Chapter 11
Agricultural Residue-Derived Sustainable Nanoadsorbents for Wastewater Treatment

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Abstract Water resources are getting contaminated globally in a very fast manner due to natural and anthropogenic practices. If this happens with such a pace, it will lead to freshwater scarcity. Therefore, economically feasible, easy to use and technically simple technologies for water treatment must be developed proactively. Adsorption technique, among the other water treatment technologies, might be favorable for the said purpose in terms of techno-economic aspects (cheap, universal, and eco-friendly). However, conventional adsorbents like clay, silica gel, activated carbon, limestone, and activated alumina have certain inherent issues which

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make their real-world application limited. Therefore, emerging nanoadsorbents may be employed as a replacement of conventional adsorbents in wastewater treatment. Nanoadsorbents have high surface area, porosity, and tunable characteristics. The challenges with the application of nanoadsorbents for wastewater treatment include identification of low-cost and sustainable adsorbent precursor materials. The agricultural residue-derived nanoadsorbents have a potential to deal with the above challenges. A variety of agricultural residue-derived adsorbents such as nanosilica, nanocellulose, nanobiochar and their composites have been developed and used for wastewater treatment. This chapter gives an overview of the available wastewater treatment technologies and covers the development and application of agricultural residue-derived nanoadsorbents for wastewater treatment including the concepts like operating mechanism, regeneration and selection of adsorbents. Chapter ends with the conclusions and potential recommendations.

Keywords Wastewater treatment · Agricultural residue · Adsorbents · Nanotechnology · Nanobiochar · Emerging pollutants

11.1 Introduction

Industrialization and rapid population growth have polluted water resources globally and caused a challenge of freshwater availability. This is particularly important when the demand of freshwater doubles every two decades. Approximately 40% of the global population (from 80 countries) is facing water deficiency. About 500 billion m^3 fresh water is used by industries every year (Ali et al. 2021). Industries such as fertilizer, paper and pulp, steel, sugar, textile, thermal power plant, etc. contribute majorly towards water pollution. Water resources are being polluted due to unwanted entry of various pollutants.

Pollutants may basically be classified as conventional and/or emerging pollutants. Conventional pollutants include fluoride, nitrate, and trace metals while emerging pollutants comprise but not limited to steroid, hormones, pharmaceuticals and personal care products, artificial sweeteners, surfactants (Ahamad et al. 2020), antibiotics, sunscreens (Caliman and Gavrilescu 2009), naturally occurring algal toxins, steroids, endocrine disruptors and their degradation intermediates (Preda et al. 2012), gasoline additives, fire retardants, plasticizers, and microplastics (Browne et al. 2015). Emerging pollutants are present in trace amount (ng/L–μg/L), but their long persistence in the environment significantly affects water quality, health of human and animals and ecosystem. Further, pollutants may be classified as inorganic, organic and biological in nature. A constant flux of heavy metals and other inorganics originated from industrial and municipal wastewater, mine drainage is contaminating surface waters and sediments (Hoque and Philip 2011). Organic pollutants include fertilizers, plasticizers, polybrominated biphenyls, phenols, detergents, greases, formaldehydes, oils, hydrocarbons, pharmaceuticals, and pesticides (fungicides, herbicides, insecticides) (Ali et al. 2012). Major sources of organic pollutants are chemical and agricultural industries. Bacteria, viruses, fungi, algae, and amoeba are the examples of biological pollutants which affect human health and may cause nausea, rheumatoid arthritis, kidney damage, chronic diseases, circulatory system, and nervous disorders (Ali 2012).

Monitoring of emerging pollutants is difficult due to their low concentration but advanced separation techniques (liquid-liquid extraction, polymer grafted matrix, magnetic nanoparticles based solid phase extraction) (Moliner-Martínez et al. 2011) and analytical techniques (GS-MS, LC-MS, LC-MS-MS) (Hernández et al. 2007), capillary electrophoresis (Moliner-Martínez et al. 2011) are capable of detecting emerging pollutants even at trace level. Efficient, selective and cost-effective wastewater treatment techniques are necessary to develop in the above scenario. Available wastewater treatment methods are filtration (Barakat 2011), precipitation (Fu and Wang 2011), ion exchange (Kurniawan et al. 2006; Peng and Guo 2020), advanced oxidation processes (García-Montaño et al. 2006; Dhaka et al. 2017), biological treatment (Aksu 2005), reverse osmosis, distillation, electrochemical dialysis (Gunatilake 2015), and adsorption (Kwon et al. 2016; Patel et al. 2019, 2021; Kumar et al. 2020). The process of wastewater treatment is becoming expensive regularly as the prescribed standards for discharge are getting more and more stringent.

Adsorption is one of the prominent wastewater treatment techniques due to low operational and maintenance cost and ease of operation (Gupta et al. 2012; Singh et al. 2018). The efficiency of adsorbents depends upon its specific surface area, pore volume, and available binding sites (Hassan and Carr 2021). A number of conventional adsorbents, namely activated carbon, silica gel, clays, limestone, chitosan, and zeolites are used for wastewater treatment (Krstić et al. 2018). Different pollutants like dyes (Muhd Julkapli et al. 2014), heavy metals, metalloids, pesticides, and pharmaceuticals (Patel et al. 2019) have been removed using adsorption process (Dawood and Sen 2014; Singh et al. 2018; Rathi and Kumar 2021).

