Chapter 5 Thermochemical Conversion of Biomass into Value-Added Materials for Effluent Treatment Applications



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Abstract Lignocellulosic biomass has been explored for the synthesis of various value-added materials due to its wide availability and environment-friendly nature. Apart from being studied as a potential feedstock for the synthesis of fine chemicals and generation of biofuels, these biomasses have also shown a wide range of applications in effluent treatment processes. Many agricultural waste biomasses had shown potential in effluent treatment, even in their raw form. Activated carbon prepared by the pyrolysis of biomass has yielded promising results as adsorbents and catalysts support the removal of both conventional and priority pollutants from effluents. Moreover, composite materials including metal oxide composites, magnetic materials, catalyst supports, polymer composites, and graphene composites prepared by the thermochemical conversion of biomass are being explored in tertiary treatment processes for the removal of targeted pollutants from the aqueous phase. Hence, this chapter is aimed to discuss the application of biomass-based value-added materials for effluent treatment applications.

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Abbreviations

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5.1 Introduction

Humanity dates back to not a decade or a century but a millennium. Since existence began, the production of wastes in many forms originated particularly from natural sources. The most popular form of waste would be wood or of plant origin. In general, the term "Biomass is defined as matter originating from living plants, including tree stems, branches, leaves as well as residues from agricultural harvesting and processing of seeds or fruits" (Pang 2016). Biomass is considered to carry energy in the form of chemical bonds among hydrogen, carbon, and oxygen moieties (Pang 2019). The sources of biomass are plant products, the residue of crop farming and processing industries, fruit and vegetable waste, agro-industrial waste, household waste, urban waste, and animal waste (Wormeyer et al. 2011). Figure 5.1 shows the classification of biomass resources. They include materials consisting of cellulose, hemicellulose, and lignin (Mohan et al. 2006). As for the elementary composition, 90% of the typical biomass contains 51% carbon, 42% oxygen, and trace amounts of hydrogen, nitrogen, and chlorine (Mandapati and Ghodke 2021b). The biomass resources were calculated to be 146 billion tonnes/annum. Tropical countries like India contribute to the production of about 500 million metric tonnes/ year of biomass. This natural carbonaceous resource is mostly used or exploited as a source of fuel.

5.2 Biomass as a Source of Fuel

The rapid consumption of fossil fuel has led to its depletion (Mandapati and Ghodke 2021a; Agrawal and Verma 2022; Kumar and Verma 2021a). Various renewable resources which include biomass-based reserves, wind, solar, and geothermal resources have been explored as alternative fuels. Among these renewables,



Fig. 5.1 Classification of biomass resources

bioenergy is renewable energy sourced from biomass that is abundant and has a high utilization potential to produce energy (Pang 2019; Kumar et al. 2020; Kumar and Verma 2021b). If 10% of the biomass is exploited for energy production with 50% efficiency, it may have the potential to churn out 3.1 trillion tonnes of oil equivalent energy. This would account for the availability of 200 times the energy consumed worldwide currently (Energy Information Administration, EIA, 2017). On the other hand, the utilization of 10% of biomass for organic chemical synthesis at a 10% conversion rate will lead to the production of 1.6 billion tonnes of chemical feed materials (Pang 2019). Generally, in developing countries, 38% of the energy consumed is primarily from bioenergy produced from biomasses (Sarkar and Praveen 2017).

Biomass is a clean energy source is produced by plants by consuming CO_2 from the atmosphere through photosynthesis (Tekin et al. 2014). Moreover, these biomasses are produced in short duration ranging from months to years when compared to unsustainable fossil fuels which usually require millions of years (Collard et al. 2012). Hence, renewable energy from biomasses proves to be a sustainable source of energy supply that can also address environmental concerns.

5.3 Value-Added Pathway from Biomass for Different Applications

Biomass conversion pathways through various processes are shown in Fig. 5.2. The widely used thermochemical conversion technologies for the conversion of biomasses include but are not limited to gasification, pyrolysis, hydrothermal





liquefaction, and torrefaction (Goswami et al. 2020, 2021a). Torrefaction is a thermal pre-treatment process used in the combustion, pyrolysis, gasification, and liquefaction of biomass (Ghodke and Mandapati 2019). Pyrolysis is heating the biomass at elevated temperatures (573–973 °K) to obtain biochar and bio-oil. The hydrothermal liquefaction process is operated between 523 and 647 °K within the pressure range of 4–22 MPa for the production of bio-oil. Gasification involves the conversion of biomass into syngas at temperatures higher than 973 K.

