010). The heavy metals persist in environment due to their specific gravity which is 5 g/cm^3 or more. They become a serious hazard when they exceed some threshold. Heavy metals exist naturally and are also produced from human activities. Some of the natural means are by soil erosion, natural weathering, mining, industrial effluents, urban run offs, sewage discharge and pesticides (Igwe 2006). The heavy metals are needed by human body in small amounts, but in large concentrations, these can be toxic and dangerous. Heavy metals damage the kidney, liver, brain, lungs, blood circulation and composition. The long term exposure to heavy metals leads to disfunctioning and degenerative muscular, physical and neurological diseases like Parkinson‘s and Alzheimer’s (Jaishankar 2014). The most common heavy metals found in wastewater are arsenic, cadmium, zinc, nickel, copper and lead. Arsenic is the most abundant and most important heavy metal found on the earth’s crust. It is carcinogenic, highly toxic and found in the form of oxides and sulphides. The organic arsenics are arsenite and arsenate compounds which are lethal in nature. Arsenic dissolves in water by natural means, and through pesticides and chemical disposal (Igwe 2006).

Lead is the most widely used heavy metal due it its numerous industrial uses. Lead is used in metal plating and finishing operations, in battery industries it is emitted out as a waste, as an exhaust from automobiles; it is expelled out from factory chimneys, by smelting of ores, from fertilizers and pesticides. The concentration of lead that is discharged in air is taken up by plants and is fixed in soil and the rest is the source in drinking water. Mercury is a shiny, silvery liquid that is converted into gas which is colourless and odourless upon heating. Mercury is the most toxic and bioaccumulative heavy metal. There are so many anthropogenic sources that cause its distribution in environment like municipal water, mining, incineration, industries and agriculture wastewater. Methyl mercury is the deadly form of this metal which comes into human body from aquatic life by consuming aquatic animals. Mercury is used in pulp and paper manufacturing, in batteries, thermometers, lamps and dental amalgams. It causes acute metal poising, thus making this as a deadly element (Jaishankar 2014).

Cadmium is the 7th most toxic element on earth. It is produced as a by-product of zinc production. Cadmium remains in the body throughout life, if someone consumes it from environment and gets exposed at work. It is present in tobacco smoke, rechargeable batteries and in alloys production. It is also used in cadmium plating, coating and pigments formation. Acute and chronic intoxication can happen if someone inhales it or ingest it (Olafisoye 2013). Chromium is the seventh most abundant element. Its most common forms are trivalent Cr^{+3} and hexavalent chromium Cr^{+6}. Chromium is introduced into the environment by burning of coal and oil, fertilizers, metal plating and from tanneries, electroplating, metallurgy, wood preservation, paper and pulp formation. Cr(III) is immobile in its reduced form and is insoluble in water, whereas Cr(VI) in its oxidized state is highly soluble in water and thus mobile. The hexavalent chromium causes pulmonary disorder, oedema, liver damage and skin infection. The maximum level of this metal in water should be 0.05 mg/L as recommended by world health organization (WHO) and 0.1 mg/L in surface water according to Drinking Water Quality Guidelines. On the other hand, Cr(III) causes kidney damage and reproductive system dysfunction as well as affects the normal functioning of brain in a negative manner. Tanneries produce large concentrations of heavy metals in water, especially Cr (III) which is readily oxidized by the freely available oxygen in water and is converted into Cr (IV) which is deadly poisonous to living organisms (Logeswari 2013).

Aluminium is a third most abundant element and it is produced from mining and other activities and elevated levels of it in the environment can cause serious problems to plants and humans. There are many factors that influence the toxicity of aluminium which are pH of water and organic matter content. Due to acidity in the soil (below 5 pH) the silicon is leached down and the unstable form of aluminium stays there, causing toxicity in soil. This results in disturbance and distraction in plant and its cells like retarded root growth, small and dark leaves appearance and chlorosis. Iron being the second most abundant element, is central for the growth and survival of all organisms. There are several anthropogenic sources and mining activities that cause its introduction in environment. The iron precipitates and clog the respiration process in fishes. Iron has direct and indirect effects on aquatic animals and plants. Iron toxicity retards the growth in aquatic plants even with the minimum concentration of 1 mg/L of total iron. The acidic soil and Zn deficiency cause restriction in rice yield, bronzing of leaves and high uptake of Fe^{+2} (Jaishankar 2014).