Conventional adsorbents have issues like their high cost, low removal efficiency, fast exhaustion, and poor regeneration capacity. The performance of adsorbent may be improved via surface modification, composite preparation among the several other routes. The complex and multistep processes for modifications are either expensive or less feasible for large-scale production (Bhatnagar et al. 2013). To overcome these limitations, nanoadsorbents can be used for wastewater treatment (El-Sayed 2020). Nanoadsorbents have relatively high chemical reactivity, conductivity, large surface area, and specificity making them a preferred choice over the conventional adsorbents (El-Sayed 2020). Nanoadsorbents may be prepared through sol-gel, sono-chemical, mechanical, microwave, and chemical process (Rangari et al. 2017; Biswas et al. 2019). The use of nanoadsorbents for wastewater treatment is a win-win strategy as they can be developed using agricultural residue. Further, agricultural residue burning is a serious problem in certain areas of India; it causes loss to soil health, unbearable air pollution and the health affects. Therefore, converting this agri-waste into nano-adsorbents is a "double-edged sword" with benefits of solid waste management and wastewater treatment.

This chapter gives an overview of various wastewater treatment techniques and emphasizes over sorptive removal of pollutants from wastewater using agriculture residue-based nanoadsorbents. Efficiency of nanoadsorbents over conventional adsorbents has been discussed. Silica, cellulose, lignin, and biochar-based nanoadsorbents are being included in the discussion.

11.2 Available Wastewater Treatment Techniques

Wastewater treatment includes primary, secondary, and tertiary stages (Fig. 11.1). Primary stage includes physical processes such as screening, grit removal, and sedimentation. Secondary stage comprises biological treatment, namely aerobic, anaerobic digestion, activated sludge treatment, trickling filtration among the other process. The tertiary stage mostly includes chemical treatment of wastewater. This stage is the most important as, at this stage, toxic and harmful pollutants are converted into less toxic forms or eliminated to meet the accepted standards. These wastewater treatment stages should be collectively used to achieve better results (Gupta et al. 2012). A brief overview of the wastewater treatment techniques has been provided in the following paragraph and summarized in Table 11.1.

The screening includes filtration (i.e., removal of coarse solids) via slow sand filtration (Verma et al. 2017) is a primary wastewater treatment technique which eliminates commonly present conventional suspended pollutants from wastewater (Barakat 2011). Biological filtration (Aziz and Ali 2016), a secondary stage process, is the bacteria-derived degradation of ammonia to nitrites and eventually to less toxic nitrates. Membrane filtration techniques such as microfiltration, nanofiltration, ultrafiltration and reverse osmosis, fall under tertiary stage of wastewater treatment, are used to remove pollutants according to their particle size (Zazouli and Kalankesh 2017). Microfiltration and ultrafiltration using ceramic membranes have been reported to remove chemical oxygen demand (COD) (>87%), color (>96%),

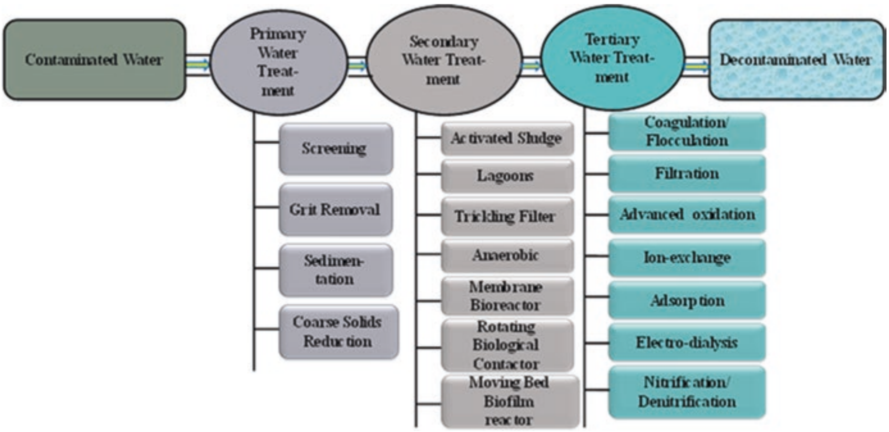

Fig. 11.1 Wastewater treatment stages

Table 11.1 A comparative evaluation of wastewater treatment processes

S. No.	Treatment processes	Advantages	Disadvantages	Cost (US$ per million L)	References
1.	Adsorption	Low operation and maintenance cost, simple design, easy to operate, efficient regeneration of adsorbents, broad spectrum of pollutants are removed	Chemical modification of adsorbent is required to increase adsorption capacity	10–200	Ali and Gupta (2006), Singh et al. (2018), Patel et al. (2019)
			Loaded adsorbent may be considered as hazardous material		
2.	Advanced oxidation processes	Efficient, quick to degrade organic pollutants	Undesirable toxic compounds may be produced	100–2000	Gupta et al. (2012), Crini and Lichtfouse (2019)
			High operational and maintenance cost		
3.	Biological treatment	Reduce BOD, COD, and removes organic and inorganic pollutants, potential energy resource	Slow process	20–200	Gupta et al. (2012), Ali et al. (2020)
			Provides environment to grow microorganisms		
			Limited operation flexibility		
			Requires larger space		
4.	Chemical precipitation	Non-selective, easy to operate	High sludge generation	20–500	Kurniawan et al. (2006), Gupta et al. (2012)
			High maintenance cost		
5.	Coagulation-flocculation	Sludge settling capability, dewatering capability, bacterial inactivation ability	Large amount of chemicals required	25–500	Leiknes (2009), Gupta et al. (2012)
			Large sludge generation		
6.	Electrodialysis	Selectivity towards pollutant removal	High energy consumption	15–400	Gupta et al. (2012), Ali et al. (2020)
			Membrane fouling		
			High operational and maintenance cost		

