

Adsorption of Heavy Metals and Phenol from Aqueous Solution onto Fly Ash as Low Cost Adsorbent: A Review

Christina Rahel, Mridula Bhatnagar

Research Scholar, P.G. Department of Chemistry, G.D.C., Bikaner Rajasthan, India

Lecturer, P.G. Department of Chemistry, G.D.C., Bikaner Rajasthan, India

ABSTRACT: Coal fly ash, which is a by-product of thermal power plants, is one of the numerous substances that cause air, water and soil pollution, disrupt ecological cycles and set off environmental hazards. On the other hand pollution by toxic chemicals has become a major problem in the global context. Amongst these heavy metals and phenols have been identified as highly toxic compounds due to their carcinogenic nature and pungent odour. Coal fly ash which is readily available and cheap makes a good candidate as an adsorbent for heavy metals and phenol. Not only will its use reduce the environmental burdens associated with its disposal, but it will also produce economic benefits. Fly ash is strong alkali material, which exhibits pH of 10–13 when added to water, and its surface is negatively charged at high pHs. Hence, it can be expected that metal ions which are cations, meaning they carry a positive charge can be removed from aqueous solutions by precipitation or electrostatic adsorption. In the same way fly ash can also be employed for the removal of phenol or phenolic compounds from many industrial wastewaters. In the present paper, efforts have been made to investigate the use of fly ash as a low cost adsorbent in the treatment of aqueous solution bearing heavy metals (Zn, Pb, Cd and Cu) and highly toxic compound phenol.

KEYWORDS: Coal fly ash, heavy metals, phenol, batch sorption, adsorbent, adsorption capacity.

I. INTRODUCTION

A. ORIGIN OF THE RESEARCH PROBLEM

Environmental pollution is the biggest menace the world faces today. It can be categorized into three major types viz. air, water and land. Air pollution arises from people's economic and domestic activities like modern agriculture, industrialization, thermal power stations, burning fossil fuel and moving vehicles which emit harmful pollutants in the atmosphere. Major sources of water pollution include industrial plants, decomposed domestic wastes, solid minerals mining activities and petroleum mining operations. Industrialization, dumping of waste at landfills and the rising human population has given rise to many human activities that cause land pollution.

Environmental pollution due to toxic heavy metals has increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Heavy metal ions do not degrade into harmless end products [1] therefore they are difficult to degrade biologically. Heavy metal contamination exists in ecosystem largely due to refining ores, mining operations, sludge disposal, metal plating, fly ash incinerators, processing of radioactive materials, paints, alloys, batteries, pesticides and preservatives [2]. Heavy metals such as Pb, Cd, Zn and Cu present in industrial wastewater, are non-biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings [3]. These toxic metals enter the food chain and are concentrated in fish and other edible organisms and become difficult to track as they move up in trophic levels [4, 5]. Due to their

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bioaccumulation and biomagnifications in the food chain they accumulate in living tissues throughout the food chain and human receive the maximum toxic impact, since they are at the top of the food chain [6].

Copper is a biological poison. A copper concentration of 0.01 mg/L can inhibit water self-purification; at a concentration of 0.0002 mg/L, water starts to become toxic for fish. Drinking water containing high level of copper is correlated with high rates of deaths from cardiovascular problems. Symptoms of acute copper poisoning include: low blood pressure, vomiting, melena, jaundice, haemolytic anaemia, and coma to death [7].

Many industries, especially electroplating, paints, cosmetics, battery manufacturing, pigments and ammunition productions are continuously releasing Zn (II) in their discharges [8]. Zinc toxicity from excessive ingestion may lead to health complications such as liver damage, respiratory incapacitation, as indicated by increased respiratory activity such as breathing rate, coughing, volume and frequency of ventilation and decrease in oxygen uptake efficiency [9].

Cadmium occurs in nature in association with zinc minerals [10, 11]. Cadmium is highly toxic because it bio accumulates and there does not exist a homeostatic control in human body for this metal. About 1-2% of ingested cadmium, if retained in body is hazardous and potent enzyme inhibitor and it has also been reported to damage liver and kidney [12] of animals and human beings.

Lead is one of the potentially toxic heavy metals and has the tendency to accumulate in soft tissues, blood and bones when adsorbed into the body [13, 14]. Lead is widely used in industries such as mining, steel, automobile, batteries and paints [15-17]. Lead can accumulate over a lifetime and even at low concentration level may cause diseases such as anaemia, encephalopathy, vertigo, anorexia, hepatitis and nephric syndrome [18].

Likewise Phenol is a serious environmental priority pollutant since it is toxic and harmful to organisms even at low concentrations. Phenolic compounds have been classified as high-priority pollutants by the USA EPA (Environmental Protection Agency, 1984). Beside the toxic effects, phenolic compounds create an oxygen demand in receiving waters, and impart taste and odour to water with minute concentrations of their chlorinated compounds [19-21]. The chronic toxicity of phenols in humans results in headache, dizziness, fatigue, nausea, vomiting, fainting, weakness and lack of appetite at high levels. Phenol can also change blood pressure and cause liver and kidney damage [22].