5.4 An Alternate Strategy for the Utilization of Waste Biomass

Biomass has a great potential to be used as a source of biofuel (Bhardwaj et al. 2021). The total biomass power generation potential of India is estimated to be 17,500 MW. However, at present, only 2665 MW of power is being generated (Kumar et al. 2015). Hence, due to the availability of abundant waste biomass materials, the management or disposal of these substances is itself a major task for environmentalists. In the global arena, "Waste to Wealth" is a term coined to utilize waste material for useful resources. Since the resource is inexpensive, green, and renewable, environmentalists focus on such processes to reduce pollution. There are several studies, where the waste biomass and its derivatives were used as a precursor material for effluent treatment processes. The biomass could be converted into a base material for catalyst preparation in the form of support or as an adsorbent material. They can be utilized for the treatment of effluents by the process of adsorption or by using an advanced oxidation process (AOP). Wherein the preparation of heterogeneous catalyst by supporting the active material on carbon support derived from biomass reduces the cost of the effluent treatment process. Hence, this chapter is aimed to discuss the thermochemical conversion of biomass into value-added materials for effluent treatment applications.

5.5 **Biomass for Effluent Treatment Processes**

It has been reported that every day two million tons of waste from various sources are discharged into water bodies worldwide. This created an impact that one in eight people worldwide are deprived of safe and clean drinking water as reported in World Water Assessment Programme, World Water Development Report1: "Water for People, Water for Life," Paris (2003). Water pollution is found to be the major reason for diseases and subsequently deaths worldwide (Vairavel and Murty 2020; Goswami et al. 2021b). In India alone, it has been estimated that approximately 580 people die due to water pollution-related illnesses every day (Clark et al. 1996). Major contaminants found in wastewater include but are not limited to dyes and

pigments, heavy metals, phenolic compounds, pharmaceuticals, agrochemicals, and endocrine disruptors (Akhil et al. 2021; Kumar et al. 2019; Kumar et al. 2021). Effluent treatment plants comprise physical, chemical, and biological treatment systems. Generally, all these treatment methods are grouped under primary, secondary, tertiary, and advanced treatment processes. Primary treatment processes aim to remove contaminants by the physicochemical processes like primary clarification (gravity settling) and coagulation/flotation. The secondary treatment processes work on the removal of the residual organics. The secondary treatment processes employ various microorganisms for reducing the COD and BOD of the effluent. Activated sludge treatment methods such as aerobic and anaerobic digestion are some of the secondary wastewater treatment methods. Tertiary treatment methods include membrane separation processes, electrodialysis, advanced oxidation processes, adsorption, biosorption, bioaccumulation, and ion exchange (Sonune and Ghate 2004). Most of these treatment processes like adsorption, biosorption, and advanced oxidation processes utilize functional materials for their operation. These functional materials like adsorbents and catalysts in case of adsorption and oxidation processes respectively are of chemical origin, which leads to secondary pollution. However, the waste biomasses and their derivatives proved to be environmentally friendly precursor materials for the synthesis of adsorbents and catalysts support materials. A simple thermochemical modification of the lignocellulosic waste materials could yield highly functional materials for wastewater treatment processes (Liu et al. 2015).

5.6 Application of Raw Biomass in the Effluent Treatment Process

Adsorption is the most widely used effluent treatment technique This is because, the used adsorbent materials have the potential for regeneration, recovery, and recycling which proved to be an added advantage at the industrial scale of operations. It is not only used for the removal of contaminants but also could be used for the recovery of precious and costly entities from the effluents (Crini et al. 2019). The physicochemical properties of the adsorbent have a major influence on the efficacy of the adsorption process. The chosen or prepared adsorbent should be easily available, economical, non-toxic, and should have good surface characteristics. They must also have high mechanical and thermal stability (Reddy et al. 2017). The lignocellulosic waste biomasses, in their raw or modified form, proved to be potential candidates for the preparation of economical and sustainable adsorbents for effluent treatment (Bhatnagar et al. 2015). Plant and agricultural waste products have earned increased interest for dye and heavy metals removal by adsorption from the aqueous solution because of their natural availability and higher removal efficiency (Garg et al. 2019; Agrawal and Verma 2021). The inexpensive waste products, after basic cleaning or some minor treatment, were explored as adsorbents. Agricultural by-products

especially those containing cellulose exhibit good adsorption potential for removing various toxic pollutants from effluents. There are numerous studies reporting the application of raw lignocellulosic materials like rice husk, oil cakes, banana peel, sugarcane bagasse, powdered leaves, etc. for the removal of different types of dyes, heavy metals, and other priority pollutants. This method of exploiting raw biomass as functional adsorbent materials proved to solve disposal problems associated with the abundant availability of these waste biomasses (Moorthy Rajendran et al. 2020). Few of the studies which deal with the application of these raw biomass materials for effluent treatment is tabulated in Table 5.1.