(continued)

Table 11.1 (continued)

S. No.	Treatment processes	Advantages	Disadvantages	Cost (US$ per million L)	References
7.	Ion exchange	High regeneration, highly selective for pollutants removal, no sorbent loss	Not effective for non-ionic pollutants (disperse dyes)	50–200	Gupta et al. (2012), Crini and Lichtfouse (2019)
8.	Membrane filtration	High removal efficiency, additives free, less chemical consumption, small space required	Limited flow rate Membrane clogging High capital cost High maintenance cost	15–400	Qin et al. (2002), Gupta et al. (2012)

total suspended solids (TSS) (~100%), and turbidity from anaerobically treated dairy wastewater (Zielińska and Galik 2017).

In case of chemical precipitation, precipitant reacts with dissolved metal ions in wastewater and converts into insoluble sludge followed by its removal via sedimentation or filtration (Zamboulis et al. 2004; Fu and Wang 2011). Precipitant like lime, limestone, alum, sodium hydrogen carbonate, and ferric chloride are used for wastewater treatment (Gupta et al. 2012). The precipitant (for example, limestone) has been reported to remove more than 90% of Cd^{2+} and Cu^{2+} from water (*p*H 8.5) (Aziz et al. 2008).

$$M^{n+}(aq) + nOH^{-}(aq) \leftrightarrow M(OH)_n \downarrow$$

Ion exchange process uses an ion exchange membrane which potentially eliminates colloidal and soluble ionic contaminants from wastewater (Kurniawan et al. 2006). The anion exchange membrane retains the anions and rejects cations. However, the cation exchange membrane retains cations and rejects anions (Barakat 2011). A combined anion and cation exchange membrane efficiently removes dissolved organic carbon (76%) and total hardness (97%) using NaCl regeneration solution (20%) (Comstock and Boyer 2014).

In case of biological methods of wastewater treatment, microbes are used to decompose organic pollutants especially emerging pollutants from water into simpler non-toxic compounds under controlled temperature and physicochemical conditions (Aksu 2005). Microbial action in the absence of oxygen to degrade organic matter from wastewater is known as anaerobic biological wastewater treatment (Eq. 11.1) (Mohan et al. 2007). Aerobic microbes (bacteria and fungi) decompose organic contaminants in wastewater in the presence of oxygen (Eq. 11.2). Aerobic digestion of enzyme pre-treated biosolids has been reported to remove emerging pollutants from wastewater collected from local municipal wastewater treatment plant (up to 90%) (Vaithyanathan et al. 2021). Cassava starch wastewater was treated using an up-flow multistage anaerobic reactor and 87.9% COD was removed within 6 h of hydraulic retention time (Sun et al. 2012).

$$\text{Organic matter} + \text{Anaerobic bacteria} \rightarrow CO_2 + H_2O + \text{Co-products} + \text{Anaerobic bacteria} \quad (11.1)$$

$$\text{Organic matter} + O_2 + \text{Aerobic bacteria}\ CO_2 + H_2O + \text{Co-products} + \text{Aerobic bacteria} \quad (11.2)$$

The wastewater treatment using oxidation process involves decomposition of organic contaminants into simpler compounds like aldehydes, carboxylates, and sulfates (Garcia-Segura et al. 2013). Numerous oxidants like chlorine (Cl_2), hydrogen peroxide (H_2O_2), Fenton catalyst (H_2O_2 + Fe(II)), Fenton like catalyst and ozone (O_3) may be used as oxidants in wastewater treatment (Saputra et al. 2011). However, when single oxidation technique is not sufficient for complete decomposition of organic pollutants, two or more oxidation techniques might be used simultaneously to generate reactive radical species such as hydroxyl free radical and sulfate radical anion which degrade organic pollutants in wastewater. This technique is known as advanced oxidation process (AOP) for wastewater treatment (García-Montaño et al. 2006). Nanoscale zerovalent iron (nZVI) impregnated biochar (BC) composite (a Fenton like heterogeneous catalyst) was prepared. The nanobiochar (nZVI to BC (1:5)) successfully degraded trichloroethylene via Fe(II)/Fe(III) redox and electron-transfer reaction pathways in aqueous solutions (Yan et al. 2015a). Advanced oxidation processes such as photo-Fenton oxidation process (Moncayo-Lasso et al. 2009), ultraviolet (UV) assisted sono-Fenton (Kakavandi et al. 2019), and ultrasonic irradiation assisted Fenton or Fenton like processes (Mahamuni and Adewuyi 2010) have been reported frequently in the literature.

