Review Paper:

Biochar based dye removal from industrial effluents: A review

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Abstract

During recent years, numerous investigations have been carried out to explore the potential of biochar to remove organic and inorganic pollutants from wastewater. In the field of dye adsorption, activated carbon is the most widely used adsorbent, but its activation and regeneration costs are high. Several alternative adsorbents are being investigated to remove dyes from aqueous media. Bio chars are a class of alternative adsorbents, which are normally produced by pyrolysis of agricultural wastes, wood, or other biomasses in oxygen–limited conditions.

Bio char is a carbon rich material produced from waste biomass by thermochemical conversion methods. It is used as a bio sorbent in removal process of various pollutants and its efficiency is strongly influenced by the characteristics of the biomass feed stock and method of production. This review aims to understand the sorption behaviour of dyes on to bio char-based bio sorbent. The mechanism describing bio sorption behaviour of biochar and the factors influencing the bio sorption behaviour process have been broadly reviewed in this study. The bio sorption model can also be used to comprehend the potential of the bio char as bio sorbent for dye removal.

Keywords: Biochar, adsorbents, sorption, pollutant, dye, biomass, pyrolysis.

Introduction

The impact of organic and inorganic pollutants on human health and the environment has become a global threat[44]. Exposure to organic and inorganic pollutants in the environment can cause serious damage to the air, pollution of water bodies, death of grass and trees, infestation of food diseases by insects, adverse effects on animals, plants and human health. These contaminants are carcinogenic, toxic and mutagenic and their presence in the ecosystem can cause loss of ecosystem quality[10].

Most of these pollutants come from domestic and commercial activities. Since all living things on earth depend on the earth's air and water resources so when these resources are polluted, the survival of all living things is directly affected. Almost two third of the earth's surface is covered with water and population growth directly leads to increased water pollution resulting from human activities[3,4].

Water is valuable for future generations and must be protected. Today, water quality is an issue of great concern[38]. Due to increasing pollution and depletion of natural resources, domestic activities have a direct and indirect impact on water quality, which affects the environment and quality of life. The textile industry produces a lot of water pollution due to excessive use of water during fabric production. Other industries also produce dyes pollution at the end of their industrial processes[28]. Nowadays, various dyes and additives are widely used in industries such as textile, paper, printing, paint, detergent, cosmetics, carpet, leather, rubber and food.

Dyes can be defined as oil or water-soluble organic compounds that produces colour. Natural dyes come from animals, plants, molluscs, minerals etc. Synthetic dyes are mostly unsaturated organic molecules. Wastewater containing these dyes cannot enter ecosystems due to its long-lasting colour, chemical stability and high biochemical oxygen demand[54]. In India, the textile industry is the largest consumer of dyes. It is estimated that 260,000 tons of dyes are released into the environment each year[16] and approximately 20% of water pollution worldwide is caused by dye industries[41]. Many countries have solid wastewater management policies and regulations with separate guidelines for each sector, with the aim of reducing the amount of pollution released into the environment.

Many industries have developed and have used different treatment strategies to treat wastewater including advanced technologies such as ion exchange, flocculation, adsorption irradiation, coagulation, oxidation, photochemical ozonation, electrochemical destruction, advanced oxidation, membrane process, nanofiltration etc. from wastewater[32,61]. In recent years, biological treatment has become the most effective technology compared to other methods. Microorganisms are primarily employed in biological treatment to break down pollutants in wastewater[25]. These organisms transform pollutants through biochemical degradation enzymatic or metabolic processes. Many types of bacteria have been used successfully to bio absorb pollutants in wastewater.

Biosorption is a technology that effectively employs biomass to adsorb contaminants in wastewater when compared to other approaches[3,4,19,48]. The utilization of biochar-based adsorbents to remove contaminants from waste water resources has been the focus of recent environmental remediation research[43]. The functionality of the biochar group, surface shape, pH, porosity, mineral content, specific surface area and adsorption capacity all affect the qualities of the biochar material. Biochar was created using a variety of raw materials and its ability to adsorb different metals was examined[13].

The main purpose of this review is to search different theories in the field of biochar derived from biomass. Charcoal acts as a dye adsorbent in aqueous solution. In this review, the efficiency, adsorption properties of dyes and the effects of different studies on the adsorption performance of biochar obtained from biomass raw materials are discussed.

