A Review on Adsorption: An Optimum Tool for COD Reduction At Tertiary Level in an Effluent Treatment Plant

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Abstract- *The amount of contaminants present in the waste water reaching the tertiary treatment is increasing day by day due to multiple synthesis and variety of products, this result into higher level of COD, BOD, turbidity, etc at tertiary level which makes it difficult to comply with the discharge norms. COD in specific is reduced at primary and secondary level but refractive COD is still a matter of concern at tertiary level. Higher COD levels means greater amount of oxidizable organic material in the effluent which accounts for the reducing DO levels in the water which may lead to anaerobic conditions which can be deleterious to the higher aquatic life forms, it also tends to accelerate bacterial growth in the rivers and consumes the oxygen levels in the river and reduces the efficiency of the other tertiary treatment units. Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater. The adsorption of organics from the waste water on different adsorbents is carried out to increase the percentage reduction of COD, characteristics, efficiency and economy of waste water by a low cost adsorbent, which is discussed in this review paper.*

Keywords- COD, Adsorption, Efficiency, Isotherms, Kinetics

I. INTRODUCTION

Since the end of the last century a large amount of products, such as medicines, disinfectants, contrast media, laundry detergents, surfactants, pesticides, dyes, paints, preservatives, food additives, and personal care products, have been released by chemical and pharmaceutical industries threatening the environment and human health. Currently there is a growing awareness of the impact of these contaminants on groundwater, rivers, and lakes. Therefore the removal of emerging contaminants of concern is now as ever important in the production of safe drinking water and the environmentally responsible release of wastewater. Hence it is imperative that it should be treated to an environmental acceptable limit.

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest. If it is desired to measure either organic or inorganic COD alone, additional steps must be taken to distinguish one from the other. COD is a defined test; the extent of sample oxidation can be affected by digestion time, reagent strength and sample COD concentration. COD often is used as a measurement of pollutants in wastewater and natural waters [22].

Although very little investment has been made in the past on water treatment facilities, typically water supply and treatment often received more priority than wastewater collection and treatment. However, due to the trends in urban development along with rapid population increase, wastewater treatment deserves greater emphasis. Several research studies showed that, treated wastewater, if appropriately managed, is viewed as a major component of the water resources supply to meet the needs of a growing economy. The greatest challenge in implementing this strategy is the adoption of low cost wastewater treatment technologies that will maximize the efficiency of utilizing limited water resources and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents. Treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater at tertiary level includes adsorption, Advanced Oxidation Processes (AOPs), ion exchange, electrochemical process, biological operations, cementation, chemical precipitation, solvent extraction, multi effect evaporators, Nanofiltration (NF) and Reverse Osmosis (RO) membranes. The adsorption processes do not add undesirable by products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design and operation, and

insensitivity of toxic substances. Among several materials used as adsorbents, Activated Carbons have been used for the removal of different types of emerging compounds in general but their use is sometimes restricted due to high cost. Furthermore when Activated Carbon has been exhausted, it can be regenerated for further use but regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin-activated carbon. This has resulted in attempts by various workers to prepare low cost alternative adsorbents which may replace activated carbons in pollution control through adsorption process and to overcome their economic disadvantages. Recently natural materials that are available in large quantities from agricultural operations have been evaluated as low cost adsorbents and environmental friendly.
Moreover the utilization of these waste materials as such directly or after some minor treatment as adsorbents is becoming vital concern because they represent unused resources and cause serious disposal problems. A growing number of studies have been carried out in recent years to evaluate the behavior of emerging adsorbents such as agricultural products and by-product for emerging contaminants removal. On the other hand industrial wastes, such as, fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry are currently being investigated as potential adsorbents for the removal of the emerging contaminants from wastewater.

This review presents the state of art of wastewater treatment by adsorption focusing in special way on removal of emerging contaminants like refractive COD.

Higher COD levels means greater amount of oxidizable organic material in the sample which accounts for the reducing DO levels in the water. This reduction in DO leads to anaerobic conditions which can be deleterious to the higher aquatic life forms. Low (generally >3 mg/L) dissolved oxygen, causes reduced cell functioning, disrupts circulatory fluid balance in aquatic species and can result in death of individual organisms, as well as large "dead zones". Hypoxic water can also release pollutants stored in sediments. Also the presence of refractory COD in the effluent tends to accelerate bacterial growth in the rivers and consumes the oxygen levels in the river and reduces the efficiency of the other tertiary treatment units.

Many conventional treatment methods have been used for COD reduction such as ion exchange, reverse osmosis, membrane filtration, etc. but the cost involved in all these methods have been reported to be very high. Of the tertiary treatment methods existing, adsorption has been proven to be effective due to the lesser land requirement and flexibility in raw material use. Adsorption involves utilization of several agricultural or industrial materials which if not properly disposed, adds to pollution; for the development of suitable carbonaceous substances which are to be used for treating water and waste water [1].