Wastewater treatment using electrodialysis technique removes ionic pollutants as high voltage across ion exchange membrane is applied. When polluted water passes through the electrodialysis cell, anionic pollutants migrate toward the anode and the cationic one toward the cathode (Gunatilake 2015). The cation exchange membrane made up of poly vinyl chloride and 2-acrylamido-2-methylpropane sulfonic acid based hydrogel was prepared. The membrane had a low electrical resistance and showed high removal efficiency for K^+ (99.9%), Pb^{2+} (99.9%), and Ni^{2+} (96.9%) (Nemati et al. 2017).

11.3 Wastewater Treatment Through Adsorption Method

Adsorption is an efficient and cost-effective wastewater treatment method which involves retention of pollutants onto adsorbent's surface through forces such as electrostatic attraction, hydrophobic interaction, π–π interactions, hydrogen bonding, precipitation, ion exchange, and surface complexation (Tan et al. 2015; Kumar et al. 2018; Patel et al. 2019). Adsorption can potentially be used to remove conventional as well as emerging pollutants from wastewater (Ali 2012; Patel et al. 2019). Adsorption process can remove inorganic and organic pollutants efficiently even up to 99% from water (Ali et al. 2012). Working efficiency of adsorption process depends upon concentration and type of pollutant, nature and particle size of adsorbent, structure, properties, and morphology of adsorbent like pore size, specific surface area, surface functional group, working *p*H, temperature, adsorbent dose, and contact time (Kumar et al. 2014; Patel et al. 2019). Adsorption process is preferred over the other conventional methods of wastewater treatment due to following reasons.

- Cheap adsorbents can be prepared from locally available agricultural residues and waste biomass.
- Selective adsorbents can be prepared by choosing appropriate biomass and their modification for intended application.
- Adsorption, unlike conventional wastewater treatments, generates no secondary pollutant or sludge.
- Adsorbent can be regenerated using physicochemical approaches.

11.3.1 Nanoadsorbents for Wastewater Treatment

The commonly used conventional adsorbents for wastewater treatment are clay, lime stone, activated carbon, silica gel, activated alumina, and zeolite. These adsorbents have numerous challenges associated with them (i.e., expensiveness, rapid exhaustion, surface modification, and low removal efficiency). Adsorption efficiency of conventional adsorbents, like activated carbon, decreases rapidly in wastewater treatment process. Regeneration of these adsorbents requires thermal, chemical, oxidative treatments which increase the operational cost and thus limit adsorbent's application for pollutant removal (Crini 2005; Zhou and Lei 2006). Adsorption capacity of conventional adsorbents is affected by the presence of co-pollutants in wastewater (Makeswari and Santhi 2013). Moreover, relatively low removal capacities of conventional adsorbents limit their application in wastewater treatment. This is due to the poor morphological and structural properties. Thus, it is advisable to use smart, efficient, low-cost adsorbents in wastewater treatment process.

Nanoadsorbents which are cost-effective and efficient may be used in place of conventional adsorbents. Nanoadsorbents have large specific surface area, pore size, rich surface chemistry and density of active sites (El-Sayed 2020). Nanoadsorbents have widely been used for mitigation of conventional and emerging pollutants from (waste)water (Belessi et al. 2009; Joseph et al. 2019). A variety of nanomaterials, namely metallic nanoparticles, magnetic nanoparticles, nanostructured mixed oxides, carbonaceous nanomaterials (carbon nanosheets, carbon nanotubes, carbon nanoparticles), silicon nanomaterials (silicon nanotubes, silicon nanoparticles, and silicon nanosheets), nanoclays, nanofibers, xerogels, aerogels, and polymer-based nanomaterials have been used as adsorbents in wastewater remediation (Khajeh et al. 2013; El-Sayed 2020). Synthesis procedure and operating conditions influence the structural (specific surface area, particle size, pore size, and pore volume), chemical (functional group, acidic/basic character, surface potential, water solubility, stability) and thermal (conductivity, stability, heat capacity, volatile content) properties of nanomaterials. Different nanoadsorbents (graphene, Fe_3O_4, alumina, magnetite, carbon nanotube, TiO_2, Al_2O_3, mesoporous carbon, $MnFe_2O_4$, and nano-zerovalent iron) have been synthesized by chemical vapor deposition, spray pyrolysis, thermal evaporation, vapor phase transport, electrodeposition, laser ablation processes, ion sputtering, coprecipitation using surfactants, chemical solution decomposition, and sol-gel method (Sharma et al. 2009; El-Sayed 2020). Sol-gel method is widely used for the synthesis of nanoparticles due to low cost, eco-friendliness, and homogenous product formation (Li et al. 2011).

Adsorption capacity of nanomaterials can be enhanced by modification such as composites formation and coating with other materials. For example, the composite of TiO_2 and carbon nanotubes has large surface area and active sites than the individuals, therefore having high removal capacity for pollutant removal (Ilisz et al. 2003; Hurt et al. 2006). Nanoparticles have been modified to increase the adsorption capability of the respective materials as the adsorption capacity is directly related to surface properties (Afkhami et al. 2010). Neat nanoparticles generally have a tendency to agglomerate in the absence of colloidal stability. So, the surface modification provides colloidal stability to nanoparticles (Crane and Scott 2012). Surface of nanomaterials can be modified through different mechanisms, namely ligand exchange, hydrothermal reduction, co-condensation, surface coating, covalent binding, grafting, and coprecipitation (Manyangadze et al. 2020). Modification of silica and iron nanoparticles has been sucessfully performed by hydrothermal method (Manyangadze et al. 2020). Nano size alumina, synthesized by chemical immobilization and modified with 2,4-dinitrophenylhydrazine was successfully removed Cr^{3+} (97.4%), Cd^{2+} (80.4%), and Pb^{2+} (97.0%) from wastewater (Afkhami et al. 2010).