Preparation of biochar - Raw materials

Biomass can be defined as the organic material that is obtained at the end use of animal and plants origin. It is an important raw material in the preparation of biochar. In general, municipal waste can be divided into non lignocellulosic and lignocellulosic groups which includes animal and human waste and wood /wood products respectively. This biomass can be directly converted into bioenergy, chemicals and waste products through various thermal and chemical methods. This thermochemical process includes pyrolysis, gasification, hydrothermal carbonization, liquefaction etc. Pyrolysis is the most cost-effective way to produce biochar, bio-oil and syngas.

Selection of biomass: Different types of biomasses considered as agricultural wastes such as rice husk, coconut shell, walnut shell, seaweed, algae residues, peanut shells, etc. can be used to produce biochar. The composition and various factors such as cellulose, hemicellulose and lignin in the biochar preparation vary depending on the type of thermal degradation. Depending on the kind of feedstock material utilized, different components like cellulose, hemicellulose and lignin have different compositions and amounts in formed biochar[13]. During the pyrolysis process, these ingredients experience thermal deterioration or degradation at various temperatures.

The first step in the degradation process is the breakdown of hemicellulose at 200–260 °C, cellulose at 230–350 °C and lignin at 300–500 °C. To generate biochar, it is best to employ a combination of biomass feedstock from various sources, such as forestry waste, agricultural waste, field waste and manures, as each type of feedstock is not always available[46]. The type of feedstock utilized to make the biochar and the adsorption processes employed determine the capacity of the biochar to be absorbed.

Development of biochar: Thermochemical conversion methods such as pyrolysis, hydrothermal carbonization (HTC) and gasification are the most commonly used conversion technologies for biochar synthesis. Pyrolysis is considered as the most efficient and economical technology for biochar production[58], providing the best biochar yield[56]. In pyrolysis, biomass is converted into biochar by heating it at 200^0-900^0 C in an oxygen free atmosphere[2].

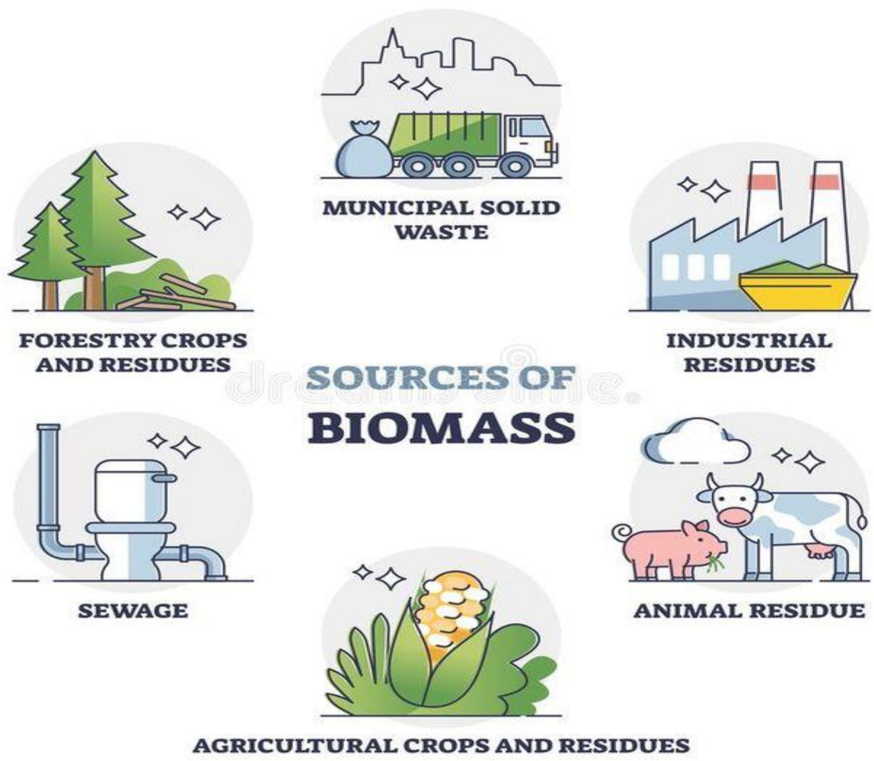

Fig. 1: Sources of Biomass

Fig. 2: Biochar production

The pyrolysis is divided into slow, medium and flash depending on parameters like temperature, residence time, heating etc. Hemicellulose, cellulose and lignin are organic compounds which are broken down during the thermal degradation process of biomass raw material components. As a result, there are variations in the amount of pyrolysis products. The properties of biosolids, bio-oil and biogas vary depending on temperature, heating rate and length of storage. Using heat and pressure in the presence of water, hydrothermal carbonization converts biomass to biochar. The reaction must be kept at a high temperature (1600–800 °C) and liquid state (>1 atm)[49-52]. Depending on the kind of feedstock material utilized, different components like cellulose, hemicellulose and lignin have different compositions and amounts in formed biochar[13].