Background: Industrialization has not only brought development and prosperity with it, but it has also brought so many problems. One of them is control over pollution. Industries produce high quantity of waste, which is discharged in water directly without any treatment. Electroplating, leather, tannery, textile, pigment and dyes, paint, wood processing, petroleum refining, photographic film production etc., emit large concentrations of heavy metals in water. The conventional methods of treatment of heavy metal contamination include chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electrodialysis, etc., all of which are expensive, energy extensive and produce toxic by-products. Safe and economical treatment of metals has been searched and from this effort, adsorption technique has emerged out as a most promising alternate option to treat heavy metals from different environmental samples like industrial, agriculture and municipal (Mills-Knapp et al. 2012).

Adsorption: Adsorption is a very effective, reasonable and eco-friendly technique. It is a process of transformation of liquid into the surface of solid and binds with the solid surface through physical and chemical interaction. It is a partition process which is used to separate a desired element from the reaction mixture. The components of the liquid phase are attached to the solid adsorbent surface. An adsorption process can be either batch, semi-batch and continuous. Adsorption is an interaction of the surface and the group that is to be adsorbed. Adsorption can be physical or chemical depending upon the intermolecular forces.

Physical adsorption: Van der Waal's force of attraction is a driving force for this type of adsorption and occurs in any state like solid, liquid or gas. In this type, the atom and molecule are not disturbed of any element upon this interaction. Physical adsorption occurs at low temperature and under certain conditions.

Chemical adsorption: Chemical adsorption involves a chemical reaction between adsorbent and adsorbate. It is also called activated adsorption which involves strong interactions of ionic and covalent bond. The adsorption of pollutants on solid adsorbent happens when the pollutant travels from the bulk solution to the absorbent surface. A film of pollutant is formed on the adsorbent surface or the intra particle diffusion happens (Bajpai 1999).

Low cost adsorbents: The naturally occurring materials that are locally and commonly found are very encouraging as low cost adsorbents such as industrial and agricultural wastes. An ideal adsorbent should be highly selective in terms of separation, thermally and mechanically stable and does not foul, and that adsorbent should be regenerative and less soluble in liquid.

Agricultural waste adsorbents: The chemically modified and enhanced agricultural waste has been extensively used as adsorbent to remove heavy metal contamination from industrial waste. The plant based adsorbents are rice husk, neem bark, black gram husk, waste tea, Turkish coffee, walnut shell, etc. Some more adsorbents like papaya wood, maize leaf, teak leaf powder, *Coriandrum sativum,* lalang leaf powder, peanut hull pellets, sago waste, saltbush leaves, tree fern, grape stalk wastes are studied. The chemically modified agricultural waste is much more efficient and enhanced in working. The benefits of using agricultural wastes for wastewater treatment include easy technique, modest processing, superior adsorption ability, selective adsorption of heavy metal ions, economical, easy availability and easy regeneration. On the other hand, the use of untreated agricultural wastes as adsorbents can also fetch a number of problems such as small adsorption ability, elevated chemical oxygen demand (COD) and biochemical oxygen demand (BOD) as well as total organic carbon (TOC) due to discharge of soluble organic compounds contained in the plant materials. There are many factors that affect the adsorption capacity, these factors are pH, temperature, contact period, initial concentration of metal, agitation rate, dosage of adsorbent, etc. (Lakherwal 2014).

Industrial waste adsorbents: There are many types of industrial waste or by-products which can be used as adsorbents to remove heavy metals from effluents. These by products are natural, economical and easily available. These by-products or wastes are slightly processed to enhance their adsorption capacity. Industrial by-products such as fly ash, blast furnace slag, waste slurry, lignin-a black liquor waste of paper industry, coffee husks, tea factory waste, sugar beet pulp, waste pomace of olive oil factory, battery industry waste, and waste biogas residual slurry are all industrial waste adsorbers for heavy metal removal (Barakat 2011).

There are few environmental samples considered, from which the heavy metals removal techniques are analysed on the basis of their efficiency, percentage removal, cost and availability.