11.3.2 Agricultural Residue-Derived Nanoadsorbents for Wastewater Treatment

Agricultural residue-derived nanoadsorbents may remove pollutants efficiently from (waste)water. The use of agricultural residue-derived nanoadsorbents is a win-win strategy for wastewater treatment and its management simultaneously. The use of such nanoadsorbents will not only help in wastewater remediation but also serve as a smart remedy for agricultural wastes management which is otherwise a big challenge in itself. Herein, we have presented an overview of selected studies of agricultural residue-derived nanoadsorbents used for wastewater treatment. A summary of such nanoadsorbents has been provided in Tables 11.2 and 11.3.

Table 11.2 Inorganic pollutants removal in water using agricultural residue-derived nanoadsorbents

Agricultural waste	Materials	Surface area (m^2/g)	Contaminants	*p*H	Equilibrium time (min)	Adsorption capacity (mg/g)	References
Bagasse biomass	Carbon nanotube coated biochar	359	Pb^{2+}	4.0–5.0	–	122	Inyang et al. (2015)
Corn straw	Nanocomposite (Zr@MCS)	43.9	PO_4^{3-}	<7.0	60	29.2	Hu et al. (2020)
Cotton wood	Biochar/AlOOH nanocomposite	–	As^{5+}	–	720	1.74	Zhang and Gao (2013)
Cotton wood	Biochar/AlOOH nanocomposite	–	PO_4^{3-}	–	360	135	Zhang and Gao (2013)
Pine wood	zerovalent iron/biochar nanocomposite	13.6	As^{5+}	4.0	60	124	Wang et al. (2017)
Rice hull	Magnetic biochar/ZnS nanocomposites	–	Pb^{2+}	6.0	720	368	Yan et al. (2015 b)
Rice husk	Nanoadsorbent	–	Pb^{2+}	8.0	70	3.78	Kaur et al. (2020)
Sugarcane leaves (*Saccharum Officinarum*)	Nanoadsorbent	75.4	Pb^{2+}	7.0	30	148	Kaliannan et al. (2019)
			Zn^{2+}	7.0	30	137	
Walnut shell	β-cyclodextrin/chitosan	82.0	Cr^{6+}	2.0	–	206	Huang et al. (2016)
Wheat straw	Nanocomposite Ws-N-La	78.7	PO_4^{3-}	3–7	–	30.0	Qiu et al. (2017)
Wheat straw	Graphene/biochar nanocomposite	17.3	Hg^{2+}	7.0	72 × 60	0.85	Tang et al. (2015)

Table 11.3 Organic pollutants removal in wastewater using agricultural residue-derived nanoadsorbents

Agricultural waste	Materials	Surface area (m^2/g)	Contaminants	pH	Equilibrium time (Min)	Adsorption capacity (mg/g)	References
Artichoke leaves	Sodium hydroxide coated nanobiochar	8.82	Metformin hydrochloride (MFH)	6.0–7.0	–	36.0	Mahmoud et al. (2020)
Bagasse biomass	Carbon nanotube coated biochar	359	Sulfapyridine	6.0–7.0	300	31.0	Inyang et al. (2015)
Banana peel	Cellulose/SiO_2 nanocomposite	8.92	Methylene blue	10.0	120	78.7	Ali (2018)
Corn stalks	Magnetic Fe_3O_4 nanoparticles coated biochar	–	Crystal violet	6.0	–	349	Sun et al. (2015)
Cotton wood	Biochar/AlOOH nanocomposite	–	Methylene blue	–	12 × 60	85.0	Zhang and Gao (2013)
Cotton wood	Graphene coated biochar	–	Methylene blue	–	–	174	Zhang et al. (2012)
Dendro wood	Nanobiochar	28.5	Oxytetracycline	9.0	–	113	Ramanayaka et al. (2020)
Pine wood	Nanobiochar	47.2	Carbamazepine	6.0	360	18.4	Naghdi et al. (2019)
Rice straw	Nanocomposite of SiO_2-Fe_3O_4	–	Penicillin G	8.0	180	164.7	Fakhrian and Baseri (2020)
			Amlodipine Besylate	8.0	180	229	
Sugar-beet pulp	Hydrogel nanocomposites (starch-based)	–	Crystal violet	9.0	71	2500	Moharrami and Motamedi (2020)
			Methylene blue	9.0	146	1428	
Wheat straw	Magnetic nanobiochar	296	Tetracycline	–	12 × 60	263	Li et al. (2020)
			Hg^{2+}			127	
Wood pulp	Cellulose nanofiber	–	Congo red	–	–	664	Pei et al. (2013)
			Acid green 25	–	–	683	

11.3.2.1 Silica-Based Nanoadsorbents

An amorphous silica based bionanoadsorbent (particle size: 10–50 nm, yield: 81%) was developed using rice husk via hydrothermal technique. The adsorbent successfully removed methylene blue (65% within a minute) from aqueous solution. Thermodynamic studies indicated the spontaneous and endothermic nature of adsorption process (Tolba et al. 2015). Rice husk residue-derived nanosilica (SiO_2) modified with polyelectrolyte polydiallyldimethylammonium chloride (PDADMAC) polymer was prepared by Pham and others. The modified SiO_2 with PDADMAC removed 92.3% amoxicillin antibiotic from aqueous medium. The mechanism involved was electrostatic attraction between cationic (PDADMAC polymer) and anionic surface (SiO_2). Non-electrostatic hydrophobic and lateral interactions were mainly responsible for amoxicillin (negatively charged) sorption onto modified nanosilica through induced electrostatic attractions (Pham et al. 2018).