B. INTERDISCIPLINARY RELEVANCE

India has the fifth largest coal reserves in the world. The Indian coal is characterised by its high ash content (45%) and low sulphur content. The power sector is the largest consumer of coal followed by the iron, steel and cements segments. In India, coal will continue to remain a major source of fuel for power generation. At present, about 60% power is produced by using coal as fuel, which results in the production of about 112 million tonnes of ash per annum. As per the available estimates it is expected that ash generation will reach 175 million tonne per annum by 2012 and 225 million tonne by 2017 [23]. Coal fly ash world's fifth largest material resource which is a by-product of the coal combustion process for energy generation is recognized as an environmental pollutant. Fly ash is hazardous as its disposal require large quantities of land, water and energy, its fine particles, if not managed well, can become airborne and causes respiratory problems when inhaled. Fly ash present in air settles on leaves and crops in agriculture fields around the power plant and lowers the yield [24].

On the other hand increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and phenols which lead to several health problems in animals, plants and human beings [25]. Most of the industries discharge their wastewater and effluents containing toxic materials into rivers without adequate treatment leading to a number of serious environmental problems due to their non-biodegradability and persistence to accumulate in the environment elements such as food chain [26]. As a result of the degree of the problems caused by heavy metals and phenol pollution, it is essential to remove these toxic materials from waste water before its disposal.

In recent years, the need for safe and economical methods for the removal of heavy metal ions and phenols from contaminated water has developed research interest towards the production of low cost wastewater treatment methods. The current physio-chemical processes for heavy metal and organic compounds removal like

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Website: www.ijirset.com

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chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation recovery etc. are extremely expensive, give incomplete removal and are inefficient in treating large quantities [27-28]. In view of this, it can be expected that metal ions or organic materials can be removed from aqueous solutions by precipitation or electrostatic adsorption as these methods are found to be superior compared to the other techniques for water reuse in terms of low initial cost, flexibility and simplicity of design, ease of operation, environmental friendly, insensitivity to toxic pollutants and does not result in formation of harmful substances [29].

Fly ash, a particulate material generated by the combustion of pulverized coal in thermal power plants [30] is recognized as an environmental pollutant [31]. Globally, over 600 million tonnes of fly ash is produced during combustion of coal all over the world, which requires large dumping sites for its safe disposal posing a serious environmental problem. Since the production of fly ash is an environmental hazard, applications for the utilization of fly ash have been undertaken worldwide over the years. Some applications of fly ash in land fills, road construction, cement production, and zeolite syntheses have been widely used. However, fly ash recycling is still not sufficient and novel applications have to be explored. Therefore, it is desirable to take proper and efficient control measures to overcome this problem. Now a day many of researchers are using fly ash as an adsorbent for the removal of various organic and inorganic pollutants on account of its higher specific surface area, narrow particle size distribution, strong alkaline nature, high unburnt carbon content, the porosity of adsorbent and low cost or zero cost as it is a waste material from thermal power plants [32-37]. Conversion of fly ash which is a waste material of thermal power plants into a low cost adsorbent would provide a conventional means for waste utilization and controlling water pollution by inorganic and organic wastes, a subject, which has necessitated research interest towards the development of safe and economical methods for pollution control. In this review paper efforts were undertaken to evaluate the effectiveness of fly ash as a low cost adsorbent in the removal of heavy metals (Cu, Zn, Cd and Pd) and highly toxic compound phenol from their aqueous solutions under varying experimental conditions based on articles published recently on this key issue.

II. THEORETICAL ORIENTATION

A. HEAVY METALS: SOME GENERAL INFORMATION

The term ‘heavy metals’ refers to any metallic element which has a high density, specific gravity or atomic weights between 63.5 and 200.6 and is toxic or poisonous even at low concentration [38-42]. However, chemical properties of the heavy metals are far more important as compared to their density. Heavy metals include lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), copper (Cu), zinc (Zn), chromium (Cr), iron (Fe), arsenic (As), silver (Ag) and the platinum group elements [43]. Heavy metals occur as natural constituents of the earth crust as their ores in different chemical forms, from where they are recovered as minerals [44] and are persistent environmental pollutants. They enter the body system through food, air and water and bio-accumulate over a period of time disrupting the health system of human beings, plants and animals. Certain heavy metals like Fe, Cu, Zn, Ca and Mg are nutritionally essential for a healthy life, but large amounts of any of these may cause acute poisoning, whereas some others like As, Cd, Pb and Hg are of no known bio-importance in human biochemistry and physiology and their consumption even at very low concentrations can be toxic [45-46]. Chronic heavy metal intoxications damage central nervous system, lungs, kidneys, liver, the cardiovascular and gastrointestinal (GI) systems, endocrine glands and bones and may increase the risk of some cancers. Heavy metals can be emitted into the environment by natural and anthropogenic pollutants like industrial wastewaters from mining, metal processing, pharmaceuticals, tanneries, pesticides, rubber and plastics, organic chemicals, lumber and wood products [47-48]. Therefore to avoid health hazards it is essential to remove these toxic heavy metals from waste waters before their disposal.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

