LITERATURE REVIEW OF REMOVAL OF HEAVY METALS USING COCONUT SHELL BASED CHARCOAL

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Abstract - Heavy metals present in waste water are posing major threats to living organisms and its removal is therefore of huge concern now. Among other techniques available, adsorption is one of the easiest and cost effective ways of water treatment. The treatment becomes even more cost effective if sorbents can be prepared from renewable and cheap sources like agro wastes. Activated carbon produced from coconut shells can be used to remove heavy metals. 70% removal of copper is found with an initial concentration of 2 ppm, pH of 5 and adsorbant dosage of 10 g/L. Activated carbon can be modified by converting it into composites. Activated carbon-iron oxide nano composite gave a removal of 87% with the same initial parameters.It can be considered as future expansion of the paper.

Key Words: ppm-parts per million

1. INTRODUCTION

1.1. ACTIVATED CARBON

Activated carbons are extremely versatile adsorbents and have major industrial significances. They have high specific porosity and hence enhanced surface area. Thus, they are used in wide range of applications concerned particularly with the removal of species by adsorption from the liquid or gas phase. Activated carbons can be considered to be composed of non-graphitic, non-graphitizable carbons with a highly ordered microstructure [1].

Activated carbon has been in use since ancient times. The origin of activated carbon (AC) is associated with Ancient Egypt (1500 BC), when the Egyptians make use of its adsorbent characteristics for water purifications and medicinal purposes[2]. The first recorded case dates back to 3750 BC, when both the Egyptians and Sumerians used wood char for the reduction of copper, zinc and tin ores in the production of bronze, and also as a smokeless fuel. The use of activated charcoal in medicinal applications is first recorded in Thebes (Greece).Hippocrates suggested the use of wood char for treatment of drinking water. The use of activated carbon as a gas phase adsorbent was first recommended by Dr. D. M Kehl, who used wood char to mitigate odours emanating from gangrene.

The application of activated carbon on an industrial scale started in England in 1793 AD when wood char was found as a capable decolourising agent in sugar industry. It was then replaced by bone charcoal which was proved to be a better adsorbent than wood char. Activated carbon was used extensively as an adsorbent for gaseous adsorbates by the middle of 19th century. Carbon filters came to be used widely in sewer ventilation systems to remove nasty odour and in gas masks to prevent inhalation of toxic vapours.

Kayser in 1881 used the term adsorption to describe the binding of gas molecules on char. Activated carbon, as it is in its present form, was first discovered by R von Ostrejko. He is best considered as the father of/inventor of activated carbon. He suggested two ways to synthesise activated carbon:

• The carbonization of lignocellulosic materials with metal chloride (a form of chemical activation).

• The mild gasification of chars with steam or carbon dioxide at high temperatures (thermal or physical activation

The first commercial chemically activated carbon was produced in Aussig in 1914; raw material used was saw dust and zinc chloride was the activating agent. It came to be known as carboraffin.

The First World War triggered the massive production and application of activated carbons. It was then that activated carbon based gas masks were developed to adsorb poisonous gases used by foes as a war weapon. Since then, the production and utilisation of activated carbon has increased every decade, especially due to the implementation of more stringent environmental regulations regarding treatment of water resources, clean gas application and economic recovery of valued chemicals [1].

1.2 ACTIVATED CABON PREPARED FROM AGRO WASTES

Among the various types of chemical and physical methods developed for the treatment of effluents, adsorption processes utilizing activated carbon are preferred because of its ease of application with good efficiency. However, commercial activated carbon is very expensive and non-renewable, which limits its practical utility, particularly for a large-scale setting. To overcome these drawbacks, production of activated carbon from cheap and renewable precursors, which are mainly agricultural by-products and

wastes like coconut husks and coconut shells, have been investigated[3].

Coconut shells are excellent materials to produce activated carbon due to their high carbon content and hardness[4]. Coconut shell is composed of carbonaceous materials like lignin, cellulose and hemicellulose[5, 6]. Activated carbons produced from coconut shells have a tighter, more microporous structure than their coal based counterparts. This is due to the inherent pore structure of the coconut shell precursor compared to the coal precursor. This microporosity itself makes it a very efficient adsorbent.

