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A systematic review of biomass-derived materials for wastewater remediation of contaminants

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ABSTRACT

Nowadays, a significant amount of wastewater containing hazardous contaminants is produced due to the fast growth of industrialization and urbanization activities. If this wastewater is not properly treated, it poses greater risks to the environment and has an impact on the counties' economies and quality of life. As a result, legislators, policymakers, and the scientific community have been increasingly interested in the development of sustainable, economical wastewater treatment technologies. Therefore, in order to develop effective technologies and realize the concept of wastewater cleanup, a comprehensive strategy is urgently needed. This view may be influenced by adsorption using agricultural waste-based adsorbents, which have many benefits over current wastewater treatment methods. This review guarantees a comprehensive examination of the possible use of agricultural waste-based natural sustainable adsorbents for effective removal of contaminants (dyes and heavy metal). For the critical literature analysis, a number of variables that affect the adsorption efficiency-such as adsorbent dosage, concentration, contact duration, pH, and temperature-as well as the best-fitting models have been supplied. Additionally, future work should focus on process engineering to improve the efficiency of green catalysts in order to increase process economy.

Keywords: Agricultural waste, Adsorption, Contaminants, Waste water

Introduction

Water is one of the most precious and important natural resources on the earth. It is very crucial for all living creatures in its pure state because it constitutes the majority of living tissues and the concept of life is impossible without water. Water is also known as a universal solvent because of its good solubility power. It plays an indispensable role in the world economy. The need for pure water is continuously increasing. With growing population and industrialization, the obtainable supplies are speedily diminishing. Water contamination is a recent issue of concern for the whole world. According to the central pollution control board, the gross per capita water availability would decrease by 2050 (Central Pollution Control Board MINARS/36/2013-14), and the total demand for fresh water would be rising rapidly and creating water stress. Further, drinking water is not accessible in many regions of the world even though 70% of the earth is covered by water. The quality of water resources has degraded at a very fast rate due to various organic and inorganic pollutants released from anthropogenic as well as natural sources. Water contamination is a serious concern as it affects living entities from recreation, domestic, fishing, transportation, and other commercial activities (Yadav *et al.*, 2019). Water pollution is caused by many factors like inadequate sewage treatment, chemical wastes, industrial effluents, petroleum refining wastes, marine dumping issues, fertilizers and pesticides used in agricultural activities radioactive waste material, thermal power plants, Animal excreta in rural areas, etc. The contaminated water contains various inorganic and organic contaminants, some of which are highly persistent, toxic, and carcinogenic. In water, more than 700 chemical contaminants have been reported (Yadav *et al.*, 2019). Major toxic organic pollutants include pesticides, polynuclear aromatic hydrocarbons (PAHs), plasticizers, phenols, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), fertilizers, greases, oils, nitrogen, bleach salts, biological contaminants like viruses, bacteria, protozoan, parasites, and drug residues, primary inorganic pollutants include arsenic, lead, cadmium, mercury, chromium, and many other (toxic) metals, along with nutrients such as nitrate and phosphate. Waste water regulations are established in some countries to reduce human and environmental exposure to hazardous chemicals. In the same line, the Central Pollution Control Board (India) set various standards for the discharge of waste water effluents into the any water body, for example biochemical oxygen demand 30 ppm, chemical oxygen demand (COD) 250 ppm, pH 5.5–9.0, manganese (mg/L): 1.0, chromium (mg/L): 0.05, copper (mg/L): 2.0, and iron (mg/L): 3.0 (Maity *et al.*, 2019). Many studies have been carried out for the purification of wastewater and to preserve freshwater sources. Many techniques have been demonstrated as efficient to eliminate pollutants from wastewater (Buruga *et al.*, 2019). Among the various water treatment techniques adsorption is considered to be one of the most successful techniques in the field of separation technology, particularly in

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wastewater treatment processes. Therefore, the main objective of this review article is to provide information on the application of various sustainable low-cost alternative adsorbents such as agricultural solid waste materials in the removal of heavy metal and dye from contaminated water. This review article also provides various research results and a compilation of up-to-date development on the current state of knowledge on various agricultural solid waste-based adsorbents and their application in the broad field of separation and purification of water and wastewater pollutants. This review is focused on two major contaminants like dyes and heavy metals.

Dyes are the coloring agents that have two components chromophores and auxochromes, chromophores are responsible for producing color, and auxochromes are responsible for the solubility of molecules in water and enhance the affinity of dye molecules towards the fibers. Dyes are classified in several ways based on their chemical structure, color, application, and particle charge in the solution. Each class of dye has a very unique chemistry; some dyes react chemically while some are held by physical forces. Usually, dyes are divided into two classes, natural dyes, and synthetic dyes. The sources of natural dyes are animals and minerals. With the rapid growth of industrial activities, natural dyes couldn't meet the needs of people's demand, so synthetic dyes are developed and used particularly in fabrics and textile industries. Synthetic dyes include ionic dyes (cationic and anionic) and non-ionic dyes (vat and disperse) based on their particle charge upon dissolution in aqueous application medium. Classification based on chemical structure includes Azo, Anthraquinone, Indigoid, Nitroso, Nitro, Triarylmethane dyes. Soluble dyes are classified as acidic, mordant, metal complex, direct, basic, and reactive. Insoluble dyes are azoic, sulfur, vat, and disperse dye. Among all these dyes azo dyes are widely used and account for 65-70% of the total dyes produced.

The annual production of dyes about 5×10^5 tonnes has been estimated and usually employed in various industries like papers, plastics, processing of food, cosmetics, tannins of textiles, pharmaceutical etc (Goodman *et al.*, 2018). Approximately 100 tonnes/year dyes are discharged in water streams. Srivastava *et al* reported that most of Indian textile industries have been consuming more than 100L of water for the processing of 1 kg textile thus they discharge a huge amount of coloured wastewater in the environment that causes pollution of surface and ground water resources (Aruna *et al.*, 2021). According to WHO and UNICEF, 2000 report approximately 70–80% of all illnesses in developing countries are caused by different water contaminants, particularly affecting women and children (WHO and UNICEF, 2000). The toxicity of dyes are due to their components like aromatics, amines and trace of heavy metals such as Cd, Cu, Pb, Zn and Co (Zhou *et al.*, 2019). The presence of organic compounds in dyes cause the reduction in penetration of sun light in water that may affect the photosynthesis of aquatic life (Pearce *et al.*, 2003). Most of dyes are carcinogenic, mutagenic, or teratogenic to all living beings which affects the many functions of human body like dysfunction of kidney, liver, brain and reproductive system and central nervous system (Kadirvelu *et al.*, 2003). Acid red used in food and textile industries, colour photography which is Carcinogenic and affects the marine life also toxic to flora and fauna (Behnajady *et al.*, 2007). Acid yellow used in dyeing wool, silk, leather and polyamide fibers and harmful to the environment (dos Santos *et al.*, 2017). Crystal violet used in paper and textile industries, temporary hair colorant responsible for pollution of the groundwater in Basel which causes vomiting, jaundice, quadriplegia & tissue necrosis (Appusamy *et al.*, 2014; Li, 2010; X. Tan *et al.*, 2016). Eriochrome Black T which degrades the water quality, causes eye and skin allergies (Srivastava *et al.*, 2017). Methylene blue and Azo dyes which are majorly used in various industries like dyeing cotton, wood, silk and food industry (chilli powders, eggs, garlic curry sauce, and palm oils) are mutagenic & carcinogenic to humans causes eye burns or sometimes permanent injury to the eyes, nausea, vomiting, and mental confusion, liver and urinary bladder tumours in mammals (Daud *et al.*, 2019).