Adsorption Process-

- **Mechanisms and Definitions :-**

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid or liquid– solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater. If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption. In this case, the attraction interactions are van-der Waals forces and, as they are weak the process results are reversible. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance. On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called chemisorption. Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favorable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

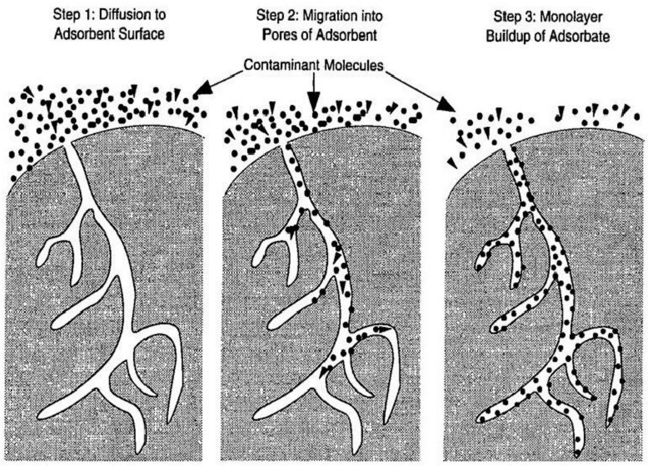

Fig- Adsorption Mechanism

- **Adsorption Isotherms :-**

In a solid–liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general equation,

$$q_t = \frac{(C_0 - C_t)V}{m}$$

Taking into account that adsorption process can be more complex, several adsorption isotherms were proposed. Among these the most used models to describe the process in water and wastewater applications were developed by

(1) Langmuir Isotherm
(2) Brunauer, Emmet and Teller (BET) Isotherm
(3) Freundlich Isotherm

The Langmuir Isotherm is described by the following equation,

$$\frac{q_e}{q_m} = \frac{b\,C_e}{1 + bC_e}$$

The Brunauer, Emmet and Teller (BET) is described by the following equation,

$$q_e/q_m = (BC_e)/\left((C_S - C)[1 + (B-1)(C_e/C_S)]\right)$$

The Freundlich Isotherm is described by the equation,

$$q_e = K_F C_e^{1/n}$$

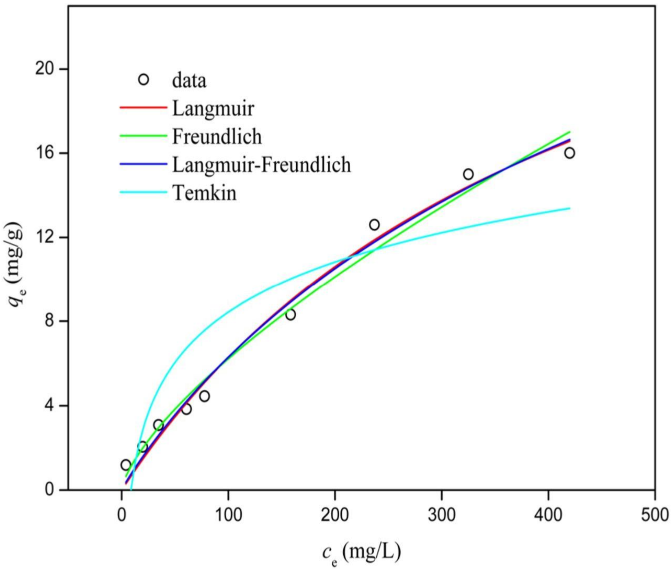

Fig- Adsorption Isotherms

The Langmuir adsorption model is valid for single-layer adsorption, where as the BET model represents isotherms reflecting apparent multilayer adsorption. So, when the limit of adsorption is a monolayer, the BET isotherms reduce to the Langmuir equation. Both equations are limited by the assumption of uniform energies of adsorption on the surface.

- **Factors Affecting Adsorption :-**
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The factors affecting the adsorption process are:

(1) Surface area (2) Nature and initial concentration of adsorbate (3) Solution pH (4) Temperature (5) Interfering substances and (6) Nature and dose of adsorbent.

Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent. The major contribution to surface area is located in the pores of molecular dimensions.

The physicochemical nature of the adsorbent drastically affects both rate and capacity of adsorption. The solubility of the solute greatly influences the adsorption equilibrium. In general, an inverse relationship can be expected between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place. Molecular size is also relevant as it relates to the rate of uptake of organic solutes through the porous of the adsorbent material if the rate is controlled by intra-particle transport. In this case the reaction will generally proceed more rapidly with decrease of adsorbate molecule.

The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups.

Another important parameter is the temperature. Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature.

Finally, the adsorption can be affected by the concentration of organic and inorganic compounds. The adsorption process is strongly influenced by a mixture of many compounds which are typically present in water and wastewater. The compounds can mutually enhance adsorption, may act relatively independently [1].

Removal of Emerging Contaminants by Adsorption-

Emerging contaminants are defined as compounds that are still unregulated or in process of regularization and that can be a threat to environmental ecosystems and human health. The words ‘‘emerging compounds’’ encompass a huge quantity of pollutants, including PPCPs, synthetically and naturally occurring hormones, industrial and household chemicals, nano-materials, and some disinfection by-products (DBPs), as well as their transformation products. Sources and pathways of emerging compounds into the environment depend on how (and where) they are used and how the products containing them are disposed.

The most of emerging compounds are sent to conventional Waste water Treatment Plants (WWTPs) that allow only partial removal of micro-pollutants by stripping, sorption, and biological degradation.

Stripping is negligible compared with the other ones because most of emerging compounds are characterized by low volatility property.

Sorption on primary and secondary sludge is more important than stripping process. It occurs like absorption on the lipid fraction of the sludge, especially on the primary sludge, and adsorption onto sludge through electrostatic interactions between positively charged compounds and negatively charged microorganisms surface.

In the last years many studies were carried out to remove emerging pollutants by adsorption process. The most used adsorbents were commercial ones (such as natural clays, minerals, and activated carbons).

- **Commercial Adsorbents:-**

  - **Activated Carbon**

Activated carbon prepared from different source materials (e.g. coal, coconut shells, lignite, wood, etc.) is the most popular and widely used adsorbent in waste water treatment throughout the world. Its application in the form of carbonized wood (charcoal) has been described first in the medical lore. The history also shows to purify impure water by boiling it in copper vessels, exposure to sunlight and filtering through charcoal.