Table 1.1 Main Properties of Heavy Metals

Property	Copper(Cu)	Zinc(Zn)	Lead(Pb)	Cadmium(Cd)
Atomic number	29	30	46	48
Atomic mass, (g/ mol)	63.54	65.39	207.2	112.41
Density, (g.cm-3)	8.96	7.133	11.35	8.65
Melting point, (K)	1356.6	692.73	600.65	594.1
Boiling point, (K)	2840	1180	2013	1038
Electronic shell	[Ar] 4s ¹ 3d ¹⁰	[Ar] 4s ² 3d ¹⁰	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	[Kr] 4d ¹⁰ 5s ²
Specific gravity	8.96	7.133	11.35	8.65

B. FLY ASH: ITS PHYSICOCHEMICAL CHARACTERISTICS AND USE AS A LOW- COST ADSORBENT

In India 70% of the total electric power is obtained from coal-based thermal power plants resulting in the production of about 112 million tonnes of ash per annum, which is expected to reach 175 million tons in near future [49]. Fly ash an inorganic, non-combustible by-product of burning coal at electric power plants is composed of unburnt carbon particles which solidify as spherical, glassy particles [50] that are carried away by the flue gases in the form of ash and are separated from the exhaust gases of coal-fired thermal power plants using electrostatic or mechanical precipitators, bag houses or scrubber systems [51].

The most serious problem associated with coal-based thermal power plants is the disposal of huge quantities of fly ash which is considered a toxic waste as it requires large dumping sites for disposal and pollutes land, water and air causing environmental dangers. At thermal power plants, fly ash is collected and disposed by using two methods, wet disposal and dry disposal methods with more than 65% of fly ash disposed off in landfills and ash ponds. More than a third is disposed off in dry landfills constructing a dry embankment (dyke). In the wet system, fly ash is mixed with water and sluiced and is hydraulically transported as slurry through pipe to a nearby settling pond or dumping site [52, 53].

The utilization rate of fly ash in India is around 40%, and the rest is disposed of on land. Under dry disposal method, fly ash can mainly be used for land reclamation and dense packing of mine fills which can provide scope for the environmental friendly huge volume utilization but is possible only if fly is available near such mining sites. Besides these disposal methods potential avenues of fly ash utilization as an engineering material primarily stems from its pozzolanic nature, spherical shape, and relative uniformity enabling it use [54] in India as

- Portland cement and grout
- Roads and embankment construction
- Structural fill
- Waste stabilization and solidification
- Underground mine stowing
- Substitute for cement clinkers
- Improvement of soft soil properties
- Road sub base
- Fly ash bricks
- Fill material
- Admixture in concrete

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

- Agriculture purposes

Fly Ash is regarded as a complex heterogenous mixture of ferroaluminosilicate minerals with Al, Si, Fe, Ca, K and Na being the predominant elements [55]. However, composition of fly ash varies widely depending on coal source and combustion process. Due to presence of minute sized potentially toxic heavy elements like arsenic, antimony chromium, vanadium, molybdenum, mercury, selenium and cadmium etc. fly ash has been considered hazardous for living organisms, plants and animals.

The discharge of wastewater into environment containing elevated levels of heavy metals and toxic pollutant phenol without proper treatment has adverse environmental effects. Thus conventional methods like chemical precipitation, filtration, chemical oxidation or reduction, ion exchange, electrochemical application and biological treatment are applied for removing dissolved heavy metal ions and phenol from industrial wastewaters [56]. But these pollutant removal processes have some inherent shortcomings and limitations. Therefore adsorption process is applied for pollutant removal from wastewaters because of convenience, simplicity of design and easy operation but again high cost adsorbents are a problem in a country like India. Hence fly ash which is a waste product of thermal power plants can be used as a potential adsorbent due to its porous structure and high surface area [57] for the removal of inorganic and organic pollutants, thereby also reducing its harmful impact on the environment and solving the problem of disposal associated with its massive production in our country.

III. TECHNOLOGIES AVAILABLE FOR REMOVAL OF INORGANIC AND ORGANIC POLLUTANTS FROM AQUEOUS SOLUTIONS/WASTEWATERS

A. GENERAL CONSIDERATIONS

There are a number of wastewater treatment technologies that are available for treating organic and inorganic pollutants present in industrial effluents. Basic techniques available for the treatment of industrial waste water containing heavy metals and highly toxic organic compound phenol are mainly divided into three categories, physical, biological and chemical. Because of the high cost and disposal problems, these conventional methods have their own limitations and drawbacks so a combination of these methods is often applied to obtain the desired results. Conventional physiochemical methods used for removing effluents from industrial wastewaters include adsorption, coagulation, chemical precipitation, ultra filtration, electrochemical oxidation, biological methods, ion exchange, enzyme treatment, solvent extraction, disinfection by ozone, photo catalysis, etc [58, 59]. However, these conventional methods give incomplete pollutant removal and are often expensive and difficult to maintain due to expensive equipment and monitoring systems, high energy costs and extra cost of treating the resultant sludge generated before disposal [60]. Table 1.2 summarizes the main advantages and disadvantages [61-64] of the various physio-chemical treatments presented in this study.