Heavy metals belong to class of inorganic pollutants having atomic weight between 63.5 to 200.6 and specific gravity greater than 5, present in sludge, fertilizers, municipal waste, pesticides, mines residues and smelting industries (Halim *et al.*, 2003). Industrial wastewater contains heavy metals like lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel. Among these, lead, cadmium, mercury and arsenic heavy metals show carcinogenic effects on human health. These may damage central nervous function, the cardiovascular and gastrointestinal systems, lungs, kidneys, liver, endocrine glands, bones, stomach cramps, skin irritations, vomiting, nausea, respiratory disorders, anaemia and mental fever. Heavy metal causes various types of cancers Parkinson's disease, multiple sclerosis, muscular dystrophy and Alzheimer's disease.

2. Need for water remediation

According to United Nations estimation, three is ten people deficit ingress to clean drinking water. Contaminated drinking water cause many diarrhoeal deaths per year. Only 3% of ground water is present in pure form and can be used for drinking and domestic purpose (Senthil Kumar *et al.*, 2019). The amount of various new type contaminants ever increasing in hydrological environments and the availability of pure water is shrinking continuously that's why by 2025 half of the world population will be living in drinking water- deficient areas, so to avoid these difficulties and toxic effects, the water remediation becomes more challenging (Goodman *et al.*, 2018).

3. Techniques for waste water treatment

It was more from 80s that people started giving much attention to the dye removal methods because of the hazardous effects of dyes on living things such as aquatic and human life. In the late 90's, there were two dye removal methods contained only preliminary water purification processes such as equalization and sedimentation. Because at that time there were no dye effluents discharge limit and the selection of dyes application and uses were not given a major attention to their environmental impact. At that time the chemical composition of most of the dyes used in the industry was unknown. After primary processes like equalization and sedimentation secondary treatments such as the use of filter beds for biodegradation comes in picture. There are several waste water treatment techniques to treat the waste water containing dyes and heavy metals. The major classes of these technologies are (i) Physical (ii) Chemical (iii) Biological (Fig. 2). All of these techniques are discussed below with their positive and negative aspects.

3.1 Biological methods

Numerous microorganisms like enzymes, fungi, algae, bacteria are studied for biodegradation and bioaccumulation of dye particles. These microorganisms have ability to biodegrade and bioaccumulate the dye particles. Various conventional biological dye removal methods are adsorption by microbial biomass, algae degradation, enzyme degradation, fungal cultures, microbial cultures as well as pure and mixed culture. Microbial biomass like mixture of organic living organisms fashioned to adsorb only selected dye molecules not all dyes. In algae degradation method algae consumes dye particles for self-growth. In enzyme degradation method extracted enzyme used to degrade dye molecules. This method have advantages like cost effective, high efficiency, non-toxic, reusability but its use is limited due to unreliable amount of enzyme production. Based on oxygen demand, biological methods divide in two classes, aerobic and anaerobic. In aerobic conditions, bacteria secrete the enzymes to breakdown the organic compounds present in the wastewater. Some of the aerobic bacteria used for dye removal are *Bacillus* sp., *Enterococcus* sp., *Pseudomonas* sp. It has been found that a number of Triphenylmethane dyes, such as magenta, pararosaniline, crystal violet, malachite green, brilliant green and ethyl violet can be efficiently decolorized (92–100%) by the strain *Kurthia* sp. (Sani & Banerjee, 1999). (Delee *et al.*, 1998; Forgacs *et al.*, 2004) demonstrate the po

tential of anaerobic treatment applications for the degradation of a wide variety of synthetic dyes present in waste water. Some of anaerobic bacteria used for dye removal are *Escherichia coli*, *Clostridium* sp. (Bhatia *et al.*, 2017; Sarayu & Sandhya, 2012). (Razo-Flores *et al.*, 1997) reported that the two azo dyes mordant orange 1 and azodisalicylate can be reduced and decolorized using methanogenic granular sludge under anaerobic conditions and (Van der Zee *et al.*, 2001) gives the feasibility of decolourization of 20 azo dyes by the application of anaerobic granular sludge. The efficiency of biological treatment system is highly affected by many factors like sensitivity of microorganism towards seasonal changes, toxicity of some chemicals and requirement of large land areas for construction of bioreactors.

3.2 Chemical methods

Various conventional chemical contaminants removal methods are advanced oxidation process, fenton reaction dye removal, electrochemical destruction, oxidation, ozonation, photochemical and ultraviolet irradiation. All of these methods have many advantages and disadvantages discussed in the text below (Katheresan *et al.*, 2018). In ultraviolet irradiation method UV light is used to decompose the dye particles in wastewater and this method produce no sludge, weakens foul odours but having drawbacks like energy depletion, high cost, limited treatment times. Ozonation is an effective dye removal method in which the ozone produced from oxygen is utilize to remove contaminant particles, it can be used in its gaseous state, doesn't increase wastewater volume, no sludge generation, quick reaction. But have limitations like extremely short half-life, high cost, and produce toxic by-products. Oxidation is the common chemical dye removal method in which, many oxidising agents are use to treat dye effluents, these

oxidising agents completely convert complex structure of dye molecules in to carbon dioxide and water. Usage of catalyst with oxidising agents can increase the rate of process and take short time to complete the reaction. This method have disadvantages like not cost effective, the activation of hydrogen peroxide agent is difficult, pH dependent process and requires catalyst for efficient removal. In fenton reaction method Fenton's reagent (mixture of catalyst and hydrogen peroxide) are used to remove dye particles from wastewater, can remove soluble and insoluble dyes and all toxins from effluents which contain solid contents also. Negative aspects of this method are like it cannot remove disperse and vat dyes, produce high iron sludge, take long time. Electro-coagulation or non-soluble anodes are use in electrochemical destruction method to treat the dye wastewater. Advantages of this method are no sludge production, used chemical don't get consumed and disadvantages are production of additional hazardous material, high cost of electricity, high flow rate as compared to other methods. Advanced oxidation process involves multiple oxidation process done simultaneously to remove dye particles and toxic materials but it is expansive and non-flexible method. It produced undesirable by-products and pH dependent method. Chemical dye removal methods are commercially unattractive because these are costly as compared to physical and biological dye removal methods, requires high electrical energy for power equipment or reactors in which chemical dye removal take place, requirement of chemicals as well as reagents at large scale is an issue. Another undesirable characteristic of this method is the generation of toxic secondary pollution resulting at the end of a chemical dye removal process presenting an additional disposal problem.