Activated carbon is produced by a process consisting of pyrolysis of raw material followed by activation with oxidizing gases. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600-2,000 m2/g.

Most studies concerning the removal of micro-pollutants in aqueous solution by adsorption are carried out by using activated carbon. However, with the aim of implementing the technology at full scale application, studies of water and waste water are most significant. For this reason in this section only works concerning emerging contaminants found in drinking water and in wastewater will be discussed.

Researchers studied the behavior of two kinds of carbons: a conventional activated carbon and two modified lignite carbons prepared utilizing a high-temperature steam and methane/steam. The conventional one showed as horter bed life than modified lignite carbons. Indeed lignite variants removed 3–4 times longer than did commercial carbon.

It is obvious that the presence of organic matter can block pores of activated carbon and, for this reason, the removal percentage decreases if compared with results of tests carried out on model water.

The problem of organic materials in water gets worse for wastewater treatment and greater carbon doses or a combination of different treatments are needed to reach a good removal percentage and to control the problem of fast deterioration of adsorbents. Some study showed that membrane filtration prior to PAC adsorption may lead to improved elimination rates for adsorbable and low molecular weight micro-pollutants and PAC addition into wastewater of MBR pilot plant significantly improved removal rates.

- **Clays**

Natural clay minerals are well known from the earliest day of civilization. Because of their low cost, high surface area, high porosity, and abundance in most continents, clays are good candidates as adsorbents. There are many kinds of clay:

smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and Fuller's earth (attapulgite and montmorillonite varieties). The adsorption capacities depend on negative charge on the surface, which gives clay the capability to adsorb positively charged species.

- **Minerals**

Another class of adsorbents includes natural minerals. This comprises of zeolite and goethite. Zeolite is typically used for the removal of dyes and heavy metals. Like clay minerals, adsorption capacity is linked to negative charge on the structure.

- **Low Cost Adsorbents :-**

Although, activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of pollutants from water, its widespread use is sometimes restricted due to the high costs. Attempts have been made to develop low-cost alternative adsorbents which may be classified in two ways:

(1) On basis of their availab
ility, i.e.
(a) Natural materials (wood, peat, coal, lignite etc.)
(b) Industrial/agricultural/domestic wastes or by-products (slag, sludge, fly ash, bagasse fly ash, red mud etc.)
(c) Synthesized products
(2) Depending on their nature, i.e.
(a) Inorganic
(b)Organic material

- **Agricultural Waste**

The basic components of the agricultural waste materials include hemi cellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing a variety of functional groups. In particular agricultural materials containing cellulose show a potential sorption capacity for various pollutants. If these wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent, if developed, can reduce the treatment of waste waters at a reasonable cost. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness.

The agricultural solid wastes from cheap and readily available resources such as almond shell, hazelnut shell, poplar, walnut sawdust, orange peel, sawdust, rice husk, sugarcane bagasse, coconut burch waste and papaya seeds have been investigated for the removal of pollutants from aqueous solutions.

Sawdust is one of the most appealing materials among agricultural waste materials, used for removing pollutants, such as, dyes, salts, and heavy metals from water and wastewater. The material consists of lignin, cellulose, and hemicellulose, with polyphenolic groups playing important role for binding dyes through different mechanisms. Generally the adsorption takes place by complexation, ion exchange and hydrogen bonding.

The agricultural waste materials have been used in their natural form or after some physical or chemical modification. Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloricacid, nitric acid, sulfuric acid, tartaric acid, citric acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), and dyes for the purpose of removing soluble organic compounds, colour and metal from the aqueous solutions have been performed [1].

Adsorption as Green Technology-

The literature studies showed above highlighted that adsorption process can be considered an efficient treatment for the removal of emerging compounds from water. It allows reaching good removal percentage and, furthermore, being a physical process, does not imply by-products formation, which could be more toxic than parent compounds. It is obvious that adsorption process is encompassed in an integrated treatment system which involves many factors, such as available space for the construction of treatment facilities, waste disposal constraints, desired finished water quality, and capital and operating costs. All these factors imply the achievement of the optimal operating conditions for low-cost high efficiencies.

The most used and studied adsorbents are certainly activated carbons both for synthetic and real water (surface water and wastewater). In spite of large use of them, the overall idea is to reduce the use of activated carbon because of high costs.

Therefore, scientific world is looking for low-cost adsorbents for water pollution. In addition to cost problem, another important factor pushing toward low-cost adsorbents is the use of agricultural and industrial waste products in order to extend the life of waste materials without introducing into the environment new materials as adsorbents and to reduce costs for waste disposal therefore contributing to environmental protection. Anyway a suitable non-conventional low-cost adsorbent should:

(1) Be efficient to remove many and different contaminants,
(2) Have high adsorption capacity and rate of adsorption, and
(3) Have high selectivity for different concentrations.

Adsorption Efficiency-

The adsorption efficiency depends on the nature of adsorbent used, the water composition, and operating parameters. During water filtration the contaminants adhere to the surface of these adsorbent granules or become trapped in its small pores on the surface of the adsorbate and this process is known as Adsorption. The different processes in which adsorption can be implied are sand filtration, dual media filtration, carbon filtration, etc.