5.7 Biomass-Derived Activated Carbon for the Effluent Treatment Process

Many studies reported raw agricultural biomass as an adsorbent for the removal of organics and inorganics from simulated effluents. However, most of these raw biomasses were found to lack desired adsorption efficiency and were mechanically unstable. The efficiency of these biomasses could be enhanced by carbonization and activation using thermal and chemical treatment methods. The physical treatment includes carbonizing the material at a temperature of around 500 °C under an inert atmosphere using nitrogen or argon supply. The carbonized material is then activated at higher temperatures using suitable activating agents like steam or CO₂. The chemical treatment method involves the impregnation of the cellulosic biomass with various strong acids and bases like NaOH, KOH, HCl, H₂SO₄, ZnCl₂, etc. The impregnated material is then carbonized at higher temperatures at around 500 °C to obtain activated carbon (AC) (Rodríguez-Reinoso and Molina-Sabio 1992). The schematic for the preparation of AC through physical and chemical methods is presented in Fig. 5.3. AC is proved to have superior adsorptive and mechanical properties when compared to raw biomasses owing to increased surface area and porosity (Zhang et al. 2019). AC derived from different biomass has varying properties. The properties of AC depend on the precursor material, type of carbonization and activation, and activation temperature and duration. AC is the widely studied adsorbent material for treating effluents which contain all types of pollutants including the emerging contaminants from effluents (Yahya et al. 2015). Moreover, AC also finds its application as catalyst support in many reported studies in advanced oxidation processes which are discussed in Sect. 5.8.4. The application of biomassderived AC is not limited to effluent treatment methods, and thus they are used in various fields such as gas purification (Ma et al. 2008), supercapacitors (Yang et al. 2014), and medicinal applications (Lakshmi et al. 2018). Few of the studies on the application of biomass-derived activated carbon for water and wastewater treatment is summarized in Table 5.2.

Table 5.1 Application of ra	iw biomass for effluent treating	hent	
Raw biomasses	Target pollutants	Maximum monolayer adsorption capacity "qm" (mg/g)	References
Dyes			
Guava leaves	Remazol brilliant blue-R	93.12	Debamita et al. (2020)
Coffee husks	Congo red	38.65	Vairavel et al. (2021)
Neem leaf powder	Coomassie violet	39.64	Divya et al. (2020)
Sugar cane bagasse	Congo red	38.20	Zhang et al. (2011a, b)
Almond shells	Direct red 80	22.42	Ardejani et al. (2008)
Jujuba seeds	Congo red	55.55	Reddy et al. (2012)
Jackfruit peel	Methylene blue	285.71	Hameed (2009)
Lotus leaf	Congo red	45.89	Meghana et al. (2020)
Heavy metals			
Neem leaf	Cd(II)	157.80	Sharma and Bhattacharyya (2005)
Cucumis melo rind	Fe(II)	4.98	Othman and Asharuddin (2013)
Coffee residues	Cd(II)	39.52	Boonamnuayvitaya et al. (2004)
Coconut husk	Pb(II)	2.75	Abdulrasaq and Basiru (2010)
Durian shell	Cr (VI)	117	Edokpayi et al. (2015)
Sugarcane bagasse	Cd(II)	189	Karnitz et al. (2007)
Cassava tuber bark waste	Zn(II)	83.3	Horsfall et al. (2006)
Wheat bran	Cd(II)	101	Ozer and Pirincci (2006)
Phenol			
Tea waste	Phenol	154.39	Pathak et al. (2020)
Garlic peel	Phenol	14.48	Muthamilselvi et al. (2016)
Rice straw	Phenol	5.78	Sarker and Fakhruddin (2017)
Lantana camara	Phenol	112.5	Girish and Murty (2014)
Vegetal cords	Phenol	6.21	Cherifi et al. (2009)
Endocrine disruptors			
Barley husk	Bisphenol A	19.94	Balarak (2016)
Walnut shell	Bisphenol A	38.5	Dovi et al. (2021)
Raw fibric peat	Bisphenol A	6.48	Zhou et al. (2011)



Fig. 5.3 Chemical and physical activation methods for the preparation of biomass-derived activated carbon

5.8 Biomass-Based Composite Materials for Effluent Treatment

Biomass-based materials either in their raw form or with thermal and chemical modification demonstrated to be an efficient low-cost material for the adsorption of various organics and inorganics from simulated effluents. Furthermore, recent studies suggest that these biomasses can also be fused with other functional materials and could be actively applied in various treatment processes. These biomass-based composites include but are not limited to metal oxide composites, magnetic materials, polymeric materials, and graphene-based composites. The schematic representation of the same is presented in Fig. 5.4.