## 1.3. METHODS OF PREPARATION OF ACTIVATED CARBON

Two methods are available for the production of activated carbon from carbonaceous materials:

- Chemical activation

- Physical activation

Physical activation is a two-step process involving carbonization and then activation using steam, oxygen or carbon dioxide. Carbonization is the process of converting organic material into charcoal and this releases flammable and non-flammable gases, water, liquid tar, etc. During carbonization, non- carbon elements like hydrogen, oxygen, etc. are eliminated as volatile species and the residual carbon atoms arrange themselves into stacks of randomly cross-linked aromatic sheets. These random arrangements of aromatic sheets leave interstices which give rise to pores[7]. Activation process aims at enlarging the pores on carbon by breaking the bonds between hydrocarbons, which in turn enhances the surface area and adsorption property. Activation using steam and carbon dioxide occurs by the following reactions:

$$C + H_2O \rightarrow \quad H_2 + CO$$

$$C + CO_2 \rightarrow \quad 2CO$$
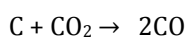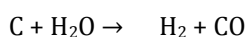
The reaction of steam with carbon is endothermic and is catalysed by the carbon surface, which finally leads to the production of water gas.

$$CO + H_2O \rightarrow CO_2 + H_2$$
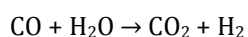
Since these reactions are endothermic, external heating is required to drive the reactions

Chemical activation can be done by impregnating raw or pre carbonized material with an activating agent and pyrolysing in the absence of oxygen. The most commonly used activating agents are phosphoric acid, hydrochloric acid, sulphuric acid, alkalis namely and sodium hydroxide and potassium hydroxide, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are commonly used for the activation of lignocellulosic materials. Among them, phosphoric acid is the more preferred activating agent because of its low environmental impact when compared to zinc chloride. The resultant charcoal is washed, dried and ground to required size.

A combination of both physical and chemical activation processes are carried out to produce activated carbon for specific applications like gasoline vapour control, gas storage, etc. For this, lignocellulosic precursors are first treated with chemical activating agents and then again activated under carbon dioxide flow[8].

1.4. STRUCTURE OF ACTIVATED CARBONS

The major constituent of activated carbon is the element carbon comprising 85-95% of it. In addition heteroatoms like oxygen, sulphur, nitrogen and hydrogen are also found which depends on the raw material, preparation and activation procedures.

Microcrystalline structure of activated carbon differs from graphite with respect to interlayer spacing. The layers are less ordered in activated carbons compared to graphite and this is due to the presence of heteroatoms in activated carbon. Biscoe and Warren proposed the term turbostratic for such a kind of structure.
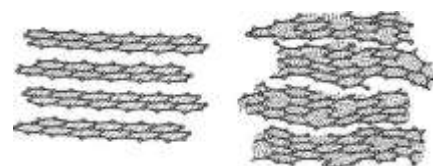

Fig.1. Graphite, turbostratic

In 1950's, the studies of Rosalind Franklin suggested that activated carbons are mainly composed of non-graphatisable carbon (which cannot be transformed into crystalline graphitic structure even at high temperatures). According to her, small graphitic crystallites are joined together by cross links in activated carbons, even though she couldn't explain the nature of crosslinks. More recent studies suggest that non graphatisable carbon has a fullerene structure containing pentagonal and other non-hexagonal rings I addition to hexagons. This structure could explain the porosity of carbons and some other properties. But this structure too could not be confirmed using diffraction studies[9],[7].

2. APPLICATIONS OF ACTIVATED CARBON

Activated carbon has two broad application classes, namely liquid and vapour phase purification. Such sorbents are used to purify a wide range of liquid systems like potable water, waste water, industrial process water and so on[10]. Removal of taste and odour contaminants and harmful pollutants from potable water is the major application and

for this purpose activated carbon has been in use since long time back. Activated carbons are useful in removing precious metal catalysts after synthesising pharmaceutically active ingredients. Sugar decolourisation is yet another important application of these sorbents. One of the important recent applications is the colour removal from natural gas liquids. Activated carbon has applications in realms other than purification like recovery of gold from cyanide leaching solutions, storage of gases like hydrogen and methane and electrodes for double layer capacitors and catalysts.

Activated carbon of lignocellulosic origin is widely being used for pollutant removal. Lignocellulosic activated carbon is widely used in industrial sector for operations like petroleum refining, air pollution treatment and volatile organic compounds adsorption. Activated carbons produced by varying parameters like temperature, heating rate, gas flow rate, activating agents and so on have been found very effective in removing polluting gases like sulphur dioxide, nitrogen dioxide, and hydrogen sulphide[11].