The economical and easily available adsorbent would certainly make an adsorption- based process a viable alternative for the treatment of wastewater containing pollutants. Selection of an appropriate adsorbent is one of the key issues to achieve the maximum removal of type of pollutant depending upon the adsorbent and adsorbate characteristics. The effectiveness of the treatment depends not only on the properties of the adsorbent and adsorbate, but also on various environmental conditions and variables used for the adsorption process, e.g. pH, ionic strength, temperature, existence of competing organic or inorganic compounds in solution, initial adsorbate and adsorbent concentration, contact time and speed of rotation, particle size of adsorbent, etc [1].

II. MATERIALS & METHODS

Generally, COD is removed using chemical precipitation, microbial treatment, advanced oxidation process, chemical treatment, etc. These methods are very costly and are quite less affordable for large scale treatment of wastewater that is rich in COD. Thus we opted for adsorption using cheap adsorbent.

Ademiluyi, F. T.; Amadi, S. A. And Amakama, Nimisingha Jacob has aimed at adsorption and treatment of organic contaminants using activated carbon manufactured from waste Nigerian bamboo. Initialy the waste Nigerian bamboo was carbonized at 400°C-500°C and activated with acid at 800°C. At the end of the column fiber glass was used to support the activated carbon. Then, experimental batch equilibrium data was correlated by Freundlich and Langmuir isotherms. The adsorption data fitted well into the Freundlich isotherm. Breakthrough time of about 1.5 hours was observed for the fixed bed adsorption process. Adsorption of organics from the refinery waste on the activated carbon prepared was examined at 28°C for every 1-1.5 hours. The reduction was found to increase with time upto an extend and then became constant. The overall reduction was found to be around 60-65%. The studies indicated that the acid activated coconut shell carbon had higher adsorption for organic matter expressed as chemical oxygen demand (COD), than calgon carbon at all carbon dosages used [2].

Gazala Sayed carried out a study on the effluent collected from a Common Effluent Treatment Plant (CETP) which includes effluents from variety of industries like textiles, leather, paints, pharmaceutical, etc. Whose effluents have a high load of COD, TSS, TDS, etc. The aim of the research was to find out the maximum reduction efficiency in the above parameters along with colour and odour removal amongst the Activated Carbon filtration, Sand filtration and Dual Media filtration. The setup was as followed that the effluent from clarifloculator was connected to the aeration tank wherein 24hrs aeration was supplied followed by the filter i.e Activated Carbon, Sand Filter and Dual media filter alternately and the flow rate was adjusted to optimum. After carrying out the study for seven days it was found that the reduction efficiency by Sand filtration was in the range of 60-75% and that of Dual Media filtration was in the range of 70-80%. And lastly the reduction efficiency by Activated Carbon filtration was found to be in the range of 80-85% and the water was treated to drinking water quality. The iodine content in the activated carbon is responsible for treatment of water. Research also shows that, activated carbon filters are extremely effective as primary filters and have the added benefit of organic load reduction resulting in cost savings with reduced chlorine demand and safer water. On completing the treatability study using different filters each for seven day study, it was found that Activated Carbon is the best adsorbent. It gives maximum reductions in colour and odour [3].

Seyed Hosseini, Nekoo; Fatemi and Shohreh has investigated that application of Granular Activated Carbon (GAC) in adsorption process for the advanced treatment of municipal and industrial waste water turns out to be an auxiliary treatment method for biological treatment of waste water to overcome the problems of biological basin in oil refineries. The experimental and modeling study in batch and fixed bed column accompanied with dynamic modeling of COD adsorption from DAF were been performed in this study. In this work, GAC was examined for reduction of COD from biological treatment units to achieve to the environmental and design regulations. For simulation of the real feed COD of the oily wastewater from DAF unit of Tehran Refinery was carried out by the commercial Iranian made AC for approaching to the desired level. Different adsorption tests were performed for determining the maximum adsorption capacity at different temperatures (25°C and 40°C), bed lengths, feed flow rates and feed concentration to have a proper insight for appropriate design of a GAC fixed bed. To scale up the adsorption unit for reduction of COD to less than 100 ppm for working at ambient temperature with an inlet COD concentration of 420 ppm, a bed with 12 m height and 1 m diameter should be designed for treating 338 m3/hr of waste water. The adsorption capacities were deduced from equilibrium adsorption isotherms using the Langmuir isotherm model [4].

Emmanuel O. Aluyor and Olalekan A. M. Badmus carried out a comparison between the adsorption efficiency of activated carbon prepared from animal horns (AHC), which is both a waste and a pollutant and a commercial activated carbon (CAC) with respect to uptake of the organic components responsible for COD of industrial wastewater. The commercial activated carbon is regarded as the most effective material for controlling the organic load. However, due to its high cost and about 10-15% loss during regeneration, unconventional adsorbents like fly ash, peat, lignite, bagasse pith, wood, saw dust, periwinkle shells, etc. have attracted the attention of several investigations and adsorption characteristics have been widely investigated for the removal of refractory materials for varying degree of success. This study is aimed at analyzing the adsorption capacity of activated carbon prepared from animal horns on industrial wastewater effluent and also to demonstrate the use of activated carbon prepared from animal horns as an alternative media over conventional activated carbon. This study deals with the results of the batch adsorption tests to establish adsorption isotherms and adsorption capacity of the activated carbon prepared from animal horns (AHC) for the removal of COD in wastewater. The adsorption process was examined in terms of its equilibria and its kinetics. The effect of pH, contact time and adsorbent dose were investigated. The most effective pH was found to be 5 for AHC and 6 for CAC. The equilibrium data for COD removal fitted the Linear, Langmuir and the Freundlich models. Hence, trend of COD removal by AHC, 95.67%, is comparable to that of CAC with 96.34% efficiency. These results show that granular activated carbons made from agricultural waste (animal horn) can be used with greater effectiveness for organic matter removal from industrial wastewater [5].