5.8.1 Biomass-Based Magnetic Materials for Effluent Treatment

Generally, nanoparticles have promising potential to be used in various effluent treatment technologies. However, the application of these nanoparticles in water and wastewater purification is limited. This is due to the fact that, the spent nanomaterials after application tends to escape into the aquatic environment causing secondary pollution. The removal and recovery of the spent materials in their nanoform is not economical. Recently, materials coated with magnetite nanoparticles are considered

		Activation of a	dsorbents				
		Physical		Chemical		Maximum monolayer	
Biomass-derived activated carbon	Target pollutants	Temperature (K)	Activating agent	Temperature (K)	Chemicals used	adsorption capacity "q _m " (mg/g)	References
Dyes	-		,			ò	
Pomegranate peel	Direct blue 106	I	I	773	ZnCl ₂ , H ₃ PO ₄ ,	54.05	Amin (Amin 2009)
Orange peel	Direct navy blue 106	1	1	393	H_2SO_4	107.53	Khaled et al. (Khaled et al. 2009)
Pineapple waste	Methylene blue	1	1	773	ZnCl ₂	288.34	Mahamad et al. (2015)
Rice husk	Acid yellow 36	373	steam	1	1	86.9	Malik (2003)
Sugarcane bagasse pith	Reactive orange	I	I	873	H_3PO_4	3.48	Amin (2008)
Grape processing waste	Methylene blue, Metanil yellow	I	I	873	ZnCl ₂ ZnCl ₂	417 386	Saygili et al. (2015)
Apple pulp and peel	Methylene blue	I	1	I	H_3PO_4	278	Hesas et al. (2013)
Palm flower	Amido black 10B	1	I	413	H_2SO_4	4.03	Nethaji and Sivasamy (2011)
Heavy metals							
Dairy waste Sugar beet	Pb(II) Pb(II)	873 873			1 1	248 197	Inyang et al. (2012)
Hazelnut shell	Ni(II)	1	1	423	H_2SO_4	11.64	Demirbas et al. (2002)
Canna indica	Cd(II)	I	I	873	HCI	189	Cui et al. (2016)

 Table 5.2
 Biomass-derived activated carbon for effluent treatment

Corn straw	Cu(II)	I	I	873	I	12.5	Chen et al.
	Zn(II)	I	I	873	I	11.0	(2011)
Pine bark	Pb(II)	723	I	I	1	3.0	Mohan et al.
Oak bark	Pb(II)	723	I	I	Ι	13.1	(2007)
Peanut shell	Pb(II)	I	I	823	H ₃ PO ₄ , HNO ₃	35.5	Xu and Liu (2008)
Corn stalk	Cd(II)	1	1	873	ZnCl ₂	32.4	Youssef et al. (2004)
Phenols			-				
Bamboo charcoal	Phenol	473	I	I	1	24.96	Ma et al. (2013)
Banyan root	Phenol	I	I	773	КОН	26.95	Nirmala et al. (2019)
Date-pit	Phenol	1173	CO ₂	I	1	262.3	El-Naas et al. (2010)
Rattan saw dust	Phenol			973	КОН	149.25	Hameed and Rahman (2008)
Dates' stones	Para- chlorophenol	1	I	773	ZnCl ₂	102.04	Aldoury and Sabeeh (2014)
Corn husk	Phenol Para-nitrophenol	1 1	1 1	773 773	FeCl ₃ FeCl ₃	8.445 11.668	Mishra et al. (2019)
Pharmaceutical wastes							
Pine sawdust	Sulfamethoxazole	I	I	923	FeCl ₂ , KOH, KNO ₃	.19.09	Reguyal and Sarmah (2018)
Tea waste	Sulfamethazine	973	Steam	I	I	10	Rajapaksha et al. (2016)
Giant reed	Amoxicillin	973	Microwave	I	I		Chayid and Ahmecd (2015)
							(continued)

		Activation of a	dsorbents				
		Physical		Chemical		Maximum monolayer	
Biomass-derived activated	Taraat nollutante	Temperature	Activating	Temperature	Chemicals	adsorption capacity "q _m "	Dafarancas
CalUUII	1 ai get pullutalits		aguit	(VI)	noen	(mg/g)	NCICICINCS
Cassava waste	Oxytetracycline	I	I	773	КОН	3.33	Luo et al. (2018)
Olive stones	Paracetamol	1	1	773	H_3PO_4	108.3	Garcia-Mateos et al. (2015)
Moringa seed	Diclofenac	1	I	723	H_3PO_4	121.112	Bagheri et al. (2020)
Cauliflower roots	Chlortetracycline	773	I	I	I	81.30	Qin et al. (2017)
Wheat straw	Ketoprofen	1	I	973	HCI	72.46	Wu et al. (2018)
Endocrine disruptors							
Agave Americana leaf fibers in combination with tannin	Tetracycline	1173	I	I	I	87.21	Selmi et al. (2018)
Argun nut shells	Diuron	573	I	I	I	833.33	Zbair et al. (2020)
Argun nut shells	Bisphenol A	573	I	I	I	1162.79	Zbair et al. (2020)
Pistachio nut shells	Caffeine	I	I	493	HNO ₃	22.6	Roman et al. (2018)
Montmorillonite/rice husk hydrochar	17α-ethynyl estradiol	I	I	452	Methanol	138	Tian et al. (2018)
Sawdust hydrochar	Tetracycline	I	I	1073	КОН	423.7	Chen et al. (2017)

Table 5.2 (continued)