DISCUSSION

Techniques for removal of heavy metals from industrial wastewaters: The metals from coal combustion effluent are removed well by potentiometric titration. For this purpose, two natural materials were analysed, which are wood ash and bone ash. The removal efficiency depends on pH, metal ion concentration, ash content and a slight influence of temperature. The wood ash acts as a good adsorbent than the bone ash at 5 pH, 20°C and C_s 0.2 g.L-1. Wood ash adsorbs metal ions better than bone ash. Wood ash adsorbed Cr (III) two times higher than the bone ash. Wood ash also adsorbed other toxic heavy metals like Cd (II) four times higher and Zn (II) 12 times higher than bone ash. The purpose of the comparison between the two is to find the best absorber. The wood ash removed 67.9% nickel, 99.1% of Cr (III) at 0.2 g.L-1 of wood ash. Hence, it can be said that wood ash is the best adsorbent for Cr (III) removal (Chojnacka 2009).

Chromium, copper, lead, mercury and cadmium are the major toxic environmental pollutants that are generated from mining activities. Heavy metals are a threat because they persist in the environment. The general trend is shifting from the use of conventional adsorbents to the use of biosorbents (Wan Ngah 2007). The chemically modified cassava waste with thioglycollic acid to modify the biomass has been used for the removal of three metal ions Cd, Cu and Zn from waste effluent. Within 20-30 minutes, the adsorption of these metals was about 60-80% by chemically modified biomass. The binding sites were enhanced by chemical modification. The increase in the concentration of reagents lead to increase in incorporation, which increases the adsorption capacity of cassava waste. Cassava is a serious threat to environment because it releases bad smell during decomposition. The good thing about cassava is that it adsorbs trace metals from solutions. The cassava waste is pH dependent and the reaction occurs within 30 minutes which shows its stability and speed. The metals can be recovered from the biomass and the biomass is biodegradable which makes it environment friendly. The cassava waste is readily available and inexpensive and can recycle metals from it (Horsfall 2003).

In this study, a comparison of different biological techniques has been made and the results showed that biological treatment options are the best for the removal of heavy metals with the efficiency of up to 90%. The methods which were studied are trickling filter, biosorption, activated sludge process and various anaerobic methods (Lakherwal 2014).

The tannery industries are most beneficial to the social and economic boom of any country and thus the emissions that are being generated are discharged to nearby streams without sufficient treatments. Thus, the experiments were performed to check the contamination reduction capacity of Cs-g-PBA/bent nanocomposite with different pH, contact time and adsorbent dosage. The maximum removal percentage of chromium VI was 97.81% at the optimum pH 3, optimum contact time of 420 minutes and 5 g of adsorbent in sample with satisfactory sufficient removal along with other parameters of similar maximum satisfactory results for turbidity, total hardness and TSS. Hence, it is concluded here that chitosan-g-poly (butyl acrylate)/bentonitenano composite is an excellent adsorbent for the removal of chromium and other impurities (Nithya 2016).

In a study, eucalyptus was investigated as a good removal adsorbent of chromium from industrial effluent. It was investigated using *Eucalyptus tereticornis* bark with various parameters including the 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 per litre. Maximum chromium removal capacities of the treated bark biomass were 70% and 94% from 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, and chrome plating effluent treated biomass was 2227, 3885 and 4003 kcal/kg, respectively, with an increase in chromium laden biomass. The results revealed that chromium loaded bark biomass can be disposed of by incineration or used in furnace as a fuel (Sharma 2011).

In a study, local clay has been considered for the removal of Zn, Pb and Cd ions from wastewater. This clay is also called Sarooj clay. The chemical and physical properties of clay as well as pore size distribution, specific surface area and microscopic structures were analysed to study the characteristics of clay. For this purpose three different types of clays were analysed such as, washed clay, treated clay and thermally treated clay (removal of Zn, Cd and Pb ions from water by Sarooj clay). It is known that conventional treatment technologies for heavy metals recovery are expensive and produce an enormous quantity of sludge. The use of inactive non-living biomass of microbial or plants as biosorbents is new and innovative for heavy metals removal from metallurgical industries. The biomass of *Aspergillus niger, Penicillium chrysogenum, Rhizopus nigricans, Ascophyllum nodosum, Sargassum natans, Chlorella fusca, Oscillatoria anguistissima, Bacillus firmus* and *Streptomyces* sp. have high metal adsorption capacities ranging from 5 to 641 mg g^{-1} mainly for Pb, Zn, Cd, Cr, Cu and Ni ions (Ahluwalia 2005).