S. Vasanthaaj, Sathiyavimal S. and N. Hemashenpagam invented that combining activated carbon with sand can tend to better reduction in the physico-chemical parameters of the waste water. The samples were processed within 24 hours after collection. Initially the waste water was made to pass through two filters. The first one containing sand followed by other containing carbon for filtration. Finally when the clarified water is drawn out of the filter, it shows that there is a considerable reduction in the physico-chemical parameters then that of the untreated municipal water. The BOD value was dropped as 128 mg/l to 55 mg/l after filtration, COD value was reduced from 310 mg/L to 178 mg/L, TDS was reduced from 2058 mg/L to 1250 mg/L, TSS was reduced from 1520 mg/L to 710 mg/L, carbonate reduced from 23 mg/L to 12 mg/L, the hardness dropped from 50 mg/L to 4.5 mg/L and pH was reduced to 6.85 from 6.93 based on physico-chemical parameters the treated municipal waste water was suggested fit for irrigation purpose [6].

Sunil J. Kulkarni, Sonali R. Dhokpande and Dr. Jayant P. Kaware have aimed on the removal of the organic and inorganic pollutants from the waste water as they are the cause of concern in current scenario of rapid industrialization. Utilization of fly ash has gained much attention in public and industry, which will help to reduce the environmental burden and enhance economic benefit. The technical feasibility of utilization of fly ash as a low-cost adsorbent for various adsorption processes for removal of pollutants in air and water systems has been studied by various researchers. Instead of using commercial activated carbon or zeolites, a lot of researches have been conducted using fly ash for adsorption of nitrogen oxides, oxides of sulphur, organic compounds, and mercury in air, and cations, anions, dyes and other organic matters in waters. It is recognized that fly ash is a promising adsorbent for removal of various pollutants. Chemical treatment of fly ash will make conversion of fly ash into a more efficient adsorbent for gas and water cleaning. Fly ash as an adsorbent is very good alternative and attracts great application. Hence, in the present research, bagasse fly ash was used as an adsorbent for removal of various pollutants like organic matter, phenol, chromium and acetic acid. The effect of parameters like contact time, adsorbent dose, pH and particle size was studied and optimum values of these parameters were reported. The optimum adsorption times for COD, phenol, chromium and acetic acid were found for appropriate reduction. It was observed that fly ash adsorption shows the percentage removal of 88-92% at optimum adsorbent time and the optimum pH for fly ash was observed to be 2. Also the percentage removal remained constant for the finer sized particles [7].

Samiksha Gaikwad & S. J. Mane has aimed to minimize the industrial pollution by implementing an advanced wastewater treatment technique like adsorption for the removal of organic and inorganic compounds from industrial wastewater. As adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutant removal. For removal of the organic contaminants from industrial waste water adsorption has become one of the best effective, economical and environmentally essential method. The Current research has focused on modified or innovative approach that more adequately address the removal of organic pollutants. Adsorption capacity of adsorbent principally depends on the characteristics of materials as specific surface area, pore size, and its distribution. In present study, it was aimed to carry out experiments using low cost material Sugar cane bagasse from sugar manufacturing unit and coconut shell activated carbon for reduction of COD from the pharmaceutical industrial wastewater. Pharmaceutical industries are one of the problematic groups due to disposing of highly toxic industrial effluents, which creates the harmful effects on marine environment. This study focused on the use of low cost adsorbents such as sugarcane bagasse fly ash and coconut shell activated carbon to adsorb COD content of the pharmaceutical industrial wastewater. By combination and individually, adsorbents were used for treatment of waste water with different dosages and contact time. The results of COD removal were up to 46 % for sugarcane bagasse ash and 68 % for coconut shell activated carbon and for the combination of both, removal of COD was up to 50%. Hence coconut shell activated carbon gives maximum reduction efficiency at constant time than sugarcane bagasse fly ash and combination of both the adsorbents. The problems will arises regarding the disposal of exhausted adsorbent can be solved either by activation or incineration or disposal after proper treatments [8].

R. Elliss Yogesh & Dr V. Sekaranhas noticed that the tannery effluent contains lot of organics and inorganics as well as heavy metals which causes environmental impacts when disposed without proper treatment. Removal of metals from wastewater is achieved principally by the application of several processes such as adsorption, sedimentation, electrochemical processes, ion exchange, biological operations, cementation, coagulation/flocculation, filtration and membrane processes, chemical precipitation and solvent extraction. The biological materials usage as adsorbents in treatment of tannery effluent has been focused during recent years. The usage of activated carbon as adsorbent reduces the concentration of Cr (VI) ions which tends to possess mutagenic and carcinogenic properties. Hence its relationship with the COD reduction of the tannery wastewater was explored in this study. Thus the treatment of tannery effluent before its disposal should be done. The COD of the tannery effluents are higher in nature, because it has high organic and inorganic loads. Therefore the treatment of tannery effluents is challenging one. They opted for activated carbon adsorbent treatment of such heavy metals. Hence in this study the COD removal efficiency of activated carbon and the optimum condition for maximum removal was studied. The batch experiments were conducted with different dosage (0.2, 0.4, 0.6, 0.8 & 1g/L) of activated carbon, contact time (20, 40, 60, 80, 100 & 120 minutes) and varying pH (2, 4, 6, 8, 10 & 12) to achieve the maximum COD removal efficiency. The optimum condition and their maximum percentage of COD reduction were identified and were found to be around 60-62% [9].