Silica based bionanoadsorbents were prepared using barley and wheat grass with 92.4 and 93.0% of silica content, respectively. The barley and wheat grass based adsorbents successfully removed Ni^{2+} (95% and 90% removal, respectively). The mechanism involved was electrostatic interaction between negatively charged surface of bionanoadsorbent and Ni^{2+}. Pseudo-first-order and Freundlich model described the adsorption kinetics and isotherm results, respectively (Akhayere et al. 2019). Further, a green bionanoadsorbent (99.6% pure nanosilica, 20 nm size) was prepared using rice husk and modified with polydiallyldimethylammonium chloride. The adsorbent removed beta-lactam cefixime efficiently (93.5% within 90 min) from aqueous solution. The electrostatic attraction between positively charged modified nanosilica and negatively charged cefixime was the major adsorption mechanism operated in removal process (Pham et al. 2020).

A thermally stable, efficient, eco-friendly, cost-effective, recyclable Fe_2O_3-enriched nanosilica (SiO_2-Fe_2O_3) was prepared from rice straw to remove Penicillin G (95%) and Amlodipine Besylate (65%) from aqueous solution. Langmuir adsorption isotherm and pseudo-first-order kinetic model indicated multilayer adsorption of pollutants on the heterogeneous adsorbent surface. The removal efficiency of SiO_2-Fe_2O_3 was 30% greater than pure Fe_2O_3 which indicates its effectiveness as an adsorbent for antibiotics removal (Fakhrian and Baseri 2020). Another cost-effective green bioadsorbent (silica nanoparticles) was synthesized using *Saccharum ravannae*, *Saccharum officinarum*, and *Oryza sativa* leaf biomasses through chemical method. Synthesized silica nanoparticles quantitatively removed Pb^{2+} and Cu^{2+} (>95%) from wastewater (Sachan et al. 2021).

11.3.2.2 Cellulose-Based Nanoadsorbents

Cellulose nanofibrils were prepared using wood pulp treated with glycidyltrimethylammonium chloride via mechanical disintegration. The adsorbent efficiently retained congo red (0.95 mol/kg) and acid green (1.10 mol/kg) from wastewater (Pei et al. 2013). A green, recyclable cellulose-derived nanoadsorbent was prepared using sugarcane bagasse via bleaching treatment followed by acid hydrolysis. The developed adsorbent removed methylene blue efficiently (35 mg/g within 60 min) from wastewater. Langmuir and Freundlich adsorption isotherms indicated the possibility of both mono- and multilayer adsorption. The adsorbent could be used successively up to six cycles in both adsorption and desorption processes (Kardam et al. 2017). An efficient, carboxylcellulose nanofiber bioadsorbent was prepared using Australian spinifex grass via nitro-oxidation treatment. The adsorbent successfully removed Cd^{2+} (84%) from aqueous solution. At low concentrations of Cd^{2+} (<500 ppm), electrostatic interaction was prominent between the carboxylate groups of the adsorbent and Cd^{2+}, while at high Cd^{2+} concentrations (>1000 ppm) dominant operating mechanism was precipitation followed by flocculation or coagulation (Sharma et al. 2018).

Banana peel-derived Cellulose/SiO_2 nanocomposite (particle size: 20 nm) was prepared using template-assistant method. Nanoadsorbent efficiently removed methylene blue (58.8 mg/g) from wastewater. The removal of pollutant followed Langmuir adsorption isotherm and pseudo-second-order kinetic model (Ali 2018). A starch-derived magnetic hydrogel nanocellulose crystal was prepared using sugar-beet pulp via acid hydrolysis method. The nanocomposites were used to remove methylene blue and crystal violet dyes from wastewater. Electrostatic force of attraction between anionic surface of modified nanocellulose and cationic dyes was main sorption mechanism (Moharrami and Motamedi 2020). Rice husk-derived magnetic carboxylcellulose nanofiber adsorbents (suspension, freeze-dried and nanocomposites) were prepared using TEMPO-oxidation method and used to remove Pb^{2+} and Ln^{3+} from wastewater. Among these, the adsorption capacity of nanocellulose suspension was maximum for Pb^{2+} (193.2 mg/g) and Ln^{3+} (100.7 mg/g). Electrostatic attraction between the negatively charged surface of adsorbent and metal ions was the main removal mechanism (Zhan et al. 2020).