The below mentioned techniques are most expensive and often not feasible. When effluents are dissolved in large volumes at low concentrations (less than 100mg/L), these treatment procedures generally become ineffective [65] so there is a research need to develop efficient and low cost wastewater treatment methods.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

**Table 1.2 Comparison of Technologies for Heavy Metal and Organic
Pollutant Removal from Wastewaters**

Technology	Advantages	Disadvantages
Chemical precipitation	little capital investment, simple operation, accomplished with very little equipment	may require working with corrosive chemicals, increasing operator safety concerns, sludge generation, for high concentrations difficult separations, extra operational cost for sludge disposal,
Chemical coagulation	Most commonly used, easy application, very effective, dewatering, sludge settling	High cost, large consumption of chemicals, ineffective in soft waters
Chemical oxidation/reduction	Mineralization, high degree of chemical specificity possible	Chemicals required, risk for acute toxicity, any intermediates and by-products may be hazardous
Ion-exchange	Operating convenience, high regeneration of materials, selective method	High cost, less number of ions removed, highly selective
Electrochemical methods	Metal recovery, no consumption of chemicals, pure metal can be achieved	For high concentrations, expensive, initial solution pH and current density
Adsorption with new Adsorbents	Easy operating conditions, having wide pH range, high meta- binding capacities	High capital cost, low selectivity, exothermic process, production of waste products
Adsorption using activated carbon	High efficiency(99%), most of effluents can be removed, long life (high capacity)	High cost of activated carbon, no regeneration, can generate carbon fines, performance depends upon adsorbent
Reverse osmosis	Converts hard water to soft water, requires less maintenance, pure effluent	Removes healthy minerals like calcium and magnesium, expensive, membrane scaling
Electrodialysis	High separation selectivity, minimal pretreatment of feed required, high membrane life	High operational cost due to membrane fouling and energy consumption, problem of corrosion, large amounts of by-products are formed
Photocatalysis	Removal of metals and organic pollutant simultaneously, low cost and fewer maintenance requirements, high optical efficiency, less harmful by-products	Long duration time, water overheating, reactant contamination, limited applications
Membrane process and ultrafiltration	Less chemical consumption, less energy consumption, high efficiency, less solid waste produced, effective in eliminating most particles	High cost, regular cleaning is required, cannot remove any dissolved inorganic substance, low flow rates, removal % decreases with the presence of other

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

		effluents
Hybrid methods (flotation-filtration)	Lower capital cost, highly selective, high membrane fluxes	Airflow should be appropriate, not possible to use horizontal membranes, Slugs are not suitable for flotation

B. BIOLOGICAL TREATMENT

Biological treatment is a process using micro-organisms, fungi, bacteria, yeasts, algae, green plants and their enzymes [66, 67] to accumulate and degrade different pollutants mainly organic, by aerobic or anaerobic decomposition. In this process methods such as microbial degradation, bioaugmentation, activated sludge, extended aeration, fungal decolonization, adsorption by (living or dead) microbial biomass and bioremediation [68-72] are commonly used to remove all biologically-degradable material from the industrial wastewater and to transform them harmless. Biological remediation methods are more economical, reliable, simple and environmentally friendly when compared with other physical and chemical processes [73]. However bioremediation is limited to those compounds that are biodegradable and is usually more time consuming than other treatment processes. Degradation mechanism is hardly known and difficult to control and organic compounds like phenol strongly reduce biodegradation of other components which makes this process so difficult. Removal of heavy metals by biodegradation is not so efficient as heavy metals are toxic to most micro-organisms and cause problems in biological waste treatment plants so genetically engineered (GE) micro-organisms have been used for the removal of heavy metals such as Cd, Hg, Ni, Cu, As and Fe [74-76].