Chambre, Andre tested the hypothesis that granular activated carbon filters have a longer useful life and greater filtering efficiency with no associated performance defects than bonded filters. This paper concludes that types of carbon filtration, how to activate charcoal by chemical and steam activation. To test this hypothesis, a third-party laboratory (IBR Laboratories) analyzed the adsorption efficiency of an Air Science granular loose fill filter and a dimensionally identical bonded carbon filter from RSE Incorporated based on the SEFA benchmark testing methods. The results of this study verify that under similar laboratory settings, Air Science granular carbon filters have a higher filtering efficiency and will maintain safe operating conditions for a longer period of time than similarly-sized bonded filters. Air Science granular carbon filters are also easier for operators to change out, have greater stability in shipping/packaging, and offer a variety of chemical impregnation options to meet specific filtration needs [10].

Uma Muknadan and Shilpa S. Ratnoji has invented that with utilization of an agricultural by product, risk husk for the removal of COD from sewage can improve its removal efficiency. As of the tertiary treatment methods existing, adsorption has been proven to be effective due to the lesser land requirement and flexibility in raw material use. Adsorption can involve utilization of several agricultural or industrial materials which if not properly disposed, adds to pollution, to develop suitable carbonaceous substances that can be used to treat water and wastewater. One such product is Activated carbon. Activated carbon can be either commercial or the one synthesized from any renewable resource. Commercially activated carbon is very costly. Hence manufacturing activated carbon from low cost and easily available raw materials is an innovative idea. Agricultural materials like rice husk, neem leaves, fruit peels etc. are being extensively used for research in wastewater treatment, which prevents several types of pollution due to dumping or open burning. Utilization of low cost renewable materials like agricultural and industrial wastes, which are sources of material and energy recovery stresses on the principle of waste minimization and cleaner production. In this study, rice husk which is an agricultural waste was used to prepare activated carbon to remove COD from raw sewage. Rice husk was processed into Rice Husk Activated Carbon (RHAC), a more useful form, by using phosphoric acid. The characteristics of raw sewage like pH and initial COD and the characteristics of adsorbent were measured. The mechanism of removal of COD by adsorption onto RHAC was studied by Batch process, under varying adsorbent dosage and pH of the solution to find the optimum conditions. RHAC was found to remove around 89-91% COD [11].

Saad A. Al –Jlil has determined COD and BOD reduction from domestic waste water using sedimentation, activated sludge, sand filter and activated carbon. Fly ash can be used as a promising adsorbent for removal of various types of pollutants from waste water. Low-cost adsorbents of different origins like industrial waste material, bagasse fly ash and jute processing waste can also be used for removal of organic matter from the waste water. The COD and BOD concentrations play a very important role in the reuse of these waste effluents. Adsorption based innovative technology developed with low cost carbonaceous materials showed good potential, more so for COD removal from the domestic waste water. Hence they studied COD and BOD reduction of domestic waste water using discarded material based mixed adsorbents (MAC) and commercial activated carbon (CAC) in batch mode. Under optimum conditions the mean maximum COD and BOD reduction was around 92% and 96% respectively. Other water quality parameters such as TSS, TDS, NO_2, TKN and PO_4 showed significant reduction except NO_3 which increased significantly using different materials in the waste water treatment plant (WTP). The sewage treatment system using different materials showed excellent potential for COD and BOD removal from domestic waste water. Also, the concentration level of COD and BOD in the treated water was within the permissible limits for industrial cooling and agriculture use especially for landscape development [12].

Mahmad farhan, Abdul Wahid, Amina Kanwal and J. N. B Bell has aimed to prepare an activated carbon from saw dust of Dalbergia sissoo, Cedrus deodara and Eucalyptus spp. using H_3PO_4, H_2SO_4 and $BaCl_2$ as activating agents. Adsorption by using activated carbon had a long and productive history. Activated carbon is considered very effective for removal of dyes COD, BOD and heavy metals from waste water. Research efforts are going on to develop activated carbon–based innovative technology with low cost carbonaceous materials. Any carbonaceous waste material can be converted into activated carbon, thus its significance is two folds. Firstly, it removes pollutant from wastewater and secondly, converts solid waste into useable activated carbon. Some of the low cost industrial waste/by-products that can be used for activated carbon with varying success including Bagasse [23], Pecan shell [24], Coconut fiber [25], Date nut [26] and peels of Avocado fruits [26]. This study was designed to synthesize activated carbon from indigenously available sawdust to test their efficiency in paper mill wastewater treatment (with particular emphasis on colour/COD reduction) and optimization of conditions for maximum efficiency of activated carbons and maximum treatment. The activated carbons were evaluated for reduction in colour and COD of a real paper industry effluents using batch-mode method to explore the effect of operating parameters (contact time, amount of activated carbon, wastewater concentration, solution pH etc). Statistical analysis revealed that all the activated carbons were significantly different in their efficacy for wastewater treatment. Cedrus deodara based activated carbon was most efficient; showed 93% COD reduction with 100% colour removal and brought other physico-chemical parameters of wastewater within the permissible limits of WHO and NEQS. The maximum percent reduction of COD and colour with Dalbergia sissoo activated carbon was 80% and 91%, respectively while with Eucalyptus spp., activated carbon; it was 74% and 85%, respectively. The effectiveness of activated carbon synthesized from sawdust of different plants for wastewater treatment was in the following order: Cedrus deodara > Dalbergia sissoo > Eucalyptus spp. The quality of wastewaters after treatment was found to be appropriate for direct discharge into streams and irrigation purpose. This study proved highly successful in addressing the local problem of paper industry effluents using locally available wood processing byproducts [13].