11.3.2.3 Lignin-Based Nanoadsorbents

An organosolv lignin nanobioadsorbent was prepared using steam-exploded rice straw biomass. The adsorbent removed methylene blue from wastewater (40.0 mg/g). The adsorption kinetics data were simulated by pseudo-first-order and pseudo-second-order models. Langmuir adsorption isotherm indicated the monolayer adsorption of methylene blue (Zhang et al. 2016 b). Lignin supported carbon nanotubes efficiently removed Pb^{2+} (235 mg/g) and oil droplet (98.3%) from aqueous solution. Tridimensional structure, presence of ample oxygen functional groups, large specific surface area, water dispersibility, and mechanical stability of adsorbent made it an effective adsorbent for Pb^{2+} removal. Pore diffusion and interaction between oxygen functional groups on the adsorbent surface and Pb^{2+} were the responsible removal mechanisms (Li et al. 2017).

A cost-effective, recyclable, poly(ethyleneimine)-grafted-alkali lignin nanobioadsorbent fabricated with lanthanum hydroxide nanoparticles was prepared. The adsorbent successfully removed phosphate at high concentration (50 ppm, 94%, 60 min) and low concentration (2 ppm, 99 %, 15 min) under wide *p*H range (3.0-9.0). Surface precipitation and ligand exchange were the main operating mechanisms for adsorption (Zong et al. 2018).

Lignin-based nanoadsorbents (alkali lignin and lignin nanoparticles) were prepared and used successfully to remove Basic Red 2 (alkali lignin: 55.2 mg/g and lignin nanoparticle: 81.9 mg/g) from aqueous solution. The adsorbents were prepared via acidification of black liquor from paper factory waste. Alkali lignin was further modified by ethylene glycol treatment. Surface morphology and chemistry were confirmed by SEM and FTIR studies, respectively (Azimvand et al. 2018). An efficient, green, cost-effective, chitosan composite with nanolignin was developed and used to remove methylene blue (83%) from wastewater. The lignin was extracted from palm kernel shell using acid and tetrahydrofuran (Sohni et al. 2019). Pseudo-second-order kinetic model and Langmuir adsorption isotherm described the monolayer adsorption. Thermodynamic studies indicated the spontaneous endothermic adsorption of pollutant onto nanocomposite surface (Sohni et al. 2019).

Alkali lignin-based Pd nanoparticles were prepared via two different methods, namely loading followed by regeneration and regeneration followed by loading. The developed adsorbents removed toxic Cr^{6+} by reducing it into less toxic Cr^{3+}. The adsorbent formed via regeneration followed by loading reduced Cr^{6+} completely within 5 min (Chu et al. 2021). Lignin-based nano-trap multifunctional adsorbent was prepared via inverse-emulsion copolymerization method. The adsorbent removed soft metals (Ag^{+}, Hg^{2+}, Cd^{2+}) and borderline metals (Pb^{2+}, Cu^{2+}, Zn^{2+}) quantitatively (>99%) from aqueous solution to the level of permissible limit in drinking water. The silver-laden nanocomposite demonstrated antimicrobial activity towards *Escherichia coli* (99.68%) and *Staphylococcus aureus* (99.76%) (Xiao et al. 2019).

11.3.2.4 Biochar-Based Nanoadsorbents

An engineered graphene-coated nanobiochar was prepared using cotton wood and used to remove methylene blue efficiently (174 mg/g) from aqueous solution. The synthesized nanobiochar was 20 times more efficient than unmodified biochar. The adsorption mechanism involved in removal process was strong π–π interactions between fused aromatic rings of dye and the graphitic sheets of biochar (Zhang et al. 2012). A zinc modified novel nanobiochar was prepared using sugarcane bagasse and removed Cr^{6+} from wastewater (~102 mg/g). The adsorbent worked even after sixth cycle of regeneration with a gradual decrease in performance (84.16–59.75 mg/g only). The working efficiency, regeneration capability, and economic feasibility made it an effective adsorbent (Gan et al. 2015). A nano zerovalent iron supported biochar was prepared using rice husk for industrial wastewater treatment through batch adsorption studies to remove methyl orange (98% within 10 min) (Han et al. 2015). Structural and physicochemical properties of biochar were confirmed by TEM, BET, and XRD techniques (Han et al. 2015).

A cost-effective, easily separable graphene modified nanobiochar composite was prepared using wheat straw. The adsorbent effectively removed phenanthrene and Hg^{2+} from aqueous solution. Structure and morphology studies indicated the higher removal capacity of nanobiochar as compared to pristine biochar. The operating mechanism was π–π interactions. The larger surface area, greater thermal stability, and presence of ample functional groups on nanobiochar improved its adsorption capacity. Surface sorption and surface complexation were the pathways for Phenanthrene and Hg^{2+} removal (Tang et al. 2015). A pine derived nano zerovalent iron modified biochar was prepared and the adsorbent used to remove As^{5+} (124.5 g/kg within 1 h) from aqueous solution. The anoxic condition was more effective (about 8%) than the oxic conditions for removal of As^{5+}. Surface complexation and the reduction reactions were responsible removal mechanisms. Regeneration and high adsorption capacity of biochar makes it an effective adsorbent (Wang et al. 2017).