C. CHEMICAL METHODS

Chemical processes used in conjunction with physical and biological processes are designed to bring about some beneficial chemical transformations by means of chemical reactions involving the complete breakdown of the hazardous species to less or non-hazardous by-products, or to a different and more readily separable form, in which further treatment becomes possible. Many of the processes in this section, chemical precipitation, electrolytic recovery, adsorption/ion exchange, solvent extraction, coagulation or flocculation combined with flotation and filtration, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone) and irradiation processes are those used frequently for treating aqueous hazardous wastes, effluents and waste waters containing metals and other inorganic species [77]. Heavy metals can be removed from inorganic effluent as metal hydroxides by using chemical precipitation method which is pH sensitive but presence of other aqueous organic ligands in wastewater can hinder precipitation thus resulting in decreased metal concentration with the problem of excessive sludge production [78]. For toxic organics including phenol, chemical oxidation by ozone and chlorine has been reported effective with maximum removal efficiency using ozone as an oxidant and several factors influence the effectiveness of this oxidation process. Generally, chemical processes have an inherent disadvantage compared to physical operations in that they are additive processes and poor process control can lead to very high reagent consumption. In some chemical processes like chemical precipitation only limited number of hazardous substances for which suitable insoluble species exists can be used with sophisticated chemistry and process requirements and are often impractical other than when very high value materials are involved [79, 80]. Furthermore, in these methods there is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Although these methods are efficient for the treatment of industrial wastewaters contaminated with pollutants, they are very expensive, extremely dangerous to use and require high consumption of energy.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

D. PHYSICAL METHODS

Physical methods include processes in which removal of substances is accomplished by the use of naturally occurring forces, such as gravity, electrical attraction, van der Waal forces, physical barriers and no gross chemical or biological changes occur in the chemical structure of the target substances. Physical methods of wastewater treatment include screening, mixing, sedimentation, flotation flocculation, filtration, equalization, comminuting, grit removal, oil and grease removal, adsorption, gas transfer and barriers such as deep bed filters, bar racks, screens and membrane [81]. The major disadvantages of physical process such as comminuting, grit removal is that they return material to the wastewater flow which causes problems if flow is agitated, increase plastics and rags on air diffusers and accumulate synthetic solids thus decreasing the separation efficiency. Whereas membrane filtration processes have the disadvantage of formation of metal hydroxides, which clog the semipermeable ion-selective membranes causing membrane fouling to occur thus making this process very expensive [82]. Among physical wastewater treatment methods, liquid-phase adsorption is currently considered to be the most potentially feasible alternative for wastewater treatment because of its simplicity of design, sludge free operation and low capital intensiveness [83]. This process does not require an additional pre-treatment step before its application, is insensitive to toxic pollutants and also, does not result in the formation of harmful substances.

Liquid phase adsorption is highly efficient, well-established technique for the removal of organic compounds and metal ions from various industrial effluents due to its simplicity of design, low investment in terms of both the initial costs and land, effectiveness, ease of operation and the availability of a wide range of adsorbents [84, 85]. Activated carbon is often preferred as an effective adsorbent for the removal of organic compounds [86] and heavy metals [87, 88] from wastewaters due its high adsorption capacity, characterized by a high specific surface area. It is highly porous, with heterogeneous surface consisting of several functional groups which act as potential adsorption sites and is usually prepared in small pellets or powder [89]. However, commercial activated carbon (CAC) is expensive with irreversible nature of adsorption which limits its use as an adsorbent on a large industrial scale. Therefore, research has been conducted on a wide variety of sorbents which fulfil all the properties of activated carbon but at the expense of low cost as compared to activated carbon. Some of the reported low-cost sorbents include bark, tannin-rich materials, seaweed, algae, fly ash, chitosan, dead biomass, xanthate, zeolite, clay, peat moss, bone ash, leaf mould, moss, iron-oxide-coated sand etc.

Fly ash particles are generally spherical in shape ranging in size from 0.5 μm to 100 μm . Components of fly ash vary depending upon the combustion technology and composition of the coal being burned, but all fly ash includes considerable amounts of silicon dioxide (SiO_2), Calcium Oxide (CaO) also known as lime, aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3). Fly ash has potential use as suitable sorbent to remove heavy metals and organic compounds [90] from aqueous solutions because of its particle size distribution, water holding capacity and highly porous and large surface area. Its effectiveness increases with high carbon content and its alkaline nature makes it a good neutralising agent [91]. Therefore, it is evident that these properties enable use of fly ash as a low-cost adsorbent to efficiently remove heavy metals and organic compounds from aqueous solutions as it is readily available at no or little cost without any regeneration process.

IV. REVIEW OF RESEARCH AND DEVELOPMENT ON THE SUBJECT

A. REMOVAL OF HEAVY METALS AND PHENOL USING CONVENTIONAL ADSORBENTS

Conventional adsorbents such as activated carbon, silica gel, activated alumina and bauxite, ion exchange resins and activated clay have been used extensively by previous researchers to remove heavy metals and other organics dissolved in water due to their high adsorption capacity. The most effective method for the removal of dissolved heavy metals and organic material is sorption on activated carbon [92], which is a highly porous and amorphous solid with higher exposed surface area for adsorption. Due to high cost of commercially activated carbon it can be prepared from a variety of carbonaceous materials such as anthracite coal, olive stones, rice husk, coconut shells, wood char, lignin, peat, sawdust, petroleum coke, bone char, etc [93]. Srivastava et al. [94] have studied the adsorption of phenol onto activated carbon-commercial grade (ACC) and laboratory grade (ACL). The liquid-phase adsorption of phenol from water using several different types of