Potato peel hydrochar	Pramipexole Dorzolamide	1 1	1 1	473 473	КОН КОН	60 60	Kyzas and Deliyanni (2015)
Rice straw hydrochar	Tetracycline	1	1	573	K ₂ CO ₃	714	Liu et al. (2014)



Fig. 5.4 Biomass-based composites for effluent treatment

very promising in the environmental remediation process. Since the magnetic particles are superparamagnetic (they are magnetized only with the external magnetic field), they can be recovered easily by the external magnetic field and reused without any loss of the functional materials (Nethaji et al. 2013). Hence, magnetic materials like iron oxide nanoparticles are extensively studied as functional materials for their application in water treatment owing to their magnetic properties. However, these iron oxide nanoparticles tend to agglomerate in the solution, thereby decreasing their efficiency. Hence, biomass-based materials supported by iron oxide nanocomposites were studied and successfully applied to overcome these drawbacks (Mehta et al. 2015). Biomass-based magnetic composites are mainly used in the adsorption process, and there are few studies which deals on the application of these materials in photocatalytic oxidation (Pang et al. 2016). Though several methods like hydrothermal reactions, sol-gel methods were reported, the co-precipitation method is most commonly employed for the preparation of magnetic composites. In the co-precipitation method, the biomass, or biomass-derived materials like activated carbon (AC) are dispersed along with the iron precursors like ferric chloride or ferrous sulfate. The iron salt in the precursors is then reduced using various reducing agents under continuous stirring, thus depositing the iron oxide nanoparticles onto the matrix of the raw biomass or AC derived from the biomass (Nethaji et al. 2013). The efficiency of these magnetic composites expended for the adsorptive/oxidative treatment of various pollutants from the aqueous phase along with the experimental conditions are shown in Table 5.3. The application of magnetized adsorbents derived from raw biomass and AC is presented in Fig. 5.5. Most of the studies reported an enhanced removal efficiency of the magnetic nanocomposites in comparison with the unmagnetized materials. Few adsorption studies reported a slight decrease in the efficiency, owing to the reduction in the available surface area due to the impregnation of iron oxide particles into the matrix of the biomass. Nevertheless, the ease of separation of the functional material improved considerably, thereby aiding in the regeneration and reusability of the nanocomposite materials.

	D					
				Maximum		
	Precursor			monolayer		
Biomass-based	biomass	Target	Surface area	adsorption capacity		
magnetic adsorbents	materials	pollutants	(m ² /g)	ʻ(g/gu) , (mg/g),	Inferences	References
Dyes						
Magnetic Corn	Corn cob	Methylene	153.89 (MCA)	163.93 (MCA)	The efficiency of the magnetized and	Ma et al.
cob-derived carbon		Blue	69.45	103.09	unmagnetized adsorbent derived	(Ma et al. 2015)
(MCA)			(unmagnetized	(unmagnetized	from corn cob was compared. The	
			carbon)	carbon)	magnetized carbon possessed better	
					surface area and adsorption efficiency	
					for the sorption of methylene blue	
					dye.	
Magnetic graphene	Palm Ker-	Acid Blue 113	280.39	32.2	The adsorbent had the saturation	Ying et al.
oxide-biomass activated	nel Shell				magnetization value of 33.74 emu/g	(2020)
carbon composite	(PKS)				as characterized by a Vibrating Sam-	
					ple Magnetometer. A comparison	
					study was also carried out to prove	
					that the magnetized graphene oxide-	
					PKS-derived carbon composites had	
					better removal efficiency than the raw	
					precursor and graphene oxide.	
Magnetic activated car-	Peanut	Malachite	722.34 (CO ₂	747.03 (CO ₂ activa-	Studies were performed by increasing	Guo et al.
bon from peanut shell	shell	Green	activation)	tion)	the iron oxide content in the matrix of	(2018)
			448.70 (With-	270.28 (Without	the carbon derived from the peanut	
			out CO ₂	CO ₂ activation)	shell. The surface area, porosity, and	
			activation)		adsorption efficiency increased with	
					the increase in the iron oxide	
					impregnation proving that the degree	
					of magnetization is one of the most	
					important parameters.	
						(continued)