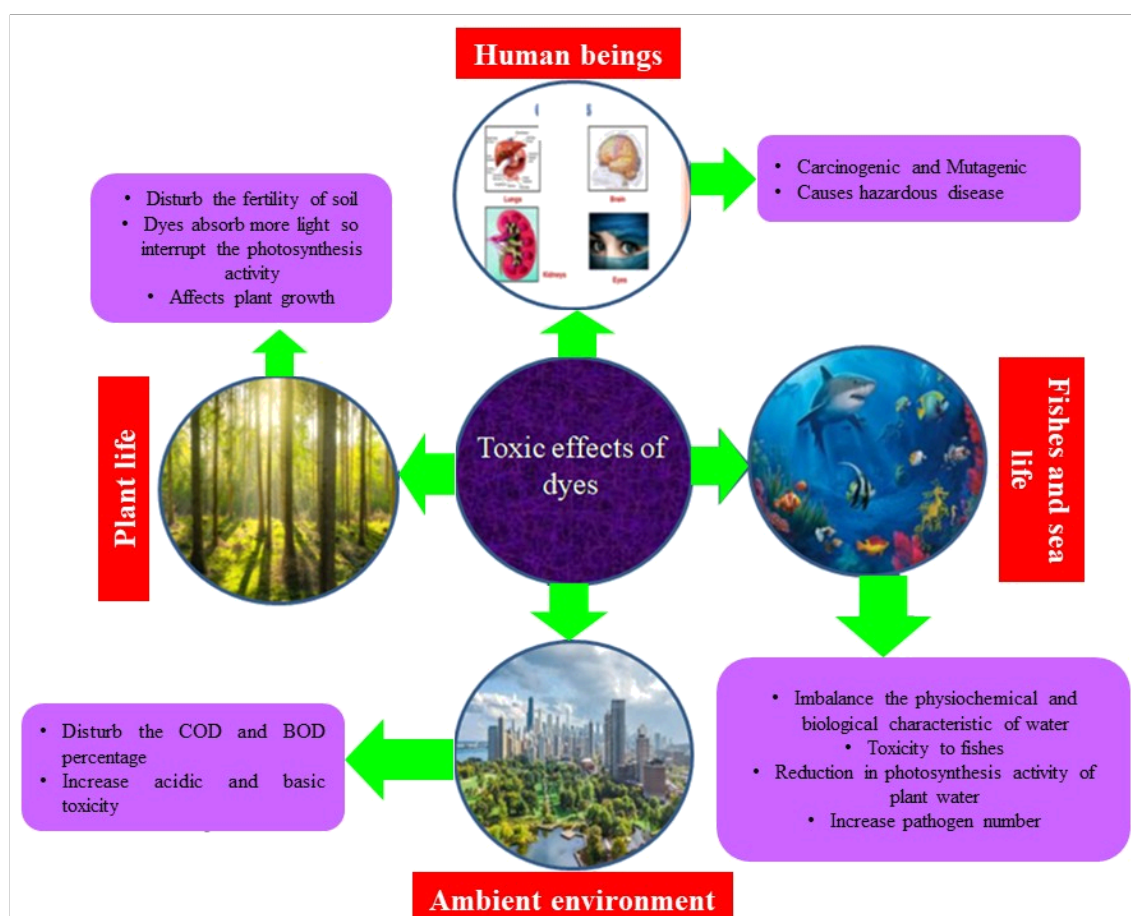


Figure 1. Toxic effects of dyes on environment and living beings

3.3 Physical methods

Among the three methods, physical dye removal methods are simple, flexible and efficient. These are the most commonly used and straightforward methods and accomplished by the mass transfer

mechanism. Various conventional physical dye removal methods are adsorption, coagulation or flocculation, ion exchange, irradiation, membrane filtration, nano filtration or ultra-filtration, reverse osmosis, and many more. All of these methods require the least amount of chemicals compare to the biological or chemical dye removal meth

ods (N. A. Khan *et al.*, 2018) and removal percentage of dyes ranging from 86.8 to 99%. Reverse osmosis is the pressure driven system in which water is passed through an extremely thin membrane leaving contaminants on one side and water on the other. Used for recycling, decolouring and desalting the water and produced pure water but its use is limited by its high cost and high pressure (Katheresan *et al.*, 2018). Membrane filtration method is effective for water recovery but costly initial investment, Easy membrane fouling and concentrated sludge production make its use limited (Koyuncu & Güney, 2013). Irradiation method uses the radiation to remove dye molecules from dye wastewater and effective at laboratory scale, but it is expansive process and require a huge amount of dissolved oxygen. Ion exchange technique produced high quality treated water but it is effective for selected contaminants (Katheresan *et al.*, 2018). Coagulation and flocculation is economical and robust method which is suitable only for removal of disperse, sulphur and vat dye effluents but this method have disadvantages like high sludge production and not effective for disperse, sulphur and vat dye effluents, pH dependent and sometimes expensive due to use of some special chemicals (Holkar *et al.*, 2016). Most of these techniques have disadvantages like high sludge production, handling and disposal problems, high pressure, expensive, technical constraints, economically unfeasible, high energy cost, chemicals required (N. Gupta *et al.*, 2016; V. K. Gupta *et al.*, 2011), etc. Among these remediation methods adsorption techniques is efficient, eco-friendly, easy to operate and cost effective. It can remove a large number of contaminants such as organic, inorganic and biological substances including soluble and non-soluble compounds from waste water without producing toxic by-products (Hassan *et al.*, 2020). The quality of water remains unchanged during adsorption process of water purification. Adsorption is the surface phenomenon in which substances from one phase adsorbed on the second phase adsorbent surface. A good adsorbent should have some important characteristics such as availability, low-cost technology, non-hazardous, high surface capacity, high abrasion resistance and stability in different environmental conditions (Shamsollahi & Partovinia, 2019). The adsorbents, which are generally used for dye wastewater treatment, are: Alumina, Silica gel, Zeolites, Activated carbon, Natural materials, low cost al-

ternative adsorbents like (a) Natural materials such as peat, wood, coal, lignite etc. (b) Industrial/Agricultural/Domestic wastes or by-products such as slag, sludge, fly ash, bagasse fly ash, red mud etc. (c) Synthesized products.

4. Mechanism of adsorption process

Adsorption mechanism depends on the properties of adsorbent and adsorbate, like nature of surface, functional sites on the surface, interaction behaviour of adsorbing molecule/ions (Siddiqui *et al.*, 2019). Magnetic activated carbon/clay composite showed that the adsorption of Pb_{II} , Cu_{II} and Ni_{II} heavy metal ions through ion exchange and electrostatic attraction took place because the positive charged ions of heavy metals attracted by the negatively charged functional groups present on the composite surface and the presence of Na^+ , Ca^{2+} and Mg^{2+} ions in the clay may be responsible for ion exchange mechanism (Le *et al.*, 2019). The adsorption of arsenite on pine cone-magnetite composite took place by Inner sphere complex and ion exchange mechanism because in case of sphere complex formation the adsorption rate increase by adding salt and the value of ion exchange coefficient increase 0.05 to 0.51 that indicates the ion exchange between arsenite and nitrate ions on the surface (Ouma *et al.*, 2018). MnO_2 /Black cumin seed composite adsorbed the methylene blue through electrostatic as well as hydrogen bonding because FT-IR spectra of methylene blue adsorbed composite shows shift in characteristic peaks of naked composite. The strength of electrostatic and hydrogen bonding was confirmed from the bonding energy determined from Temkin, and D-R models as well as thermodynamics studies (Wendler *et al.*, 2010). The removal of arsenic by $FeOH/CuO@$ waste bamboo cell took place by the synergistic effect of physical action and redox reaction mechanism. The type of adsorption mechanism can be probed with the help of FTIR which tells about shift in functional group peaks before and after the adsorption, XPS it tells about the change in binding energy peaks during adsorption process, XRD gives information about the change in crystal structure of adsorbate before and after adsorption, TEM-EDS, EDX (H. Liu *et al.*, 2020).