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Bioremediation of dyes using bio char

Biological techniques have received great attention in recent years[49-52]. In recent years, biosorption has been considered to be a fast, economical, environmentally friendly technology compared to traditional methods[19,48]. Biosorption is the process of using inactive biological materials to reduce the concentration from aqueous solutions. Biosorbents used in dye removal processes are generally obtained from agricultural wastes, industrial wastes, fungi, bacteria, algae etc.[49-52] The activity of biosorbents mainly depends on the nature of the biomass and the assay used during the biosorption process[49-52]. Good commercial biosorbents should have the following properties: high biosorption capacity[55], surface properties[39], efficient and effective separation of biosorbents[60], thermal stability[55], availability and preparation[9,35].

Nowadays, many studies on environmental remediation focus on biochar and biochar-based adsorbents[43]. The use of biochar involves studying the surface properties and adsorption properties of these materials, as these properties are important in combating pollutants[26].

Factors affecting Bio-sorption of Dye in Biochar: The adsorption capacity of biochar depends on the biochar material as well as experimental parameters such as pH of the solution, amount of biochar, temperature, initial dye concentration, contact time etc.

Bio char characteristics: Due to different operating conditions, biochar using different conversion systems has different properties and activities. Pyrolysis temperature, reaction time, thermochemical conversion type and nature of raw materials significantly affect the properties of the resulting biochar and have an impact on the adsorption activity on different dyes.

Pore size is one of the most important features controlling the adsorption mechanism which may vary from nanometers to micrometers. Various studies have shown that larger pore size is obtained by pyrolysis at high temperature, resulting in larger surface area[17]. The pH of biochar also varies with the pyrolysis temperature and the type of feedstock. The pH of biochar increases at high pyrolysis temperature[16] because higher pyrolysis temperature produces more ash and degrades acidic functional groups.

The surface characteristics of the biochar are significantly impacted by the pH of the solution. The elemental ratio of the biochar depends at different temperatures when different elements are present in the feed stock in different concentrations. The presence of different elements in different proportions in the raw material also affects the properties of biochar viz. aromaticity, polarity etc.

In general, biochar produced at high temperature provides lower H/C and O/C ratios compared to low temperature biochar. The mineral content of biochar is affected by the type of feed stock and the pyrolysis temperature as well as other physical and chemical properties. The presence of minerals in biochar facilitates the precipitation and cation exchange of pollutants in the aqueous environment.

These contaminants are removed by π-π interactions, n-π interactions, electrophilic interactions, hydrophobic interactions and hydrogen bonding interactions. In short, the nature of the biomass feedstock and the pyrolysis temperature significantly affect the physiochemical properties of the synthesized biochar. Biochar obtained by high temperature pyrolysis has high surface area, high hydrophobicity, microporosity and high adsorption capacity for pollutants[31]. The nature of the biomass feedstock also affects the surface of biochar. For example, biochar obtained from wood biomass has a higher surface area than biochar obtained from waste and animal manure, even if both are obtained from the same process[31]. Therefore, taking care of these two parameters in biochar properties makes it suitable for the adsorption process.

Bio char dosage: Many studies have been conducted to study the effect of adsorbent during dye sequestration technology in order to study the effect of adsorbent required for maximum dye removal[6]. It has been found that the dye removal rate is rapid in the first few hours and then slows down as the biochar concentration increases[8]. The increase in colour removal as the number of adsorbent increases is due to the excess of adsorption sites on the biochar surface, while the colour molecules are more easily accessible with diminished dosage of biochar. The colour removal rate per unit weight of biochar is high.

Solution pH: The adsorption capabilities, surface chemistry and dye molecule accessibility for binding sites of biochar are all directly impacted by the pH of the solution[49-52]. According to the previous studies, the optimum pH for decolourization is generally neutral or slightly alkaline. The percentage of colour removal is highest at optimum pH and tends to decrease in acidic or alkaline medium. The ability of hydrogen ions to compete with adsorbate ions for active sites on the adsorbent surface is closely related to the pH of the solution[7]. The impact of solution pH on the bio sorptive removal of methylene blue dye by biochar made from agricultural wastes was examined. The conclusion was reached by changing the solution's pH from 2 to 9 and it was observed that the dye removal efficiency of biochar increased from 40% to 90%. The biochar's sorption behaviour was attributed to its negative surface charge which promotes electrostatic interactions during the biosorption process.