The adsorption mechanism of orange fruit peel was analysed for heavy metals like Zn, Ni, Cu, Pb and Cr from industrial wastewater samples. Ni (II) was extracted with maximum adsorption of 96% at an initial concentration of 50 mg/L at 6 pH and 50°C. The adsorbent was found good for the removal of Cu(II)>Pb(II)>Zn(II)>Cr(II) after the best removal of Ni (II). The heavy metals were desorbed with 0.05 NHCl and found to be 95.83% in column process and 76% in batch process. The spent adsorbent was removed and recovered thrice from wastewater and was found to be 89% and 93.33%, respectively (Ajmal 2000).

Under various conditions of contact time, pH and temperature the removal efficiency of lead and copper ions from aqueous solution by fly ash were analysed. The fly ash adsorption capacity for Pb^{2+} and Cu^{2+} ions increased at high pH values. This endothermic adsorption process of fly ash is enhanced at low temperature by analysing the effect of temperature between 30°C and 60°C. The mechanism that involved in the adsorption of Pb^{2+} and Cu^{2+} by fly ash was precipitation and surface adsorption at fly ash (Alinnor 2007).

The use of potato peels as adsorbents is new as they are mostly discarded away. The potato peel charcoal (PPC) was researched to remove Cr (II) from industrial wastewater. Various parameters were researched such as solid liquid ratios, temperature and pH. The optimum pH for PPC adsorption was found to be 6. With the help of Van't Hoff equation, the thermodynamic parameters were analysed like Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°). All the thermodynamic data revealed the exothermic and spontaneous nature of potato peel charcoal (Amana 2008).

In batch studies, the removal efficiencies of coconut shell charcoal (CSC) and commercial activated carbon (CAC) were analysed from synthetic electroplating wastewater to remove Cr(VI). The powdered granules of (CSC) and (CAC) were modified with chitosan and oxidizing agents such as sulphuric acid and nitric acid, respectively. The statistical removal performance indicated that chitosan or/and oxidized adsorbents performed well than the unmodified and/or oxidized adsorbent in terms of adsorption level. Sulphuric acid is a very strong oxidizing agent than nitric acid and the results also revealed that the Cr adsorption capacity of sulphur oxidized adsorbent (CSC) and (CAC) was higher than the nitric acid modified and unmodified adsorbents, which are CSC: 10.88, CAC: 15.47 mg g-1, CSC: 4.05, CAC: 8.94 mg g-1 and CSCCC: 3.65 mg g-1 respectively. Thus, proving the surface modification with strong oxidizing agent boost the adsorption capacity of adsorbent (Babel 2004).

The commonly found heavy metal ions Cu^{2+}, Pb^{2+} and Zn^{2+} in industrial and municipal wastewater were investigated to be removed by pecan shell-based granular activated carbons (GACs). The metal ions adsorption of phosphoric acid, steam or carbon dioxide activated pecan shells were compared with metal ions adsorption of commercial carbon. The adsorption experiments revealed that acid-activated pecan shell carbon at doses of 0.2-1.0% adsorbed more Pb and Zn ions than any other carbons. Whereas, at dose above 0.2%, Cu^{+2} ions were adsorbed more by steam-activated pecan shell carbon. Hence, it can be said that acid and steam activated pecan shell-based GACs are better adsorbents and can replace coal-based GACs for metal ion removal (Bansode 2003).

The use of thermally activated rice husk and activated alumina in two sizes 0.3 and 1.0 mm for removal of Cr (II) were investigated. The optimum pH for removal of Cr (II) by activated rice husk was 2 and for activated alumina it was pH 4. Freundlich isotherm was applied and the concentration of Cr (II) ions by both the adsorbents increased with the increase in contact time and dose of adsorbent (Bishnoi 2004).