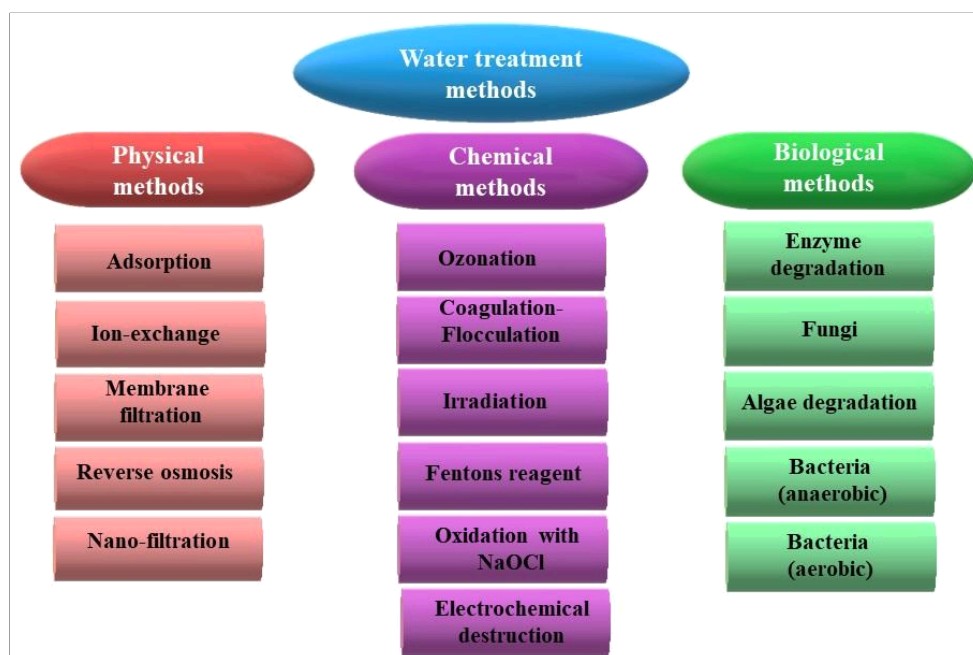


Figure 2. Classification of waste water treatment techniques

5. Biosorbents derived from agricultural waste for

dye and heavy metal removal

Agricultural waste is unwanted material obtained completely from agricultural operations directly connected to the growing of crops. Example of these waste materials are Rice husk, Sugarcane bagasse,

Coconut husk, Corn stalk, peanut hull, Natural shell huts, Wheat husk, Barley husk, Coffee husk etc. These waste materials are produced in huge amount and create disposal problem. The reuse of these waste materials and development of an ideal adsorbent is an actual task in our present time. These agricultural waste materials can be used as adsorbents for water remediation because of their effectiveness, availability, unique chemical composition, chemical stability, low cost, renewable cycle, short regeneration cycle, environmental friendliness, and green energy. Their porous structure and large specific surface area makes it easy to adsorb heavy metals and dyes. The various functional groups like acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphhydryl, carboxyl, alcohols and esters present in agriculture waste material (Salleh *et al.*, 2011; Zhou *et al.*, 2015) can be replaced by many other functional groups such as amino, sulpha, carboxyl groups of dyes and many modifying reagents. For example chemical composition of Bamboo is lignin, pentosan and cellulose so it contains a huge amount of hydroxyl groups; peanut hull contains amino, carboxyl and hydroxyl groups which are responsible for adsorption. The activated carbon produced from agricultural wastes contains high carbon content, low inorganics, require mechanical strength, low levels of ash content and low cost (Chowdhury *et al.*, 2011; Dias *et al.*, 2007; Zhou *et al.*, 2015). So the use of agricultural wastes as adsorbents in raw form or activated carbon form would provide an economic important value which helps to decrease the cost of disposal of waste and an alternative to solve environment problems. (Anastopoulos *et al.*, 2020; Bhatnagar & Sillanpää, 2010; Dai *et al.*, 2018; Ramesh, 2013; Zhou *et al.*, 2015) have discussed the various low-cost adsorbents in a number of review articles for removal of heavy metals, dyes, phenols and pharmaceutical wastes. Many researchers used agriculture solid waste such as Beech saw dust, Bagasse fly ash, Wheat bran, Eucalyptus bark, Neem leaf powder, Rubber wood saw dust, Sugarcane bagasse, maize corn cob, jatropha oil cake, Raw rice bran for water contaminants removal (Sud *et al.*, 2008). In this review, we aim to present biowaste as an environmentally benign, low-cost biosorbent for removal of various dyes and heavy metals from water effluents in raw form as well as modified form. The effect of biosorbents modification by physical, chemical and composite formation on the specific surface area and porosity was studied. Some of the advantages of using agricultural waste for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selectivity for adsorption effluents, low cost, free availability and easy regeneration (Ngah & Hanafiah, 2008). Besides, the exhausted adsorbents can be disposed of by burning and the heat used for steam generation (V. K. Gupta & Suhas, 2009).

5.1 Physical modification of biosorbents

Biosorbents can be modified by using different physical processes such as autoclaving cutting, grinding, thermal drying, milling, boiling, steaming, and carbonization these methods result in change in adsorbent surface area and particle size (Ren *et al.*, 2014). Utilization of physically modified biosorbents for heavy metal ions and dye removal is discussed below. *Cucumis sativa* peel adsorbent after grinding modification may be suitably considered as nano biosorbent due to particles having spherical shape of variable sizes from 23 to 78 nm (Shakoor & Nasar, 2019). Adsorption of Congo red dye on sugarcane bagasse adsorbent took place intra-particle diffusion model in surface area of adsorbent value of range 0.58-0.66 m²/g while adsorption of methylene blue dye obeyed by multi-adsorption stages on surface area of adsorbent value of range 1.31-1.82 m²/g. Zhang *et al.*, 2013 reported that milling of SB increases the surface area from 0.58 to 0.66 m²g⁻¹ which resulted in increase in methylene blue dye removal efficiency by 5.6%, removing 96.6% of the dye (Z. Zhang *et al.*, 2013). *Moringa oleifera* pod husk after grinding showed good adsorption capacity for crystal violet dye because grinding results in BET surface area and average diameter of pore values 2.097 m²/g and 66.268 Å (Keereerak & Chinpa, 2020). Grinding modification of fava bean peels results in macro porous adsorbent which have total surface area

and total pore volume of value 0.2108 ± 0.0035 m²/g and 0.00067 cm³/g (Ba *et al.*, 2020).