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

adsorbents such as activated carbons, activated alumina was investigated by Roostaei et al. [95]. Seco et al. [96] studied the adsorption of heavy metal ions Cu, Cd, Zn and Ni onto activated carbon and reported that adsorption of Cu ions is less sensitive to the presence of other metal ions, when compared to Ni, Cd and Zn. Silica gel, prepared by the reaction between sodium silicate and acetic acid is an amorphous, inert, non-toxic, polar and dimensionally stable form of silica. Due to large number of reactive sites silica gel has a good adsorption capacity for metal ions and phenol. Idris and Saed [97] investigated the possible utilization of silica gel sludge for the removal of phenol from aqueous solutions and observed that the adsorption capacity increased with decrease in pH. Activated alumina is a granular and highly porous form of alumina available in powder, pellet, or granule form and is prepared by treating aluminium ore so that it becomes porous and highly adsorptive for use in adsorption process. The adsorption of phenol onto activated alumina was investigated by Hassan and Hammad [98] and it was found that with the increase in the applied voltage, the phenol removal rate increased, while pH increased. The adsorption of heavy metal ions at trace concentrations was successfully studied by Akill et al. and Ceryera et al. onto surface of activated alumina [99, 100]. Therefore, adsorption of heavy metals and phenol on conventional adsorbents such as activated carbon, silica gel and activated alumina etc. have been used widely in many applications as an effective adsorbent, however, the high cost of the activation process limits their use in wastewater treatment applications [101]. The limitations on the use of these conventional adsorbents has lead to research need to find improved alternative non-conventional low-cost adsorbents which will meet several requirements such as regeneration capability, easy availability, cost effectiveness etc and will prove efficient substitutes for pollution control on a large scale.

B. NON-CONVENTIONAL LOW COST ADSORBENTS FOR HEAVY METALS AND PHENOL REMOVAL

In recent years, the increasing costs and environmental considerations associated with the use of conventional adsorbents has led to a new research work aimed at developing new low cost adsorbents that are derived from renewable resources, particularly from the waste materials. The adsorption technique involving non-conventional low cost adsorbents [102] has been shown to be highly efficient for the removal of heavy metals as well as organic compounds due to significant advantages like low cost, simplicity, availability, profitability, ease of operation and efficiency, in comparison with the conventional adsorbents which are highly expensive and non affordable by most of the developing nations. According to Bailey et al. [103] a low cost adsorbent is one which is abundant in nature, requires little processing and is an industrial waste or agricultural by-product. Several agricultural waste materials, industrial by-products, natural wastes and biosorbents have been widely utilized as an adsorbent for removing heavy metals and phenol with the advantages of being abundant, readily available, cost effective and environmentally friendly.

1.4.2.1 Natural Materials

a) Zeolite:

Basically zeolites are a group of naturally occurring or synthetic aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. Large effective surface area having strong ion exchange capacity and uniform cavities gives them superior adsorptive qualities. The residual negative charge density on their lattice is balanced by the presence of other exchangeable metallic ions which are hydrated alkali and alkaline earth cations in the pores of the framework. Due to their low costs, effective chemical and structural properties they have been used as an adsorbent, molecular sieve, ion-exchangers and catalysts [104] in the past few years. Clinoptilolite, a zeolite with open reticular structure was used by Zamzow et.al. [105] to remove Al, Fe, Cu, and Zn from copper mine wastewater. Sodium zeolite which is available in all the commercial chemical agents and is cheaper than the siliceous and aluminous zeolites can be used as cost effective adsorbent for the removal of phenol from aqueous solution. The main disadvantages are their great sensitivity to deactivation by irreversible adsorption and need of an artificial support due to their low permeability when used in column operations.

b) Clay:

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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Vol. 6, Issue 2, February 2017

Clay materials are used as strong adsorbents because of their low-cost, abundance, naturally occurring high surface areas and high cation exchange capacities [106]. The negative charge on the structure of clay gives the capability to adsorb positively charged species. Montmorillonite clay and its derivative bentonite have the largest surface area with the highest cation exchange capacity and have affinity to adsorb water in their interlayer sites. Banat et al. [107] successfully studied the adsorption of phenol from aqueous solution by bentonite. A number of studies have been conducted using montmorillonite, to show effectiveness for removing metal ions such as Zn^{2+} , Pb^{2+} , and Al^{3+} from aqueous solutions [108]. Although the removal efficiency of clays for heavy metals and phenols may not be so efficient, but their low cost and availability on large scale makes them good candidates for wastewater treatment.

c) Chitosan

Chitosan is the second most abundant naturally occurring muco-polysaccharide found in shells of crustaceans [109] like crabs and shrimps. Chitosan, produced commercially by deacetylation of chitin is an attractive material for wastewater treatment. It is being used for adsorption mainly because it has an amine functional group which is strongly reactive with metal ions and is cheap or a freely available resource. The high porosity and high hydrophilicity due to large number of hydroxyl groups [110], results in novel binding properties for metal ion such as cadmium, copper, lead, uranyl, mercury and chromium. McKay et al. investigated the adsorption of Hg(II), Cu(II), Ni(II) and Zn(II) on chitosan and found that Hg(II) had the maximum adsorption capacity [111]. The biosorption of phenol and from aqueous solutions onto was studied by Nadavala et al. [112]. The main limiting factor for many of the possible applications of chitosan is that it is easily soluble even in weak, dilute acidic solutions which render it as an insoluble biosorbent under such conditions.