Table 5.3 Biomass-based magnetic composites for effluent treatment

Table 5.3 (continued)						
	Precursor			Maximum monolayer		
Biomass-based magnetic adsorbents	biomass materials	Target pollutants	Surface area (m ² /g)	adsorption capacity "q _m " (mg/g)	Inferences	References
Heavy metals						
Magnetic biochar com- posites (MB)	Phoenix tree leaves	Chromium (VI)	83.6	55 (Magnetized Biochar)	Magnetized biochar was prepared by hvdrothermal method. The O ₂	Liang et al. (Liang et al.
				39.8 (Unmagnetized	containing groups on the surface of	2019)
				Biochar)	the biochar provided growth sites for	
				26.5 (Fe ₃ O ₄	Fe ₃ O ₄ nanoparticles.	
				nanoparticles		
Magnetic nanoparticle (Fe ₂ O ₄) impregnated	Tea waste	Nickel (II)	22.3 (tea waste)	38.3	This study does not involve the menaration of activated carbon from	Panneerselvam
onto tea waste			77 5 (mame-		tea waste Tea waste is directly	
OIIIO IEA WASIE			<i>zi</i>) (Illague- tized tea waste)		tea waster. Tea waste is unceup incorporated with Fe ₃ O ₄	
					nanoparticles. The incorporation of	
					iron oxide nanoparticles had a negli-	
					gible impact on the surface area.	
EDTAD-modified mag-	Baker's	Lead (II)/cad-	I	89.21 (Pb ²⁺)	EMB could be regenerated using both	Zhang et al.
netic baker's yeast bio-	yeast	mium (II)		41 (Cd ²⁺)	HCl and EDTA with an efficiency of	(2011a, 2011b)
mass (EMB)					greater than 90% without disturbing	
					the morphological characteristics.	
Emerging contaminants						
Fe ₃ O ₄ /Douglas fir	Douglas	Caffeine (stim-	468.2 (Douglas	Caffeine:	It was observed that the	Liyanage et al.
biochar	fir	ulant)	fir biochar)	23.9 (Douglas fir	unmagnetized adsorbent exhibited	(2020)
		Ibuprofen	322.0 (Fe ₃ O ₄ /	biochar)	better surface area when compared to	
		(Inflammatory	Douglas fir	73.1 (Fe ₃ O ₄ /Douglas	the magnetized Douglas fir biochar.	
		drug)	biochar)	fir biochar)	However, the adsorption of all the	
		Acetylsalicylic		Ibuprofen:	three pharmaceuticals were better	
				15.5 (Douglas fir		

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using the magnetized adsorbent	compared to the unmagnetized char.						
biochar)	32 (Fe ₃ O ₄ /Douglas	fir biochar)	Acetylsalicylic acid:	89 (Douglas fir	biochar)	126 (Fe ₃ O ₄ /Douglas	fir biochar)
acid (Inflam-	matory drug)						



Fig. 5.5 Biomass-derived magnetic composites for effluent treatment

5.8.2 Biomass-Based Polymer and Clay Composites for Effluent Treatment

The efficiency of a functional material in the effluent treatment mainly depends upon its available surface area and surface functionality for adsorptive removal, and oxidative potential in case of advanced oxidation processes. Hence, polymeric materials are potential candidates to be used in the adsorption process, owing to their tunable surface properties (Pan et al. 2009). Naturally occurring biopolymers such as starch, cellulose, chitosan, and alginate were widely explored for their adsorption potential due to their high surface area and variable surface functionality. Among all the above-mentioned biopolymers, chitosan is widely explored for the removal of contaminants from simulated wastewater. It is more preferred since it contains -NH₂ and -OH functional groups on its surface which can act as chelating sites for concentrating organic and inorganic moieties (Wang and Zuang 2018). However, most of these naturally occurring biopolymers exhibit weak thermal and mechanical properties. Moreover, these biopolymers exhibit swelling phenomena when exposed to the aqueous environment. Hence, most of the studies deal with crosslinking these biopolymers with mechanically strong materials like biochar, biomass-derived AC, or clay composites. Natural clay materials like bentonite, montmorillonite, kaolinite, zeolite, etc. are mostly aluminosilicates with the presence of sodium, potassium, magnesium, and calcium. The layered morphology of these clay materials with the charged surface is ideal for the adsorption of ionic contaminants from the effluent. However, these clay minerals have poor potential for the removal of non-ionic contaminants. Nevertheless, they possess strong mechanical and thermal stability. Hence, the biopolymers are generally cross-linked with clay minerals to overcome the shortcomings of both clay and biopolymers (Unuabonah and Taubert 2014). Hence, biopolymers supported with biochar, AC, and clay minerals exhibited superior adsorption efficiency with better thermal and mechanical stability as shown in Table 5.4.