(i)

Removal of lead

Plastics, finishing tools, cathode ray tubes, ceramics, solders, pieces of lead flashing etc. are the major sources through which lead enters in the environment, concentration level of lead and duration of exposure control the various biological effects. In the environment it has strong affinity to bind with many particles like oil, sediments and sewage sludge which results its removal is of great concern. Kumar *et al.*, 2016 reported that *Andes salsa* inch shell biomass adsorb lead ions at pH of 3.0 with adsorption capacity value of 17.07 mg/g and mechanism of adsorption was electrostatic attraction (B. Kumar *et al.*, 2016). Rice straw used as adsorbent showed maximum adsorption value 42.55 mg/g at pH 5.5 and 298K temperature through adsorption mechanism like electrostatic attraction and physical adsorption (Amer *et al.*, 2017). Hazelnut husk adsorb lead ions with maximum adsorption capacity of value 109.90 mg/g at optimum condition of pH and temperature was 5 and 298K (Imamoglu *et al.*, 2016). Mangosteen adsorbent adsorb lead ions with adsorption capacity of value 3.56 mg/g at optimum conditions of pH, temperature, contact time, adsorbent dose and concentration range of values 5, 298 K, 30 min, 20-250 mg/L, 1.5g/L respectively and followed Langmuir isotherm (Zein *et al.*, 2010). Coconut shell adsorb lead ions showed 0.02 mg/g maximum adsorption capacity at pH, temperature, time, adsorbent dose, initial concentration of value 10,303k, 30min, 0.5 mg/L, 0.5-5 mg/L respectively (Okafor *et al.*, 2012).

ii. Removal of chromium

Chromium is a toxic heavy metal occurs in various oxidation states but chromium (VI) and chromium (III) are of main environmental concern, which enters in to environment by many applications like tanning, wood preservation and pigments, dyes for plastic, paints, and textiles (Yu *et al.*, 2000). Various agriculture biomass based adsorbents which used for the removal of chromium were *Ficus nitida* leaves (Ali & Alrafai, 2016), Olive bagasse (Demiral *et al.*, 2008), Mango kernel (*Mangifera indica*) (Akram *et al.*, 2017) [1], Mosambi peel (Saha *et al.*, 2013), *Melaleuca diosmifolia* leaf (Kuppusamy *et al.*, 2016), Beech saw dust, Bagasse fly ash, Wheat bran, Eucalyptus bark, Neem leaf powder, Rubber wood saw dust, Sugarcane bagasse, maize corn cob, jatropha oil cake, Raw rice bran (Sud *et al.*, 2008). Coconut shell used as adsorbent for Cr_{VI} removal at optimum condition of pH, initial concentration, contact time, doses were 4.6, 10 – 200 mg/L, 100 min, 1.5g/L respectively with maximum adsorption capacity of value 40 mg/g, followed by Langmuir isotherm and pseudo second order kinetic model (Mohammed *et al.*, 2014). Tadesse reported that teff straw act as an adsorbent for the removal of chromium metal with an adsorption capacity of value 3.51 mg/g at optimum pH, temperature, value was 2.0, 298 K respectively and adsorption took place by chemisorption adsorption mechanism (Tadesse *et al.*, 2015).

iii. Removal of cadmium, arsenic, nickel, copper, mercury, zinc

Cadmium has more water solubility as compare to other heavy metals and it accumulates in environment from various sources but the long life time PVC-window frames, plastics and plating on steel are the basic sources and causes very harmful effects on human body. Nickel and its compounds have no characteristic odour or taste. The sources of nickel to the environment are nickel plating, colored ceramics, batteries, furnaces used to make alloys or from power plants and trash incinerators. Experiments were conducted on sequestration of heavy metals on various agriculture biowaste adsorbents and resulted in

good removal efficiency. Peels of peas, fig leaves, broad beans, medlar peel, wheat bran, husk of black gram straw, bagasse fly ash, bagasse, wheat bran, hazelnut shell, orange peel, maize cob, peanut hulls, jack fruits, maple saw dust, tea waste, defatted rice bran, cottonseed hulls, pinus radiata bark, mango saw dust, mustard oil cake, are the adsorbents which were tried for the adsorption of heavy metals like cadmium, arsenic, mercury, nickel, copper etc. with adsorption efficiency of range 40-100% (Sud *et al.*, 2008). Rice bran which is used for the removal of Pb (II), Cd (II), Cu (II), Zn (II) and showed more than 80% removal (Montanher *et al.*, 2005) (Montanher *et al.* 2005). Najam *et al.* 2016 reported that Raw walnut shell were used for removal of cadmium ions with adsorption capacity of value 7.29 mg/g at 6 pH by share or exchange electronics and chemisorptions adsorption mechanism (Najam & Andrabi, 2016). Sesame used as an adsorbent for removal of cadmium ions showed adsorption capacity of value 84.74 mg/g at optimum pH of value 6.0 and followed by chemisorptions mechanism (Cheraghi *et al.*, 2015). Casuarinas fruit powder and Banana stem powder were used for the removal of copper ions showed adsorption capacity 4.55 and 6.49 mg/g at optimum conditions by chemisorption and physical adsorption mechanism (Mokkapati *et al.*, 2016). Walnut shell were used for zinc ions removal showed adsorption capacity of value 7.48 mg/g at 5.0 pH and 313 K temperature by Ion exchange adsorption mechanism (Najam & Andrabi, 2016).

5.2 Chemical modification

Recently, more attention has been given for enhancing the effectiveness and adsorption capacity of biowaste adsorbents by modifying their specific properties using various techniques. Although various agriculture waste materials have been used as adsorbent for removal of water contaminants like heavy metals and dyes but the application of these untreated biosorbents causes several problems like low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the agriculture wastes. So, the modification of these biosorbents required to avoid these problems because the pre-treatment of bio wastes using different kinds of modifying agents like many base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate), mineral and organic acid solutions (hydrochloric acid, nitric acid, sulphuric acid, tartaric acid, citric acid, thioglycolic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), dye (Reactive Orange 13) can extract soluble organic compounds and remove colour of aqueous solutions. These chemical modifications generally results in oxidation of functional groups present on the surface or introduce new functional groups on the surface of biosorbent which enhance chelating efficiency, surface area and porosity. For example, Hydrochloric acid, sodium carbonate, sodium hydroxide, tartaric acid and epichlorohydrin are commonly used for the chemical modification of rice husk which remove lignin, hemicellulose, reduce cellulose crystallinity and increase the porosity or surface area results more adsorption capacity for cadmium then unmodified rice husk (Ngha & Hanafiah, 2008). But sometimes these chemical modification results decrease in adsorption capacity, for ex-

ample hydrochloric acid treated rice husk showed decrease in adsorption capacity for cadmium heavy metal ions then untreated rice husk because hydrochloric acid results in protonation of adsorption sites on adsorbent which leaves the heavy metal ions in the aqueous phase rather than being adsorbed on the adsorbent surface (U. Kumar & Bandyopadhyay, 2006). Esterification reaction between biosorbents of agriculture waste materials and acids results in increase functional groups. These extra functional groups on the surface are responsible for binding of the dye molecule and heavy metal ions which results in increase of adsorption efficiency but esterifies tartaric acid modified rice husk however significantly reduced the uptake of Cu and Pb because the chelators like nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) caused significant suppressing effect on the uptake of Pb (Wong *et al.*, 2003). Esterification of papaya seed increase the uptake of methylene blue dye from 200 mg/g to 250 mg/g but decrease for anionic congo red dye from 71.43 mg/g to 58.8 mg/g because the esterifies modification causes negative charge on the adsorbate surface (Nasuha *et al.*, 2011). Modified orange peel adsorbent showed the maximum uptake capacity for Pb²⁺, Cd²⁺ and Ni²⁺ ions were 476.1, 293.3 and 162.6 mg g⁻¹, respectively, which were about 4.2, 4.6 and 16.5 time higher than that of the unmodified biomass (Feng *et al.*, 2011). Ortho-phosphoric acid treated *Gmelina aborea* leaf powder exhibited higher performance and showed a increase in adsorption capacity from 142.86 to 1000 mg/ L which proved that modification resulted in the creation of several pores on gmelina aborea leaf powder (Solomon *et al.*, 2019).