Sunil J. Kulkarni has studied that treatment of domestic sewage and subsequent utilization of treated sewage for irrigation can prevent pollution of water bodies and reduce the demand for fresh water in irrigation sector. It has been estimated that usually 70% of the water pollution is due to domestic sewage. The COD of the waste water is indicator of its purity. Various pollutants impart COD to the water. COD removal is ultimately removal of these impurities from the wastewater. COD removal methods include: adsorption, coagulation, electrochemical, ultraviolet irradiation, and membrane-based technology. Reduction of COD can be done by various adsorbents like adsorption onto bamboo-based activated carbon, adsorbent derived from agricultural waste, adsorption using avacado peel carbon and adsorption using laterite-based constructed soil filters was carried out in this work. Hence an attempt is done to minimize the pollution parameters like colour, COD and BOD by using coconut coir activated carbon in batch and column operations and optimum values of these parameters were obtained. Although higher doses of coconut coir activated carbon are normally required for the COD and BOD removal, the operation is feasible because of low cost of coconut coir activated carbon. It was observed that in continuous column 75-80% COD removal and 78-80% COD removal took place [14].

A K A Rathi, has aimed at demonstrating adsorption as the first stage of treatment which shall increase efficiency of the subsequent biological treatment. For treating waste water from multiproduct chemical plants containing organic chemical substances in varying composition and concentration, which are difficult to degrade biologically, adsorption process in combination with other processes is considered very effective in reducing COD and colour. Adsorbents in industrial waste water treatment with adsorptive properties of adsorbents, activated carbon, inorganic adsorbents and effluent applications of activated carbon adsorption processes were reviewed. The use of activated carbon in water and waste water treatment, including the increasingly important role of adsorption for removal of specific target compounds or classes of compounds from water waste water containing complex organic substance mixtures has also been reviewed. The waste water was biologically treated and residual COD and BOD were removed further with activated carbon. Experiments were carried out on different wastewater samples from chemical plants on adsorbents like activated carbon, bentonite and lignite. The effectiveness of adsorbents in the removal of organic matter by the way of reducing COD and colour was evaluated. Considering the rate of reduction of COD obtained for different adsorbents, effectiveness and cost of the adsorbents and ease of disposal of spent adsorbents, suitable adsorbent or a combination of adsorbents could be selected for optimizing the cost of waste water treatment. The performance of lignite is observed to be comparable with that of activated carbon. Lignite is, therefore considered to be cost-effective adsorbent in reducing COD as well as colour from the waste water [15].

Vinesh V. Rakholiya and S. A. Puranikhas determined that the high cost of coal-based activated carbons has stimulated the search for cheaper alternatives. Hence low cost and non-conventional adsorbents like activated carbon, lignite, fly ash, neem tree leaves were used as adsorbents for removing COD from the industrial wastewater. Activated carbon is a commonly used adsorbent in sugar refining, chemical and pharmaceutical industries and water and wastewater treatment. Fly ash has shown quite effective adsorbent capacity for COD reduction from the industrial wastewater. Though its capacity is lower than that of commercial grade activated carbon, the low material cost makes it an attractive option for the treatment of industrial waste water which contains phenolic compounds. The study aimed at demonstrating that adsorption as the first stage of treatment increases efficiency of the subsequent biological treatment. Experiments were carried out on different wastewater samples from chemical plants on adsorbents like activated carbon, bentonite, and lignite. The effectiveness of adsorbents in the removal of refractory organics by way of reducing chemical oxygen demand and colour was evaluated. The COD and colour reduction by activated carbon was found to be around 60-70% [16].

Uttarini Pathak, Papita Das, Prasanta Banerjee and Siddhartha Datta conducted an experimental study after determination of the initial parameters of the raw wastewater generating from dairy industry which was subjected to batch adsorption study using rice husk. The COD of dairy wastewater is mainly due to milk, cream or whey. Technologies such as coagulation/flocculation process and oxidation process have been developed over the years to remove organic matter i.e. COD from industrial waste water. These methods are effective in fields of reduction and time but are expensive and require skilled personnel. They also become disadvantageous in terms of pH adjustment and generation of chemical sludge that must be treated before disposal. Adsorption technique emerges as promising technique in the removal efficiency (COD) economy and operation. Physical adsorption using activated carbon is effective in removal but has a high initial cost, low adsorption capacities, and separation inconvenience and needs a costly regeneration system. All these have simulated the search of cheaper alternatives and application of biosorption in environmental treatment has become a significant research area. Biosorption may be defined as a process wherein a solute molecule is removed from the liquid phase in contact with a solid, usually an inexpensive adsorbent which has a special affinity for the solute particles. The effects of contact time, initial wastewater concentration, pH, adsorbent dosage, solution temperature and the adsorption kinetics, isotherm, and thermodynamic parameters were investigated. The phenomenon of adsorption was favoured at a lower temperature and lower pH in this case. Maximum removal as high as 92.5% was achieved using the adsorbent. Moreover it is a cost-effective process since it is cheaply available raw material. The entire process was favoured at lower temperature and lower pH with a little adsorbent dosage [17].