Wastewater from various industries like paints and pigments, glass production, mining operations, metal plating and battery manufacturing processes are known to contain heavy metal contaminants[12].Due to the discharge of heavy metal containing waste water, industries bearing heavy metals like Cr, Cu, Ni, As, Pb, Zn, As are more hazardous than others. Because of their high solubility in aquatic environments, heavy metals are easily absorbed by living organisms. They can get into the food chain and finally will be accumulated in large amounts in human. If they are ingested beyond a limit, they can cause serious health issues and so it is essential to treat such waste waters before they are released into environment[13].Activated carbon is nowadays being commonly used in treatment of heavy metal containing effluents.

2.1 HEAVY METAL TREATMENT USING ACTIVATED CARBON

Heavy metals are defined as those metals which possess a specific density of more than 5g/cm^3 and cause adverse impacts on environment and living organisms. These metals are essential in low concentrations to maintain various biological and physiological functions, but cause severe adverse impacts when present in excess amounts[14].

Toxic metals get dispersed in the environment through organic wastes, transport, industrial effluents and power generation. When they are present in gaseous form or as particulates, they may be carried to far off places by wind. They are finally washed off to landscapes and water bodies. Contaminated water from mines and smelting units may also be carried by drainage water and this is yet another source of heavy metal pollution. Humans become exposed to these heavy metals through ingestion or inhalation[15, 16].

Heavy metals cause serious health defects like reduced growth and development, cancer, organ damage, nervous system damage, and may even lead to death. The level of toxicity depends on the absorbed dosages, route of exposure and duration of exposure, i.e. acute or chronic. These metals bind to protein sites that are not meant for them and displace natural metals from their original binding sites and thus cause malfunctioning of cells and this ultimately leads to toxicity[14].

2.2 ADVERSE HEALTH EFFECTS OF COPPER

Human beings are more likely to get exposed to copper in the form of soluble copper compounds that are commonly used in agriculture. Depending on the size of the particles, they may either remain suspended or settle into lake and river sediments. Those residing near or working at copper mines may even inhale copper containing dust. Higher concentrations of copper are found in soil near copper and brass production units. Another source of copper in soil is spreading sludge from sewage treatment plants and this copper stays strongly bound to the soil surface and direct exposure to copper occurs through skin contact. Maximum permissible limit of copper in drinking water is 1300ppb [15, 16].

Chronic copper toxicity initially affects liver since it is the first site where copper gets deposited after getting into blood. It can finally lead to liver cirrhosis and damage to renal tubules, brain and other organs. Symptoms can progress to coma, vascular collapse and death[17]. Acute poisoning can lead to gastrointestinal distresses like nausea, vomiting and abdominal pain. High levels of exposure can lead to destruction of red blood cells. Wilson's disease is a genetic disorder caused due to building up of copper in liver[18].

Conventional procedures for removing heavy metals from waste water include processes like chemical precipitation, floatation, ion exchange, electrochemical deposition, and adsorption. Among these, chemical precipitation is the widely used method.

However, the method requires a large amount of chemicals to reduce the metal to an acceptable level for discharge and has got long term environmental impacts. Every method has its inherent advantages and limitations and among all the methods, adsorption is considered a better methodology because of convenience, easy operation and simplicity of design. Activated carbons prepared from agricultural biomass offer a low cost but effective method for removal of heavy metals and other pollutants from waste water[19].

2.3 ACTIVATED CARBON COMPOSITE

Activated carbon has been modified by loading it with other materials to form a composite. Chitosan coated carbon has been synthesised and used effectively for the removal of heavy metals [20]. Activated carbon has also been

modified by loading it with metals like magnesium , metal oxides like zinc oxide and iron oxide, zeolites and anionic surfactants to produce composites which show improved adsorption of heavy metals from waste water without compromising its potential for removing organic pollutants[21]

Nano materials are gaining importance in the environment protection field. The specific properties of nanomaterial like enhanced surface area, small size, quantum effect and macro quantum tunnelling effect contribute to their extra ordinary adsorption capacity and reactivity both of which are favourable for removal of heavy metals. Nanoparticles have the tendency to aggregate due to their large surface area to volume ratio and low surface energy which in turn can affect their adsorption potential. This can be overcome to a great extent by loading them on activated carbon since this prevents their agglomeration and exposes greater area for adsorption[22].

3. REVIEW OF LITERATURE

Great deal of work has been done and is still progressing in the area of developing cheaper and more effective adsorbents for treating waste water. This is of great importance in the present scenario since waste emanating from various sources is polluting water bodies at an alarming rate. In this context, development of low cost and potent adsorbents from agricultural wastes like nut shells, rice husk, etc. is fast gaining importance.