Chemical modifications of activated carbons using acids is the most studies technique that had been used for past several decades due to its simplicity, availability of oxidizing agents and the established nature of this technique. Which introduce acidic functional groups onto the surface of activated carbon. But an acid treatment gives different effects on the certain activated carbons either increasing or decreasing their adsorption capacities. This is control by the type of activating agents, precursors, activation methods and adsorbate. Hydrochloric acid modified oil palm shell-based activated carbon showed increase in adsorption capacity for methylene blue from 243.90 to 303.03 mg/g which was 24.24% higher than unmodified oil pal shell activated carbon. Due to the adsorption of negative ions (Cl⁻ from HCl) on the positive sites on the carbon surface, which makes the surface negative and facilitating the adsorption of the positive charged molecules of methylene blue (I. A. W. Tan *et al.*, 2008). Wang *et al.* reported that 2M hydrochloric acid and nitric acid modified commercial activated carbons (BDH, F100 and BPL) resulted in decrease in uptakes of methylene blue ions due to the removal of hydroxide groups by the acidic treatment which produced acidic oxygen functional groups on the carbon surface. Which reduced the interactions between methylene blue molecules and carbon (Wang *et al.*, 2005). Ethylenediamine modified rice hull which adsorbed basic (basic blue) and reactive dyes (reactive orange) from single and binary solutions with good sorption capacity as compare to natural rice hull adsorbent. The maximum adsorption capacity in binary solution was increased by 4.5 and 2.4 times, respectively compared to those in single dye solutions.

Table 1. Biosorbents utilization for dye removal using physical modifications

Adsorbent	Dye	Qmax (mg/g)	pH	Doses	Initial concentration(mg/g)	Contact time(min)	Temperature (°C)	Adsorption Kinetic model	Adsorption Isotherm	Ref.
Gaint duckweed	Methylene blue	144.93	9	0.1-1g/100ml	10-500	0-24h	25	Pseudo first-order	Langmuir	(Waranusanigul <i>et al.</i> , 2003)
Tea waste	Methylene blue	85.16	2-10	0.2-0.6g/200ml	10-50	0-6h	r.t	Pseudo-second order	Langmuir	(Uddin <i>et al.</i> , 2009)
Banana peel (Grinding)	<i>Rhoda mine B</i>	81.07		0.04-0.5 g/30ml	25	10-70	30-60	-	Langmuir	(Singh <i>et al.</i> , 2018)
Musa acuminata peels (Grinding)	Emerald green	10.75	1-10	0.2-2g/25ml	5-25	10-70	10-80	Pseudo-second order	Langmuir	(Rehman <i>et al.</i> , 2018)
<i>Solanum tuberosum</i> peels (Grinding)	Emerald green	2.611	1-10	0.2-2g/25ml	5-25	10-70	10-80	Pseudo-second order	Langmuir	(Rehman <i>et al.</i> , 2018)
Brown seaweed sargassum	Methylene blue	142.86	7	2g/L	5-400		25 ± 2	Pseudo-second-order	Temkin and Dubinin-Radushkevich	(El <i>et al.</i> , 2018)
<i>Psyllium</i> seed powder (Milling)	Reactive orange 16	206.6	2-7	0.5 - 2 g/L	50-300	40	30	Pseudo-second-order	Langmuir	(Malakootian & Heidari, 2018)
Cassava root husk (Dried)	Direct black	46.1	2		25-500	0-72h	30-50	Pseudo-second-order model	Langmuir	(Scheufele <i>et al.</i> , 2019)
<i>Cucumis sativas</i> peel(Grinding)	Crystal violet	149.25	8	5.0g L ⁻¹	10-100	1h	25	Pseudo-second-order model	Langmuir	(Shakoor & Nasar, 2019)
Anatolian black pine (Grinding)	Crystal violet	12.36	3-10	1-15 g/L	25-200	5- 240	45	Pseudo-second-order	Langmuir	(Gemici <i>et al.</i> , 2019)
Coffee husk (Ball mill)	Crystal violet	12.036	3-9	0.1-1.5g/50ml	12.2394	0-120	25	Pseudo-second-order	Freundlich and Langmuir	(Cheruiyot <i>et al.</i> , 2019)
<i>Moringa oleifera</i> pod husk (Grinding)	Crystal violet	156.25	2-10	0.2-1.8 g/L	50-250	5-120	25	Pseudo-second order	Langmuir	(Keereerak & Chinpa, 2020)
Fava bean peel(Grinding)	Methylene blue	140	5-10	0.1-1g/100ml	3.6-100	2-20	r.t	Pseudo-second order	Langmuir	(Ba <i>et al.</i> , 2020)
Green seaweed <i>Codium</i> decorticated	Crystal violet Congo red	278.46 191.01	6	1 g/L		120	25	Pseudo-second order	Langmuir	(Oualid <i>et al.</i> , 2020)
Gaint reed (Grinding)	Reactive blue	3.940	2-10	0.25- 3g/L	10-150	10-180	20-50	Pseudo-second order	Freundlich	(Alwared <i>et al.</i> , 2020)
Mango seed kernel (Grinding)	Reactive black	2.816								
	Methylene blue	142.857	8	0.2g/30ml	20-100	10-240min	30	Pseudo first order	Langmuir	(K. V. Kumar & Kumaran, 2005)

Chemical modifications also affect the point of zero charge (pH_{pzc}) of the adsorbent and behaviour of adsorbent towards solution pH. For phosphoric acid treated sugarcane bagasse, the dye adsorption was significantly remained almost 100% for all pH values. But for sugarcane bagasse carbon it was significantly changed over the pH value 3-6 showed lowest percentage of dye removal at pH 2 (52.2%) and at the pH range of 7-10 it remain constant. As the adsorption of dyes on modified sugarcane bagasse took place by ion-exchange mechanism that did not shows effect of pH on adsorption. But on unmodified sugar cane bagasse it took place by electrostatic attraction mechanism showed effect of solution pH. Phosphoric acid treated sugarcane bagasse showed more adsorption capacity as compare to unmodified sugar cane bagasse and untreated sugarcane bagasse carbon of values 48.42, 10.98 and 5.66 mg/g respectively (Saad *et al.*, 2010). The pH_{pzc} of the sugarcane bagasse and citric acid modified sugarcane bagasse adsorbents were 5.5 and 3.4 respectively. Point of zero charge of native, Polyethyleneimine treated and immobilized sugarcane bagasse was found to be 4.8, 5.8 and 5.3 respectively.