In the batch studies, bagasse fly ash was used to remove Ni and Cd from industrial wastewater. The adsorbent used is a waste generated from sugar industry which removes 90% of Cd and Ni in 60 and 80 min, respectively. Various parameters like solution pH, adsorbent dose, adsorbate concentration, temperature and particle size were studied and the results showed that at a concentration of 14 and 12 mg/L and at a pH value of 6.0 and 6.5, maximum adsorption occurred. At the adsorbent dose of 10 mg/L optimum adsorption of metal ions was achieved. The Langmuir model suited better than the Freundlich model. The process indicated the endothermic nature of both the metal ions, and the adsorption process increased with increase in temperature. Free energy change, enthalpy change and entropy change of the adsorption process were determined by using isotherms (Gupta 2003).

Techniques for removal of heavy metals from agricultural wastewaters: The use of activated carbons is costly to remove heavy metals from effluents. To replace it, several natural and easily available materials were experimented upon. Chemically, any sort of modified versions of waste sludge and fly ash are effective and easy to be disposed off (Varma 2013). The conventional methods to remove heavy metals from agricultural wastewater are expensive. Rice husk and saw dust are two agricultural and timber industry wastes that can be used to extract chromium (VI) from agricultural wastewater. After treating these materials with sulphuric acid (a strong oxidizing agent) they are tested to determine several process parameters like pH, initial metal concentration, contact time and adsorbent dose. At low pH, maximum chromium removal was achieved. The removal efficiency of rice husk carbon and saw dust carbon was 91.75% and 94.33%, respectively at 20 g L^{-1} adsorbent dose (Bansala 2009).

The agro waste materials like bagasse, pith and saw dust were used to study the batch adsorption technique for the removal of Pb (II) from wastewater. Different parameters were studied which include effects of initial metal concentration, contact time, pH and adsorbent dose on the removal of Pb (II). Carbon derived from pith proved the best adsorbent for Pb (II) from agricultural wastewater. Lagergren rate plots were used to find the kinetics of Pb (II) removal, Weber and Morris intra particle diffusion plots were used to understand the diffusion process and Langmuir and Freundlich isotherms were used to check the applicability of the whole adsorption process. The desorption process of Pb (II) from sorbed carbon was accomplished by washing it with 0.1 M HNO_3 and carbon was recovered by washing with 0.1 M $CaCl_2$ solution and was reused (Ayyappana 2005).

In a study, the industrial wastewater discharge that carry typical heavy metals like Zn^{2+}, Cd^{2+} and Pb^{2+} ions, are removed by modified and unmodified maize cob and husk. According to the results, the maximum adsorption occurred at 495.9 mg/g for Zn^{2+} ion, 456.7 mg/g for Pb^{2+} ion and 493.7 mg/g for Cd^{2+} ion by using unmodified adsorbent. The presence of other metal ions, presence of nonaqueous solvent and modification by carboxymethylation affect the adsorption efficiency of each metal ion (Igwe 2005).

There are so many adsorbents that are low cost and have better removing efficiency which are derived from natural materials, agriculture or industrial waste. These adsorbents are compared with activated carbon to check the removal efficiency for Cd (II), Cr (III), Cr (VI), Cu (II), Ni (II) and Zn (II) from wastewater. Several parameters were compared which include pH, dose required, initial metal concentration, adsorption capacity and the price of the adsorbents. From the research it was concluded that low cost adsorbents from agricultural waste were best for the removal of heavy metals i.e., Cr(VI): 170 mg/g of hazelnut shell activated carbon, Ni(II): 158 mg/g of orange peel, Cu(II): 154.9 mg/g of soybean hull treated with NaOH and citric acid, Cd(II): 52.08 mg/g of jackfruit, compared to activated carbon (Cd(II): 146 mg/g, Cr(VI): 145 mg/g, Cr(III): 30 mg/g, Zn(II): 20 mg/g). Hence, low cost agricultural wastes as adsorbents are better for the removal of heavy metal ions from industrial wastewater than the activated carbon (Kurniawana 2006).

In another study, partially converted crab shell waste, which is made up of chitosan, was used to remove Ni from industrial wastewater. Chelating ability of chitosan makes it an excellent adsorbent. The partially converted crab shells proved excellent adsorbents and quickly removed the metals within 5 minutes. The sorption mechanism for these processes was complicated and cannot easily be explained by Langmuir or Freundlich theories. The pH parameter had no effect on the overall process (Pradhan 2005).