d) Peat:

Peat is a polar, highly porous and very dark organic material formed under waterlogged conditions from the partial decomposition of organic matter [113]. Peat contains lignin and cellulose which include polar functional groups like ethers, alcohols, aldehydes, ketones and acids that allow it to bind with a variety of metal ions. In spite of its low adsorption capacity, peat can be used as a low cost adsorbent in place of activated carbon as it has a high cation exchange capacity and the spent material can be disposed off easily. Viraraghavan and Maria investigated adsorption characteristics of peat along with other adsorbents for the removal of phenol from wastewater and found that the removal efficiency of peat was maximum when compared with other sorbents [114]. Adsorption of Zn and Cd on peat was investigated by Petroni et al., 2000 and it was observed that peat columns are able to retain the main interferent on adsorption of metal ions in solution [115]. However, disadvantages of using peat in its natural form are that it is difficult to handle because of its stringy and messy strands and has low chemical stability along with poor mechanical strength.

1.4.2.2 Agricultural Wastes

Agricultural wastes due to abundant availability pose little economic value and create serious disposal and pollution problems. A large amount of solid waste produced in the agricultural industry is normally used as a domestic fuel. However, for better utilization it can be explored as an alternative adsorbent owing to abundance in nature, low cost, porous structure and relatively high carbon content [116].

a) Rice Husk:

Rice husk, which is a relatively abundant, potentially available throughout India after harvest and low cost material, is widely being investigated as an adsorbent for the removal of various pollutants such as heavy metals and organic compounds from wastewaters. Dry rice husk contains 70–85% of lignin, cellulose, sugars, etc. and the rest part contains silica present in the cellular membrane which acts as an effective adsorbent for different materials [117]. Kermani et.al conducted studies to use rice husk for the removal of phenol from aqueous solution [118]. Removal of chromium, zinc, copper and cadmium ions from aqueous solution at optimum conditions was studied by Munaf et.al on the surface of unmodified rice husk [119].

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

b) Sugarcane Bagasse:

Sugarcane bagasse an agricultural by-product from sugar refining industries is used worldwide as fuel in the same sugar-cane industry. After energy generations in power plant ashes containing high amounts of unburned matter, silicon and aluminium oxides are produced which could be applied for waste water management strategies [120]. The adsorption of cadmium on sugarcane bagasse from aqueous solution was investigated by Khan et. al. and the efficiency of adsorption was found to depend on the pH, contact time and initial metal ion concentration [121]. Karunaratnea and Amarasinghe studies the removal of aqueous phenol from activated carbon prepared from sugarcane bagasse in a fixed bed adsorption column [122]. It however suffers with the disadvantages of high activation cost and substantial amount of sorbent loss during regeneration.

c) Sawdust:

Sawdust, a solid waste product from the wood industry is one of the possible low-cost adsorbent because it can be obtained in large quantities from sawmills at negligible price. It can be used as a potential adsorbent as it contains lignin, cellulose and hemicellulose [123] with polyphenolic groups which effectively bind heavy metal ions through different mechanisms. Saw dust has been examined successfully by a number of researchers to be a promising effective material [124] for the removal of heavy metals and phenol. Shukla et al. have investigated the adsorption capacity of sawdust for various heavy metal ions [125]. Research on the adsorption of phenol by sawdust was carried out by Jadhav et al. and it was observed that sawdust can be effectively used as a low cost adsorbent [126]. However, sawdust has a low adsorption capacity and its sorption process is pH dependent.

d) Other Agricultural Waste By-Products:

Activated carbon is one of the most popular and widely used adsorbents for removal of heavy metals and phenol from water and wastewaters. Activated carbon characterized by high surface area, microporous characteristics and high adsorption capacity still remains an expensive material in developing countries [127]. Hence, there is an urgent need to explore the feasibility of agro-based natural wastes as inexpensive materials for the elimination of pollutants from wastewaters. In recent years, researchers have worked on inexpensive materials, such as coconut shell [128], corn cob [129], palm shell [130], apple pulp [131], chickpea husks [132], grain sorghum [133], pistachio nut shell [134], jute fibre [135], olive stones and walnut shell [136], cherry stones [137], jackfruit shell waste [138], oil palm shell [139], rubber tree seed coat [140], cotton stalk [141], flamboyant [142], Ceiba pentandra hulls [143], Euphorbia rigida [144], hazelnut husks [145], wheat bran [146] and Terminalia arjuna nuts [147] etc. which are locally available and have demonstrated outstanding removal capabilities as compared to activated carbon. The adsorption capacities of different adsorbents for adsorption of heavy metals and phenol under different environmental conditions reported in the literature are compared in Table 1.3.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