Basavaraj S. Karadagi1 and Prof. G. M. Hiremath have investigated the removal of colour and COD by adsorption depending upon the effect of pH, adsorbent dosage and contact time. Currently there are various treatment processes such as oxidation process, coagulation, filtration, ozonation, membrane filtration, hydrogen peroxide, reverse osmosis processes are employed in determining the removal of COD, BOD and colour removal from the wastewater. Due to higher cost effective and disposal problems involved in the above treatment methods further investigations have been fed up. The adsorption process provides effective and alternative effect in removal of COD, colour and other parameters in treatment of waste water using low cost adsorbents which are readily available and inexpensive. Quest of non/conventional and good low cost adsorbents contributes to the sustainable development of environment and beneficiary uses in the future for commercial activities. The sawdust is readily available in local sawmills and also various activated carbons of sawdust, neem leaves, corncob, rice husk, tea leaves and agricultural wastes used in treating the industrial wastewater. COD and colour removal was the main target of this study and sawdust can easily remove the COD and colour. In the present study batch adsorption technique was used in this process by using sawdust with respect to effect of pH, contact time and adsorbent dosage with mean adsorbent dosage. The study conducted the experiments at constant pH with mean adsorbent dosage and optimum agitator speed. It was found that the optimum removal of colour was from dark green to light brown and COD removal was 78% and this result was good as compared to other processes of adsorption process. Finally from the study of adsorption process it was concluded that removal of COD and colour was effective in sawdust because of its higher capacity of adsorption and sawdust was the main key in this study. From the experiments we can say using sawdust as an adsorbent in treating textile wastewater is simple and less economical. And also sawdust not only removes COD and Colour it can also removes BOD, Total dissolved solids (TDS), total suspended solids (TSS) and Total solids (TS) [18].

Sachin Madhavrao Kanawade and Vijay C. Bhusal has determined that COD and BOD in waste water from sludge can be reduced by using low cost adsorbent like Wooden Based Activated Charcoal (WBAC) and Laterite in a column used as a stationary phase. Activated carbon is a carbon material mostly derived from charcoal. The unique structure of activated carbon produces a very large surface area of granular activated carbon typically provides a large surface area. The activated carbon surface is non-polar which results in an affinity for non-polar adsorbents such as organics. Activated carbon is very effective in applications requiring air or water purification as well as precious metal recovery or removal. The parameters like specific gravity, viscosity, total suspended solids and pH were reduced with great effect by using WBAC and Laterite as a permanent adsorbent. The fixed bed efficiencies can be compared by changing the bed ration of adsorbent. The whole study of optimizing parameters was done in column chromatography to compare the result of after treatment and before treatment. The fixed bed of WBAC and Laterite reduces COD and BOD value to 70 and 75% respectively. This is the maximum value of minimization of COD and BOD from waste water of dairy industry. Thus, it is a cheaper method for minimizing the excess sludge of wastewater treatment in various sectors. The other parameters like pH, viscosity and total suspended solids can also be effectively reduced by these techniques which might be used in various industries for the other treatment of waste water [19].

Sunil J. Kulkarni and Ajaygiri K. Goswami have determined that affordable and effective treatment of wastewater is critical issue for the developing countries. The aim of the current study is to demonstrate the use of bagasse fly ash as an adsorbent for purifying the wastewater. Various conventional treatment techniques, both biological and non-biological were been tried. Reduction of COD and colour of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon was carried. The effects of contact time, adsorbent dose and pH on the adsorption are also studied and optimum values of these parameters were reported. A packed column study was also carried out to estimate ideal adsorption time. The ideal adsorption time is the time when the ratio of final to initial concentration of the effluent for a column reaches 0.5. COD and BOD were measured as indicator parameters of water quality. The disposal of domestic sewage from cities and towns is a biggest source of pollution of water bodies in India. COD is the amount of oxygen required for the organic matter for its chemical decomposition and BOD is the amount of oxygen required for the biological decomposition. In this study, attempt was done to minimize the pollution parameters like COD, BOD by using bagasse fly ash in batch and column operation. It was observed that 90-95% removal of organic matter took place by the usage of bagasse fly ash. Also optimum values adsorbent doses; contact time and pH were obtained [20].

K. K. Sivakumar, M. S. Dheenadayalan and S. Mahalakshmi had aimed to find an alternative for the commercial grade activated carbon (CAC) which is regarded as the most effective material for controlling the organic load. However due to its high cost and about 10-15 % loss during regeneration, unconventional adsorbents like Prosopis Juliflora Carbon (PJC), peat, lignite, bagasse pith, wood, saw dust, raw tea powder and raw agricultural wastes etc. have attracted the attention of several investigations on the removal studies and hence they checked the efficiency of the Prosopis Juliflora Carbon (PJC) for removal of organic compounds i.e. COD and colour from the waste water. Adsorption characteristics have been widely investigated for the removal of refractory materials for varying degree of success. Thus the removal of organic material by adsorption onto low cost waste material has recently become the subject of considerable interest. For this purpose a system of standardized batch absorbers under steady state conditions were used to study the effect of these media. The influence of treatment contact time, adsorbent dose, initial COD concentration and agitation speed on the rate of percent removal COD was evaluated. As alternative to commercial Activated Carbon Prosopis Juliflora Carbon (PJC) blend has shown quite effective adsorbent capacity for COD removal from the domestic wastewater. The removal efficiency of the PJC is around 60-70% and that of CAC is around 70-80%. Though its capacity is lower than that of commercial grade activated carbon, the low cost material makes it an attractive option for the treatment of domestic wastewater [21].

III. CONCLUSION

The review of research work done for reduction of COD is presented here. Many types of adsorption methods and different grades and categories of adsorbents have been tried by different researchers for COD reduction from waste water. Activated carbon adsorption method is found to be the best method for reduction of COD. On an average the percentage reduction is found to be in the range of 90-95%. There is still scope for research in order to reduce physico-chemical parameters economically by using low cost adsorbent. The activated charcoal adsorption technique is also a very effective method in reduction of refractive COD from the waste water.

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