	ased polymer and elay	IN THIS STREET	month arcantive			
Biomass-based		Target		Maximum monolayer adsorption capacity		
adsorbent	Biomass precursors	pollutants	Surface area (m ² /g)	"q _m " (mg/g)	Inference	References
Biopolymer composi	ites					
Zeolite derived	Chitin	Crystal violet,	I	124 (Crystal violet),	The zeolite was synthesized	Briao et al.
from chitin		methylene		87.45 (methylene	using biopolymer chitin as a	(Briao et al.
		blue, basic		blue), 789.10 (basic	mesoporosity agent by the	2018)
		fuchsin		fuchsin)	hydrothermal method	
Bacteria-derived	B. subtilis var.	Auramine O,	I	0.05 dm ³ /mg	The kinetic data were well in	Inbaraj
$poly(\gamma-glutamic$	(natto)	rhodamine B,		(auramine O),	agreement with Boyd's	et al.
acid) (γ -PGA)		safranin O		0.02 dm ³ /mg (rhoda-	ion-exchange model	(2006)
				mine B), $0.19 \text{ dm}^3/$		
				mg (safranin O)		
Chitosan/activated	Chitosan from	Cadmium	834 (activated car-	322.58	The study indicated better	Sharififard
carbon/iron	shrimp shell, acti-		bon)		interactions between oxygen	et al.
bio-nanocomposite	vated carbon from		11.6 (chitosan)		functional groups of AC, iron	(2018)
	grape stalks		419.20 (chitosan/		ions, and amine groups of	
			activated carbon/		chitosan	
			iron			
			bio-nanocomposite)			
Zerovalent iron	Chitosan	Arsenic	69 (CIN)	I	The study shows that the	Gupta et al.
encapsulated		(V) and (III)	26 (zerovalent iron)		adsorbent is porous in nature	(2012)
chitosan					and iron particles exist in	
nanospheres (CIN)					zerovalent state and there exists	
					a complexation reaction among	
					iron, chitosan, and arsenic	
Biopolymer clay con	nposites					
Cellulose-montmo-	Cellulose	Chromium	87.09	22.2	The interaction between cellu-	Kumar
rillonite composite		(VI)			lose and montmorillonite has	et al.
					рютен піс роклинаї аррисацон	(1107)
						(continued)

lable 5.4 (continued	(1					
Biomass-based		Target		Maximum monolayer adsorption capacity		
adsorbent	Biomass precursors	pollutants	Surface area (m ² /g)	(g/gm)'mg',	Inference	References
					of the material for the effective adsorption of chromium. The XRD peaks signified the ordered distribution of clay	
					layers in the biopolymer composite	
Montmorillonite-	Alginate	Paraquat	46	0.321 mmol/g	TGA was used to determine the	Etcheverry
alginate beads		herbicides			thermal stability of the beads. The results proved that the	et al. (2017)
					thermal stability of	
					montmorillonite-alginate beads	
					was much better than alginate	
					beads	
Guar gum /benton-	Guar gum	Lead (II),	5.533	187.08 (Pb ²⁺)	The TGA results proved	Ahmad and
ite		crystal violet		167.92 (CV)	increased thermal stability of	Mirza
bio-nanocomposites		(CV) dye			biocomposites in comparison	(2018)
					with guar gum. FT-IR	
					suggested the electrostatic	
					interaction or chelation via	
					hydrogen bond formation	
					between Pb ²⁺ or CV and active	
					sites of bio-nanocomposites.	
	_				-	

Table 5.4 (continued)

5.8.3 Biomass-Based Graphene Composites for Effluent Treatment

Graphene is composed of single layers of carbon atoms densely packed which attracted tremendous attraction in late 2004. It is a "single layer of carbon atom densely packed in a honeycomb crystal lattice" (Li et al. 2019). Because of its good chemical stability and graphitized basal plane structure, graphene-based materials are widely used in different applications including supercapacitors, fuel cells, batteries, and as adsorbents in effluent treatment systems (Novoselov et al. 2012). Graphene or reduced graphene oxide is mostly synthesized by using Hummers or modified Hummers method. Various functional groups present on the edges of the graphitic planes aid in the interaction of the graphene sheets with the charged contaminants present in the wastewater. However, the graphene sheets generally suffer from stacking and agglomeration problems due to $\pi - \pi$ interactions and van der Waals forces in the aqueous phase. Hence, to overcome these limitations and to exploit the desirable properties of the graphene-based materials, various biomassbased graphene composite materials were reported for the removal of organic and inorganic compounds from simulated effluents (Nethaji and Sivasamy 2017). Biomass-derived materials like biochar, AC, and other cellulosic waste biomass were used as composite materials by crosslinking with the honeycomb structure of graphene oxides. There are also studies which had reported on the utilization of iron oxide nanomaterials for acquiring the magnetic properties reducing the stacking problem of graphene layers. The application of these biomass-based graphene composite materials for the removal of organic and inorganic moieties is presented in Table 5.5.

5.8.4 Biomass-Based Metal Oxides Composites such as Catalyst and Catalyst Supports

Heterogeneous catalysis involving metal oxides is a good example of an advanced oxidation process. Literature shows a number of methods for the enhancement of catalyst activity alongside cost reduction and efficiency maximization. Though many paths are sorted for catalyst modification, synthesis of a catalyst supported on materials with a higher surface area without diminishing the activity is a greater concern. Hence, the choice of the support material comes into the picture, wherein it must be cheap, green, and environmentally friendly with enhanced activity. Hence, carbon as catalyst support derived from biomass is a better option. Wherein, the disposal problem of the biomass itself is minimized and the resulting carbon could be used efficiently. However, activated carbon in itself has been used as a catalyst. Juhola et al. (2021) had prepared biomass–metakaolin as granular composite materials for application as a catalyst for the treatment of effluents.