Table 1.3: Adsorption Capacities of Different Low-Cost Adsorbents for Heavy Metal and Phenol Removal

Adsorbent	Pollutant (Heavy metal and Phenol)	Adsorption Capacity	Reference
Peanut husk	Pb (II)	29.14	148
	Cu (II)	10.15	
Cassava tuber bark waste	Cd(II)	26.3	149
	Cu(II)	90.9	
	Zn(II)	83.3	
Wheat bran	Cu(II)	51.5	150
	Cd(II)	101	151
Jute fibres	Cu (II)	8.40	152
	Zn(II)	5.95	
Spent grain	Cd(II)	17.3	153
	Pb(II)	35.5	
Carrot residues	Cu(II)	32.74	154
	Zn(II)	29.61	
Sugarcane bagasse	Cu(II)	114	155
	Pb(II)	196	
	Cd(II)	189	
Sugar beet pulp	Cu(II)	0.15	156
	Zn(II)	0.18	
Pinus pinaster	Cd(II)	8.00	157
	Pb(II)	1.59	
Redwood bark	Cd(II)	27.6	158
	Pb(II)	182	

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

Carbon aerogel	Cd(II)	400.8	159
	Pb(II)	0.70	
	Zn(II)	1.84	
	Cu(II)	561.71	
Vermicompost	Cd(II)	33.01	160
	Pb(II)	92.94	
	Zn(II)	28.43	
	Cu(II)	32.63	
Activated carbon from waste PET	Phenol	260	161
Activated carbon from waste tyres	Phenol	110	162
Volcanic soil	Phenol	28	163
Synthetic geopolymers	Phenol	23	164
Natural coal	Phenol	18.80	165
Activated coal	Phenol	1.48	166
Dried sewage sludge	Phenol	16	167

1.4.2.3 Industrial By-Products

The industrial by-products are available free of cost and cause major disposal problem. Some of these wastes are regenerated while others find no utilization and are disposed off. If the solid wastes could be used as low cost adsorbents, it will reduce the volume of waste materials and the pollution problem associated with its

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 2, February 2017

disposal. A number of industrial wastes such as red mud, metal hydroxide sludge and fly ash have been investigated with or without treatment as low cost adsorbents for the removal of pollutants from wastewaters as they require little processing to increase their sorption capacity. Red mud (RM), largely produced from the alumina industry emerges as a residue of the digestion of bauxite ores with caustic soda for alumina (Al_2O_3) production [168]. It is composed of fine particles of silica, aluminium, iron, calcium and titanium oxides and hydroxides, which are responsible for its high surface reactivity that enables its use as a low cost adsorbent for the adsorption of heavy metals [169, 170] and phenols [171] from wastewaters.

Another industrial solid by-product of thermal power plants based on coal burning is fly ash which is a hazardous waste generated in huge amount every year. However, high percentage of silica and alumina present in fly ash increase its sorption capacity and makes it a highly potential adsorbent for adsorption of various effluents from wastewater. It is strongly alkaline and negatively charged at high pH when added to water, so metal ions can be removed from aqueous solutions by electrostatic adsorption. Several research studies were conducted to show the effectiveness of fly ash in the removal of heavy metal ions [172-174] and phenol [175] from aqueous solutions. However, there is a research need to study more on the removal characteristics of fly ash and their effect on adsorption capacity under varying experimental conditions to reduce its environmental and health effects as well as the hazards associated with the use of heavy metals and organic compounds.

V. CONCLUSIONS

Environmental pollution generated by fly ash and industrial effluents is of special concern because they are posing a significant danger to human health and environment. Coal fly ash, which is a by-product of thermal power plants is cheap, widely available and can be used as a low cost adsorbent for the removal of phenol and heavy metals from water and wastewaters. Therefore, present paper is designed to investigate the removal of heavy metals (Zn, Pb, Cd and Cu) and organic pollutant phenol from aqueous solutions using fly ash as a low cost adsorbent. Adsorption, a physicochemical tertiary technique used in this study is one of the most effective, easiest and safest methods for the removal of heavy metals and phenols from water and wastewaters. Among other wastewater treatment methods, adsorption using fly ash is the most efficient and economical method because of its relative low cost. Fly ash, a by-product of thermal power plants requires no energy for its generation so it would serve as replacement for materials that are produced by consuming energy. Adsorption by fly ash not only reduces the hazards associated with its disposal but also contribute to the sustainability of the surrounding environment by eliminating the toxic effects of heavy metal and phenol pollution. The main advantage of fly ash as adsorbent for water pollution control are low initial and operational cost, flexibility and simplicity in design and operation, no sludge generation and no effect of toxic substances compared to conventional wastewater treatment processes. Hence, fly ash as a low-cost adsorbents may be used effectively and efficiently to treat wastewater and thus contribute to the sustainability of the surrounding environment.

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