The effect of chemical modification on the surface functional groups, specific surface area, volume and size of pores can be determined using characterisation techniques like Fourier transform infrared spectroscopy, Brunauer Emmett Teller (BET) analysis. SEM and Barret, Joyner, and Halenda (BJH) method is used for studying pore size distributions on the adsorbent surface. FTIR spectra of sodium hydroxide modified tea waste showed two new peaks formed at 2919 and 1427 corresponding to aliphatic C-H and NH_2 deformations but in case of raw rejected tea there were only remarkable shift in positions of -OH, C-O and -C-C- group peaks after adsorption, which showed methylene blue binding majorly at -OH and C-O groups. Also modified rejected tea has higher physical stability and surface activity as compare to raw tea. The changes in FTIR spectra after adsorption confirm the complexation of methylene blue with functional groups present in the adsorbents. SEM micrographs of modified rejected tea showed the surface of modified tea exhibited pores like honeycomb shape gaps and modification also did not change the actual surface texture of rejected tea and have a macro reticular with enhanced physical characteristic. The BET surface area, total pore volume and average pore diameter were measured to be 6.5 m²/g, 0.0064 cm³/g and 61 Å, respectively for modified rejected tea. The increase in adsorption capacity from 147 mg/g to 242.11 mg/g is due to formation of negative charge on rejected tea after modification with NaOH. Which increase the electrostatic attraction between adsorbent and adsorbate (Nasuha & Hameed, 2011). The Fourier transform infrared (FTIR) spectra of natural rice hull and oxalic acid modified rice hull results showed that carboxyl groups increased and there were an increase in the adsorption band corresponding to the stretch vibration of the carboxyl group (at 1736 cm⁻¹), with the position of some peaks being changed after modification (Zou *et al.*, 2011). NaOH activated prunus leaves showed more specific surface area of value 426.346 m²/g which was higher than the unmodified prunus (67.205 m²/g). NaOH treatments increase the pore volume of prunus leaves to 0.282 cm³/g and decrease the Pore diameter to 2.644 nm. Significant increase in surface area and pore volume for NaOH activated prunus leaves as compared to Dead leaves of *Prunus Dulcis* was attributed to removal

of lignin from dead leaves of *Prunus delcis* due to NaOH treatment. Leading to development of pores and hence an increase in the surface area and pore volume (Jain & Gogate, 2018). XRD technique can be used to analyze the influence of the pre-treated process on the crystallinity of the cellulose. Retreatment process remove the amorphous components of lignin and hemicelluloses results increase in crystallinity after pre-treatment, (R. Liu *et al.*, 2005). The pre-treatment of wheat straw with NaOH and HCl, which remove the hemicelluloses, lignin and pectin, resulted that the surface of Pre-WS was relatively wrinkled, and its average diameter decrease significantly to 7-10 µm (Hornsby *et al.*, 1997). Grafting of wheat straw also resulted denser surface as compare to untreated wheat straw indicated that the surfaces was covered by the graft polymerization (Lin *et al.*, 2017). Some of the chemical modifications of agriculture biowaste material biosorbents are given in Table 2 along with their maximum adsorption capacity and optimum conditions.

6. Conclusion

This review article started with brief presentation of classification of dyes, their toxic effects and several treatment techniques for waste water in which adsorption technique gain more emphasis. In adsorption technique various low cost adsorbents like agricultural solid waste materials used for removal of contaminants. Agricultural wastes materials have many functional groups which make them promising adsorbents for contaminants removal in their raw and modified form. The synthesis and applications of agricultural waste-based adsorbents for the removal of various types of heavy metals and dyes from water have been reviewed. Compare to other adsorbents agricultural waste-based composites are renewable, biodegradable, biocompatible, and economically viable. As evidenced by the literature reviewed in this paper, physical, chemical and composite modification can increase the uptake of contaminants by increasing number of active binding sites in the adsorbents, improving their ion exchange properties and form new functional groups. Effect of modification on adsorbents can be studied using various characterization techniques. Adsorption techniques using these nonconventional biomass adsorbents especially replace the use of expensive commercial activated carbon for the removal of toxic contaminants from water bodies and provide a green sustainable solution for treatment of contaminated water. These also contribute to an overall waste minimization strategy. Various composites of agriculture waste materials have been studied in which magnetic adsorbents are very helpful to recover adsorbents and control the adsorption process. Parameters such as adsorption mechanism for dyes and heavy metals removal, biosorption capacity of sorbent, temperature, biosorbent dose, initial concentration of contaminants, equilibrium time and pH of the solution were also presented. Various kinetic and thermodynamic models for adsorption process were studied. Several gaps that require attention, such as the enhancement of biosorption capacity through the modification of adsorbents, assessment of adsorbents under multicomponent pollutants, validating these materials with real industrial effluents, recovery of metal ions and dyes, regeneration studies, continuous flow of studies, use of eco-friendly chemicals for adsorbents modification to avoid secondary pollution.

Table2:- Agriculture waste material adsorbents chemical modifications and their study for dye and heavy metal removal along with optimization conditions

Adsorbent	Dye	Qmax (mg/g)	pH/Doses	Contact time/ Temperature	Initial concentra- tion	Induction of func- tional groups	Adsorption mechanism	Adsorption isotherm/ kinetic model	References
Dyes									
Ethylenediamine modified rice hull	Basic Blue(B.B) Reactive Orange(R.O)	14.68(B.B) 60.24(R.O)	4-6 0.02 - 0.10 g/20ml	0-540min	5-150 mg/l	Carboxyl and amine	chemisorption	Langmuir and Freundlich/ Pseudo-second order	(Ong <i>et al.</i> , 2007)
Phosphoric acid modified rice straw	Basic blue (B.B) Basic red (B.R)	208.33(B.B) 188.68(B.R)	2-11 0.1-1.5g/L	6h	50-350	OPO ₃ Na ₂		Langmuir/ Pseudo-first-order	(Gong <i>et al.</i> , 2007)
Hydrochloric acid treated ac- tivated carbon of oil palm shell	Methylene blue	303	6.5/ 0.1g/100ml	30h / 303K	50-500	Carboxylic and ether	Chemisorption	Langmuir / Pseudo-second- order	(I. A. W. Tan <i>et al.</i> , 2008)
Phosphoric acid modified sugarcane bagasse	Methyl red	48.42	2-12 0.2 - 1.0 mg/100 mL	15-210min/ rt	50-250	OPO ₃ Na ₂	Chemisorption	Langmuir / Pseudo second order	(Saad <i>et al.</i> , 2010)
NaOH and a cationic surfac- tant hexadecylpyridinium chloride monohydrate barley straw	Acid blue(A.B) Reactive Blue (R.B)	51.95(A.B) 31.5(R.B)	2-12 2g/L	0-120min/ 298k	50-100	C ₂₁ H ₃₈ N ⁺	Chemisorption	Langmuir/ Pseudo-second- order	(Ibrahim <i>et al.</i> , 2010)
NaOH treated rice husk	Malachite green	17.98	2-9/1g/L	10-120 298k-313k	10-100	OH	Chemical ion- exchange	Freundlich/ Pseudo-second- order	(Chowdhury <i>et al.</i> , 2011)
Esterification modified pa- paya seed	Methylene blue Congo red(C.R)	250(M.B) 58.8(C.R)	0.5g/200ml	10-180min/ 303k	50-500	RCOO ⁻	Chemisorption	Langmuir for(M.B) and Freundlich for (C.R)/ Pseudo-second order	(Nasuha <i>et al.</i> , 2011)
NaOH-modified tea	Methylene blue	242.11	0.5g/200ml	303k	50-500	OH		Langmuir and Freundlich/ Pseudo-second- order	(Nasuha & Hameed, 2011)
Oxalic acid modified rice husk	Methylene blue/ Malachite green	53.21(M.B) 54.02(M.G)	2-10/ 10 mg/20ml	480min/ 293k	20-450	COO-	Surface adsorption and Pore diffusion	Freundlich for (M.B) and Langmuir for(M.G)/ Pseudo-second-or- der kinetic	(Zou <i>et al.</i> , 2011)
Mono chloroacetic acid and 2-(dimethylamino) ethyl methacrylate (DMAEMA) modified Wheat straw	Methylene blue/ Methyl orange(M.O)	115(M.B) 506(M.O)	2-12/ 10 mg/20ml	0-60min/ rt	25-500	Amino and carboxyl	Chemisorption	Pseudo-second- order	(W. Zhang <i>et al.</i> , 2012)