Temperature: Temperature also has a significant impact that affects the adsorption capacity of biochar for removal of dye[12]. In general, temperature has a positive effect on the adsorption capacity of biochar and is directly proportional to the reaction rate[53]. With increase in temperature, the tendency of colour removal increases and after a certain limit, the adsorption does not increase. An increase in temperature increases the physio absorption, while lowering the temperature decreases the physio adsorption. This adsorbent is capable of adsorbing adsorbates at all temperatures with optimum removal at 350°C to 400°C[36]. The change in temperature with varying adsorption capacity was referred to endothermic or exothermic processes[18].

Initial dye concentration and contact time: The efficiency of the adsorption process of the adsorbent is greatly affected by the initial dye concentration. The initial increase in dye content provides a significant reason that will cause mass transfer between the aqueous and solid phases[5], but also causes increase in collisions between the adsorbent and dye molecules. In contrast, the inadequate biomass concentration is not sufficient to absorb more of the color, resulting in reduced decolorization potential due to the accumulation effect of dye molecules. The initial dye concentration has limited effect on percent dye removal by adsorption due to unavailability of required number of active sites on the surface of bio char. Removal percentage becomes saturated at a particular dye concentration[1]. Conclusively removal percent of dye molecules is high at lower dye concentration because the ratio between the dye molecule and surface sites is low.

Adsorption isotherms: Equilibrium data and concentration effects are two important factors in understanding adsorption processes. Adsorption uptake can be expressed as milligrams of dye adsorbed per gram of adsorbent and the mass adsorbed is determined by the amount of sorbate retained in the immobilized medium[40]. The adsorption efficiency of single adsorbate was evaluated based on the adsorption isotherms obtained in the same medium. Adsorption isotherms are plotted between dye absorption a nd dye concentration. These were able to define sorption isotherm like one-single parameter model, seven-two model, five-three parameter model etc.

Langmuir[23] adsorption isotherm has been used to describe gas-solid adsorption in which physical force of attraction plays the key role for binding of dye molecules to the adsorbents. He assumed that all surface sites had equal attraction for the adsorbate. Further this assumption also described equilibrium relation between the liquid phase and solid phase analytically. In general, sorption sites are uniform, one sorbate molecule reacts with one active site with no interaction with sorbed species. In the process, more than one type of functional group contribute to the bio sorption process, each of which is having different affinity for sorbing dye molecule[37]. The Langmuir model is frequently used for batch bio sorption and in most cases successfully describes the equilibrium of dye bio sorption method.

The Freunlich isotherm was initially used empirically, but was later interpreted as adsorption on heterogeneous surfaces with different support surfaces[37]. Stronger binding sites were occupied first with binding sites decreasing on increasing occupancy of the site. Features of the Langmuir and Freundlich models are integrated into a unified model for hybrid mechanism adsorption.

Adsorption Kinetics: Biosorption invariably involves rapid sorption reaction mechanism[49-52]. Pseudo-first and second-order models were used to interpret the experimental data to examine the sorption mechanism and potential rate controlling steps like mass transport and processes of chemical reaction. The effect of contact time is a crucial factor to determine the adsorption kinetics. The kinetics behind adsorption forms the basis for determining the performance of a fixed bed or other flow-through systems[30]. First-order rate equation was presented by Lagergren[22] to explain the kinetics of adsorption of oxalic acid and malonic acid to charcoal from liquid to solid phase, believed to be the earliest model of adsorption rate based on adsorption capacity.

Lagergren's first-order rate equation has been called pseudo first-order model. The cation exchange capacity of peat is attributed to the bonding between metal ions and functional groups such as aldehydes, ketones, acids and phenolic explained by Ho and Mckay in their description of the kinetic adsorption process for divalent metal ions on peat. Ho's second-order rate was another name for the pseudo-second-order equation. This formula has been effectively applied to the biosorption kinetics of a variety of dyes, including the sorption of Remazol colours by green seaweed-derived biochar and the removal of methylene blue from aqueous solution using coco-peat.

Adsorption Mechanism: The current application of biochar in the field of bioremediation has attracted research attention due to its simplicity, cost effectiveness, environmentally friendly and stable behaviour. It is necessary to understand biochar surface interactions and mechanism to ensure that specific properties of biochar are relevant to the biosorption of various pollutants. General mechanisms of biosorption of organic pollutants are interaction, pore diffusion, hydrophobic interaction, cationic and anionic interaction, coprecipitation, complexation etc. Biochar characteristics depends on the pyrolysis conditions. Biochar synthesized at high pyrolysis temperature is aromatic and acidic, less polar and has a large surface area. Hydrophobic adsorption is an adsorption method with loss of functional group containing hydrogen and oxygen.