There is another concept of using clayey soil as metal ions adsorbent from wastewater other than to be used in construction. It can be used as a low cost copper adsorber.

Adsorption isotherm models were used to understand metal ion concentration, weight of adsorbent, stirring rates, influence of temperature and pH. From the results it was concluded that 90-99% copper can be removed from agricultural effluent at a pH of 5.5. Langmuir isotherm had better shown the phenomenon of copper distribution between the liquid and solid phases in batch studies. To understand the mechanism of sorption process, rate constant, activation energy, Gibbs free energy, enthalpy, and entropy of the reaction were also calculated (Saha 2010).

The Cr (VI) from waste effluent can be removed by using neem leaves as adsorbents which was identified by experimentation in batch studies for adsorption. Among other adsorption parameters like contact time, adsorbent dosage, initial Cr (VI) concentration and pH, adsorption process was also determined by using Langmuir and Freundlich isotherm models. At pH 7 in the process, maximum Cr (VI) adsorption capacity of 10 mg/g in solution was achieved. The adsorption was achieved maximum at 1-3 pH. The activated neem leaves powder was also compared with several other low cost adsorbents and the kinetics of Cr adsorption were also evaluated (Gupta 2006). In the same manner like neem leaves, decolourized cooked tea dust (CTD) was used to remove the chromium in another research study by adsorption technique. Between the pH 2 and 11, a batch study was conducted within the agitation time of 5-60 min. The adsorbent dosage was kept as 50-500 mg/50mL and the particle size of CTD was kept as 125-750 µm for the adsorption process. Maximum adsorption of Cr (VI) was achieved at optimum pH 2 and the process showed pseudo-second order results. The desorption studies indicated 82.28% removal of the hexavalent chromium from the cooked tea dust adsorbent (Dhanakumar 2007).

In another study, teak leaves (*Tectona grandis*) were used to make activated carbon for the treatment of Pb (II) from wastewater. The air dried teak leaves were powdered and carbonized by using sulphuric acid. By using scanning electron microscope and FTIR nature of the surface of teak leaves was to be investigated. Teak leaves are easily available and economically affordable for the adsorption of Pb (II) ions as compared to commercial activated carbon, lignite and some other waste materials. With the variation in adsorption doses and different contact times, batch studies were conducted to find the Pb (II) ions removal efficiency of teak leaves. The experimental results of adsorption were interpreted by using different models like Lagergren, Bhattacharya-Venkobachar, Langmuir and Freundlich (Ahamed 2010).

Techniques for removal of heavy metals from municipal wastewaters: Municipal wastewater contains many heavy metals which are hazardous to humans and environment. The common municipal, raw wastewater and sludge contain Cd, Cr, Cu, Hg, Ni, Pb and Zn ions (Al Enezi 2004). In order to remove lead and chromium from municipal wastewater, a study was conducted on the use of activated cashewnut shells as adsorbents. The cashewnut shells were powdered and activated by using KOH and CO_2 gasification at 1027 Kelvin temperature. A mesoporous structure developed with the increase in volume from 20-28% and for 27-45% for activated carbon. The removal of Pb (II) and Cr (II) ions was excellent by using activated cashewnuts with 99.61% and 98.87% removal efficiency respectively, at optimum pH of 6.5. The Freundlich and Langmuir models showed maximum capacity for Pb (II) removal to be 28.90 $mg.g^{-1}$ and cadmium removal to be 14.29 $mg.g^{-1}$ (Tangjuank 2009).

In another study, Pb (II), Hg (II) and Cd (II) were experimentally removed by a new form of activated carbon called aerogel carbon in mono and multi-components. Batch experiments were conducted with varying metal ion concentration (mg/L) for the adsorption characteristics of aerogel carbon. The scanning electron micrographs (SEM) and EDAX spectrum of carbon aerogel surfaces before and after the adsorbent were equilibrated with the metal ion solution, clearly establish the presence of the metal ions, and some surface modifications can be observed on the carbon aerogel particles adsorption with (i) surface chemistry of the pellets on the surface of carbon aerogel and (ii) inside layers of the carbon aerogel. Applicability of the isotherm models namely Freundlich and Langmuir to predict the equilibrium uptake of Pb(II), Hg(II) and Cd(II) in mono-component, binary and tertiary system have also been tested (Kadirvelu 2008).