		References	Liou and Wang (2020)	(2021) (2021)	Saeidi et al. (2015)	Han et al. (2021)
		Inference	Graphene oxide/ordered mesoporous car- bon was prepared from rice husk using mesoporous silica as a template source	Silica was extracted from rice husk. The hybrid material was prepared by hydro- thermal method. The study also claims that the composites not only aid in recycling agricultural waste but also help in the recovery of graphene oxide from the aqueous phase	Mesoporous graphene/activated carbon composite was prepared from graphene oxide and glucose. The prepared compos- ite had a higher adsorption capacity for Pb^{2+} when compared to the reported literature	Nitrogen-containing carbon materials with different morphologies were prepared using Fe(NO ₃) ₃ through a hydrothermal method. The prepared material was used for both adsorption and photocatalytic oxidation of phenol. The photoelectrons transformed by graphite claim to be reacted with O ₂ molecules to form the superoxide radicals (O_2) for the degradation of phenol
Maximum monolayer	adsorption capacity	(g/gm, (mg/g),	1591	147.06	217.6	1
Surface	area	(m^2/g)	936	625	2012	35.40
	Target	pollutants	Methylene blue	Rhodamine B	Lead (II)	Phenol
_	Biomass	precursors	Rice husk	Rice husk	Glucose	Lentinus edodes
	Biomass-based graphene	composites	Graphene oxide-based carbona- ceous nanocomposites	Graphene oxide/silica nanocomposites	Graphene/activated carbon composite	Nitrogen-containing carbon nano-onions-like and graphene- like materials

Table 5.5 Biomass-based graphene composites for effluent treatment

Since the development of nano metal oxides as a photocatalyst under visible light irradiation for environmental remediation (Fujishima and Honda 1972). Various research has been focused on the modification of metal oxides for maximum efficiency. The preparation of metal oxide on catalyst support is highly researched. While a choice for support material activated carbon prepared from biomass is widely preferred. Devagi and Soon (2018) have reported a TiO₂/modified sago bark (biomass) for treating the sago wastewater effluent. The author chose the effluent as it had a higher chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TDS), and was acidic. The sago bark was chosen as a precursor as it is a major waste during the debarking step of the starch extraction. The modified biomass TiO₂ mixture was used as a photocatalyst for 64.92% removal with 0.2 g/L TiO₂/1% MSB (120 min of irradiation). Poudel et al. (2020) has removed As(III) from water by using agro-waste-based biomass impregnated with TiO₂.

ZnO incorporation on biomass-derived activated carbon has been widely researched by various research groups. Cruz et al. (2018) had prepared a ZnO/activated carbon (biomass derives) nanocomposite for the treatment of methylene blue dye. The ZnO nanoparticles were evenly distributed on the surface of the activated carbon. Ramya et al. (2018) has worked on the preparation of activated carbon from tannery sludge biomass. The acquired biomass was used as support material for ZnO-based nanocomposite preparation. The material was used for Cr (VI) removal from the aqueous phase. Supported biomass-based activated carbon for dye degradation has been prepared by hydrothermal technique. Waste biomass was used by Vinayagam et al. (2018) for activated carbon preparation as carbon support. Akpomie et al. (2020) recently prepared a ZnO nanoparticle along with biomass for the treatment of celestine blue dye.

Hybrid bifunctional materials have also been synthesized by various research groups comprising AC and nanomaterials which would serve both as an adsorbent and photocatalytic material. Our group has also worked in this area (Nethaji et al. 2018) and we have reported a bismuth oxybromide (BiOBr)/activated carbon hybrid material as a bifunctional nanomaterial for effluent treatment. It was a good adsorbent material and it even degraded malachite green dye under visible light irradiation. The source of AC was waste polyurethane foam trash from used car seats. The composition of the foam was a polyol with a toluene diisocyanate blend. A simple hydrothermal process was used for the preparation of the bifunctional material.

5.9 Conclusions

Biomass materials are mostly explored for their potential to be used as biofuel. However, the consumption of this biomass for the production of biofuel accounts for less than 10% of the available lignocellulosic materials. Owing to its abundant availability, most of the agricultural waste biomass is considered waste and requires a separate disposal method or a process for the same. But the utilization of these types of wastes and naturally available renewable material as a source for the production of materials for the effluent treatment itself is a boon to the environment. Most of the studies suggest that these biomasses either in their raw form or modified form proved to be an effective replacement for the synthetic materials conventionally used in effluent treatment operations. Moreover, the hybrid materials which include biomass-based composites could effectively overcome the shortcomings of their synthetic counterparts. The biomass-derived activated carbon was effectively used in various adsorptive and catalytic applications as adsorbent and catalyst support, respectively. The compatible and environmentally friendly nature of the biomasses could be explored for applications in various other unit operations in effluent treatment plants. Hence, these materials derived from the biomasses can be coined as "waste to wealth" and thus prove to be environment-friendly substitutes to treat and overcome effluent treatment problems.

Competing Interests All the authors declare that they have no competing interests.

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