Compared to this, biochar at low temperature exhibits adsorption of polar organic compounds through hydrogen bonding with various functional groups. Biochar made from agricultural crop residue is utilized to remove cationic dyes such as methyl violet, methylene blue, basic blue, rhodamine, crystal violet etc. the primary process involved is electrostatic adsorption[15]. The donor and retractor groups present in biochar generated at high temperatures interact with the two functions of dye molecules.In contrast, lower temperature-produced biochar has electron-retreating groups and π systems that operate as electron acceptors and interact with molecules that donate electrons.

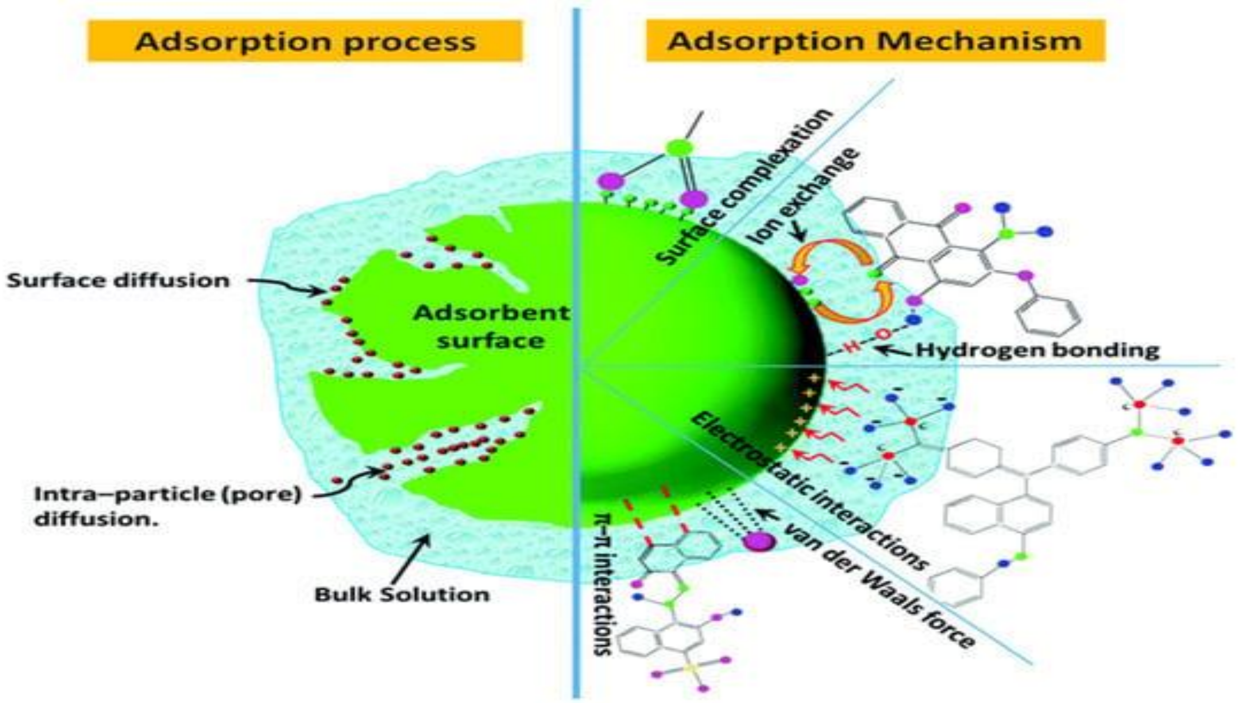

Fig. 3: Adsorption process and mechanism for dye removal from wastewater

Conclusion

This review focuses on recent advancements in the manufacture of biochar from different biomass materials and its possible use as a biosorbent for the biosorption of different colours. It offers extensive information on pyrolysis of different biomasses at different temperatures using various techniques to successfully remove dyes. The nature of the feed stock, residence period, heating rate, pyrolysis process and other factors have a significant impact on the properties and features of the resulting biochar.

Biochar's characterization tests showed that it can be employed as an effective adsorbent through conventional adsorption processes such as hydrogen bonding, electrostatic attraction, hydrophobic interactions, pore filling, π-π interaction and ion exchange. Because of its economical nature, ease of availability, ease of handling and adsorption capacity, bio char is a viable and innovative adsorbent.

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