Another approach to make activated carbon from hazelnut husks was experimented in a research to remove Pb (II) and Cu (II). The hazelnut husks were activated by zinc chloride at 973 K in nitrogen atmosphere. The surface area of activated carbon was determined to be 1092 $m^2 g^{-1}$. By applying batch study technique, the removal capacity of activated hazelnut was identified. The activated hazelnut showed good potential for metal ions removal and also showed good results in contact time, activated carbon dosage, initial metal concentration and the effect of initial dosage. By Langmuir isotherm, the adsorption of lead and copper was found to be 13.05 $mg.g^{-1}$ and 6.645 $mg.g^{-1}$, respectively (Imamoglu 2008).

In a separate study, lead ions were removed in an experiment by using coconut shell carbon. To find the metal ions removal under different concentrations, batch adsorption study was conducted. The pH factor strongly controls the Pb (II) ions adsorption by coconut shell carbon. Therefore, maximum adsorption was achieved at 4.5 pH. Using Langmuir, Freundlich and Tempkin isotherm models, the adsorption isotherms of lead were developed. With the Arrhenius and Van't Hoff equations, activation energy (Ea) and thermodynamic parameters ΔG, ΔH and ΔS were determined. The thermodynamics of lead showed spontaneous endothermic nature of adsorption process. Coconut shell carbon removed 75% of Pb (II) and was desorbed from CSC (Sekara 2004).

In another study, the coconut shells were activated by using KOH active agent. By using this active agent, surface area of coconut shell was increased and turned to be activated carbon (Hu 1999).

From municipal wastewater, copper can be removed by sewage sludge ash because it has similar chemical composition to blast furnace slag and fly ash. The characteristics of SSA that control the adsorption are specific surface area, cation-exchange capacity (CEC) and pH of zero point of change (pHZPC) were determined and their values were 24.1-25.7meq/100 g and 3.0-3.4, respectively, which shows the removal efficiency of SSA from municipal wastewater. The copper adsorption by SSA followed Langmuir model. The maximum copper adsorption was calculated to be 3.2- 4.1 $mg.g^{-1}$ by sewage sludge ash, which was close to fly ash adsorption. SSA collects copper through electrostatic attraction, surface complex formation and cation exchange. The SSA dosage required to precipitate copper hydroxide was 30-40 g/L and the equilibrium pH of wastewater to be 6.2. The removal efficiency of copper from wastewater by sewage sludge ash was more than 98% and its functioning was similar to fly ash and blast furnace slag. The SSA can be reused to remove copper (Pan 2003).

With the aim to understand the removal of Zn (II) and Cd (II) by using fly ash in wastewater, the removal efficiency of lignite-based fly ash was observed in batch experiments. The initial concentration of the adsorbate and fly ash dosage along with other parameters of contact time, pH and temperature were studied. The contact time required to attain equilibrium was two hours. The concentration of Zn (II) and Cu (II) adsorption occurred at pH 7-7.5 and the removal of metals increased with the increase in concentration of metal ions and with the dosage of fly ash and temperature. The fly ash proved itself to be as good as activated carbon. Monolayer coverage of Zn (II) and Cd (II) ions is formed at the outer surface of fly ash which is proved by Langmuir isotherm and the thermodynamic parameters suggested the endothermic nature of adsorption process (Bayat 2002).

CONCLUSION

From the review of different studies, it is concluded here that the use of conventional treatment technologies for heavy metals in different environmental samples have their own drawbacks which make them less user-friendly. Such as, they are expensive, energy extensive and produce toxic by-products. No one denies the fact that heavy metals are dangerous to environment and human health. The most common heavy metals found in wastewater are arsenic, cadmium, zinc, nickel, copper and lead along with other metals which are mercury, chromium, iron and aluminium. They have their own impacts to health of humans including chronic and acute. In order to remove them from different environmental samples, several natural and industrial based by-products have been reviewed. Their study shows that they are far more applicable to deal with heavy metals then conventional technologies such as chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electrodialysis, etc. Their operational, maintenance, availability and regeneration costs are all affordable. They are easy to deal with and give 99% removal results.

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