Ahmed Hegazi in 2013 studied the removal of heavy metals using rice husk charcoal and fly ash as adsorbants. The results showed that low cost adsorbents could be used effectively in in removing heavy metals like Fe, Pb, Ni, Cd and copper within a concentration range of 20-60ppm. Rice husk was effective in the simultaneous removal of Fe, Pb and Ni wheras fly ash was effective in removing Cd and Cu[23].

Kadirvelu, et al in 2003 prepared activated carbon from agricultural solid wastes, silk cotton hull, coconut tree saw dust, sago waste, maize cob and banana pith and used them to eliminate heavy metals and dyes from aqueous solution. Adsorption of metal ions and dyes required very short time and showed quantitative removal. The resulting carbons were economically viable for waste water treatment since all the raw materials used in this investigation were freely, abundantly and locally available[24].

Oszin, et al in 2019 produced activated carbons from chickpea husk by chemical activation using KOH and K2CO3 and examined their efficiency in removing heavy metals from aqueous solution. The maximum adsorption capacities were found to be 135.8, 59.6, and 56.2 mg/g for Pb(II), Cr(VI), and Cu(II), respectively[25].

Gueu, et al (2006) prepared activated carbon from cocnut shell and seed shell of palm tree. The activating agent used was phosphoric acid. They studied the removal of copper, lead and zinc from waste water. Amount of metal adsorbed on activated carbons increased in the order Zn, Cu and Pb [26].

Bernard, et al (2013) synthesised activated carbon from coconut shells and using it, examined the adsorption of copper, iron, zinc and lead present in electroplating waste water. Activation was carried out using zinc chloride. The pore structure of the adsorbent was investigated using SEM [12].

Song, et al (2013) studied the removal of lead ions using coconut shell activated carbons prepared by KOH activation. The adsorption data fitted well with Freundlich and Halsey isotherms. The kinetic behaviour could be explained by pseudo second order mechanism[27].

Several works have been done to increase the adsorbing power of charcoal by converting it into composites. Hayeeye, et al [2018] synthesised activated carbon gelatine composites. They studied the removal of lead using this composite and obtained a maximum adsorption of 370.37mg/L [28].

Alhan, et al (2019) synthesised ZnO –activated carbon nanocomposite with activated carbon nano zinc oxide in the ratio 9:1. With this adsorbent, they studied the examined the removal of cadmium ions from aqueous solution. The nanocomposite exhibited a maximum adsorption capacity of 96.2mg/g for cadmium ions[29].

Sharififarid (2016) et al investigated the removal of lead ions from aqueous solution using iron-activated carbon nanocomposite. Under optimum conditions, they obtained 96% removal of lead using the nanocomposite [30].

In the current study, commercial coconut shell charcoal is made to undergo acid activation and its adsorption of copper is compared with iron oxide-activated carbon nano composite.

4. MATERIALS AND METHOD OF PREPARATION

4.1 MATERIALS

Granules of coconut shell charcoal, concentrated phosphoric acid (H_3PO_4), lead nitrate ($Pb(NO_3)_2$), copper sulphate pentahydrate ($CuSO_4.5H_2O$), iron oxide nanoparticles, sodium hydroxide pellets, concentrated hydrochloric acid, deionised water.

4.2. PREPARATION

Granules of coconut shell carbon (unactivated) was purchased (supplier: Green Dust Bioprocess Engineers, Coimbatore) and crushed. The powdered carbon thus obtained was sieved using a sieve shaker with a mesh of size 44 BSS (particle size: 355 microns) .Acid activation was carried out using phosphoric acid . The sample was then

treated with 50wt% of phosphoric acid and kept in an incubator at 110°C for 24 hours .The sample was then filtered and washed several times with deionised water until the excess acid was removed. The filtrate was tested with lead nitrate solution to confirm the absence of any residual acid.The acid activated carbon was then dried overnight in an oven at 110°C and stored in air tight containers for further use[31]

5. CONCLUSION AND FUTURE SCOPE

Activated carbon produced from coconut shells can be used to remove heavy metals present in water. 70% removal of copper is found with an initial concentration of 2 ppm, pH of 5 and adsorbant dosage of 10 g/L .

The future scope of the paper include that ,activated carbon can be modified by converting it into composites. Activated carbon-iron oxide nano composite gave a removal of 87% with the same initial parameters.

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