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Table2:- Agriculture waste material adsorbents chemical modifications and their study for dye and heavy metal removal along with optimization conditions

NaOH ,Epichlorohydrin, di-ethylenetriamine and chloroacetic acid modified bamboo	Methylene blue	606	3-10/ 50 mg/50ml	15-315/ 298k	100-900	Carboxyl / diethylenetriamine	Surface adsorption and Intra-particle diffusion	Langmuir/ Pseudo-second- order	(Guo <i>et al.</i> , 2014)
NaOH modified leaves of <i>Prunus Dulcis</i>	Acid blue113	50.79	2/ 6g/L	330min	50-200		external diffusion , in- tra-particle diffusion,	Langmuir/ Pseudo- second- order	(Jain & Gogate, 2017)
NaOH modified breadnut skin	Malachite green	353	2-10/ .050g/25ml	30-240min/ 298k	0-1000		Chemisorption	Sips/ Pseudo-second order	(Taylor <i>et al.</i> , n.d.)
Jute fiber activated carbon by phosphoric acid	Methylene blue	225.64	4/ 75ml/50ml	0-4h/ 301k	50-500	OPO ₃ Na ₂	Diffusion	Langmuir /Intraparticle diffusion	(Senthilkumaar <i>et al.</i> , 2005)
<i>Gmelina aborea</i> leaf powder (<i>ortho</i> - phosphoric acid (H ₃ PO ₄))	<i>Rhoda mine</i> B	1000	3-10	0-120min/ 303-323k	200-1000		chemisorption	Langmuir/ Pseudo-second- order	(Solomon <i>et al.</i> , 2019)
<i>Grevillea Robusta</i> leaves (1N H ₂ SO ₄)	Indigo carmine	97.27	6/8g/L	40min/ 313K	20	Carboxyl	Chemisorption	Pseudo-second order	(Rao <i>et al.</i> , 2020)
Glossogyneteniuifolia leaves activator (ammonia, lauric acid solution)	Malachite green Congo red	370.4-434.8 (M.G) 37.04-37.88 (C.R)	2-10/ 2-12g/L	293-323K	100-500	-	Chemisorption	Freundlich / Pseudo-second order	(Yang & Hong, 2017)
Heavy metals									
KOH and K ₂ CO ₃ treated chickpea	<i>Pb</i> _{II} , <i>Cr</i> _{VII} , <i>Cu</i> _{II}	135.8(Pb) 59.6(Cr) 56.2(Cu)	2-10/ 2-6g/l	0-360min/ 293-313k	100-400	Metallic potassium	Chemical sorption	Freundlich/ Pseudo-second- order	(Őzsin <i>et al.</i> , 2019)
Sulphuric acid modified acti- vated carbon of corncob	<i>Cu</i> _{II}	26	2.4/ 0.5g/L	40min/ 304k	100		Physical adsorption	Langmuir / Pseudo-first-order	(M. N. Khan & Wahab, 2007)
Grafting modification of corncob biochar using acrylonitrile	<i>Cd</i> _{II}	85.65	6.8/ 50 mg/25ml	24h/ r.t	20-200	C≡N moieties	Ion exchange and ad- sorption-complexation	Freundlich/ Pseudo-second- order	(Luo <i>et al.</i> , 2018)
HCl modified oak sawdust	<i>Cu</i> _{II} , <i>Ni</i> _{II} <i>Cr</i> _{VII}	3.22(Cu), 3.29(Ni), 1.70(Cr)	4(Cu),8 (Ni),3(Cr) 40(Cu), 30(Ni), 60 (Cr)g/L	0-12h/ 293K	0.1-150		Physical adsorption	Langmuir/ Pseudo-second- order	(Argun <i>et al.</i> , 2007)
Grafted copolymerization- modified Orange peel	<i>Pb</i> _{II} , <i>Cd</i> _{II} , <i>Ni</i> _{II}	476.1(Pb), 293.3(Cd), 162.6(Ni)	5.5/ 0.05g/25ml	3h/ 303k	50-1200		Chemical sorption	Langmuir/ Pseudo-second- order	(Feng <i>et al.</i> , 2011)

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Table2:- Agriculture waste material adsorbents chemical modifications and their study for dye and heavy metal removal along with optimization conditions

Formaldehyde nd sulphuric acid modified <i>Pinus Pinaster</i> Bark	$Zn_{II}, Cu_{II}, Pb_{II}$	-	4.5-7.5/ 1g/100ml	1-12h/ 295k	10-100 ppm	-	Freundlich	(González, 1994)
$ZnCl_2$ treated Corn husk biochar	Pb_{II}	113.12	2-9/ 1-20g/l	6h/	20-1000		Freundlich	(Rwiza <i>et al.</i> , 2018)
Nitric acid treated tangerine peel	Cr, Cu, Mn, Co, Ni, Pb, Cd, Zn	28.46(Cr) , 25.65(Cu), 27.85(Mn), 26.81(Co), 26.58(Ni), 5.78(Pb), 7.48(Cd), 9.78(Zn)	3-5/ 1-4g/l	0-120min/ rt	2-5 ppm		Physical adsorption Chemisorption	(Memić & Sulejmanović, 2018)
Grafting with acrylamide (AM) and citric acid (CA) modified rice straw	Cu_{II}, Cr_{VI}	17.82(Cu), 53.88(Cr)	0.1g/100ml	24h/ 298k	10-200	Amino and Carboxyl	Langmuir/ Pseudo-second-order	(Q. Liu <i>et al.</i> , 2020)

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