A pinewood derived nanobiochar (particle size: 60 nm) removed carbamazepine from aqueous solution (95% within 3 h) following pseudo-second-order kinetic and Freundlich adsorption isotherm model. The kinetic studies showed that the addition of surfactant enhanced the adsorption efficiency by 57% and increase in pH (from 3 to 8) improved the adsorption efficiency by 2.3-fold (Naghdi et al. 2019). A magnetic nanobiochar was prepared using wheat straw via ball milling. The adsorbent removed tetracycline and Hg^{2+} from aqueous solution (>99%). The electrostatic interactions, hydrogen bonding, and π–π interaction between the surface of adsorbent and tetracycline were operating in case of tetracycline removal, while electrostatic attractions, Hg–π bond formation, and surface complexation were reported for Hg^{2+} removal (Li et al. 2020).

11.3.3 Mechanism Involved in Adsorptive Removal of Inorganic and Organic Pollutants

Adsorption is a surface phenomenon wherein adsorbate molecules accumulate onto the surface of adsorbent. The presence of various minerals and functional groups remain present on the adsorbent surface. Various physical and chemical forces (mechanism) operate during sorptive removal of pollutants from wastewater using agricultural residue-derived nanoadsorbents. These forces allow the adsorption of different contaminants on adsorbent surface. Adsorption mechanism and efficiency are influenced by precursor materials of adsorbent and the characteristics of contaminants.

The physical properties of adsorbents such as surface area and pore volume and distribution play a vital role in adsorption of pollutants. Different mechanisms reported for sorptive removal of inorganic and organic pollutants from aqueous phase using agricultural residue-derived nanoadsorbents are depicted in Fig. 11.2a, b. The operative mechanisms in adsorption processes mainly included electrostatic

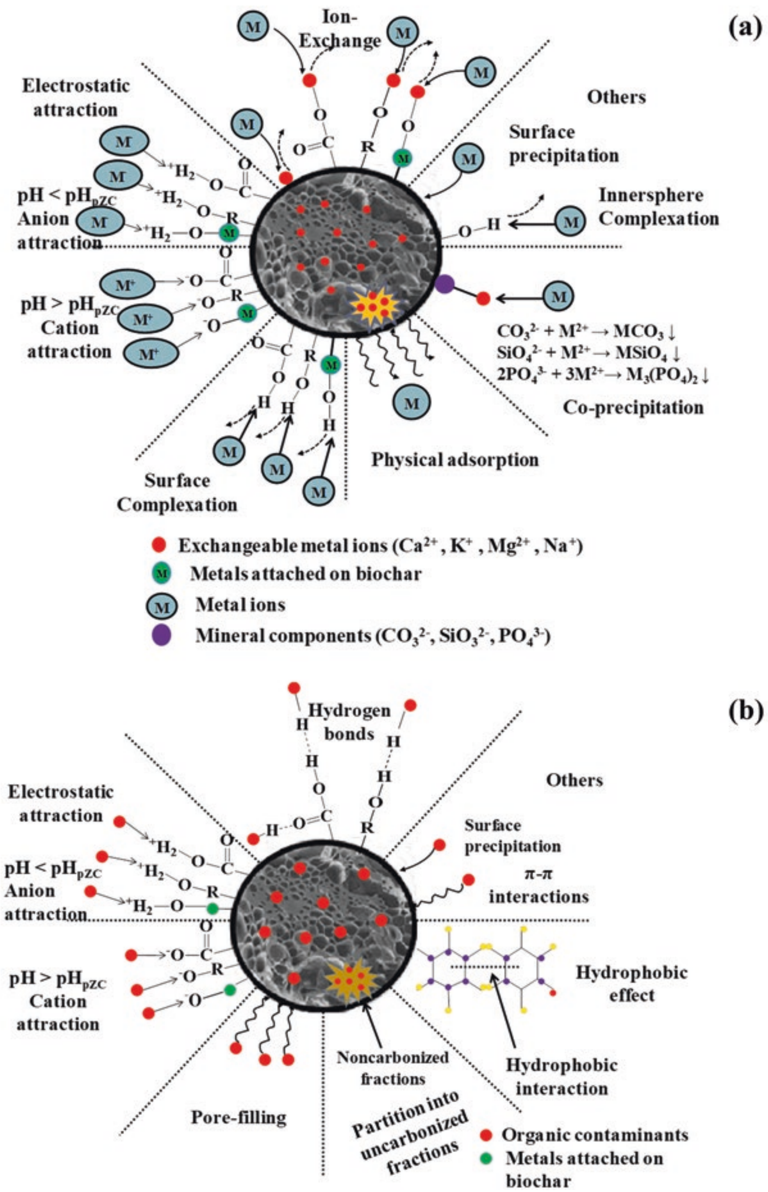

Fig. 11.2 Mechanisms involved in sorptive removal of (**a**) inorganic and (**b**) organic pollutants. (Reproduced with permission from Tan et al. 2015)

attraction, hydrophobic interaction, π–π interactions, hydrogen bonding, precipitation, ion exchange, and surface complexation (Tan et al. 2015). Interaction between adsorbate and adsorbent also depends upon operational parameters like *p*H, matrix of the solution, contact time, pollutant concentration, adsorbent dose, temperature among the others.

If the solution *p*H is less than pH_{pzc}, then the functional groups present on the adsorbent surface will get protonated and adsorb negatively charged pollutant species from the solution; on the other hand if *p*H is more than pH_{pzc} then positive charged species adsorb onto the surface. Wang et al. (2018) described various possible mechanisms between functionalized magnetic nanoparticles and metals, antibiotics, pesticides. In case of pesticides, mechanisms included hydrophobic interaction, electrostatic interaction, π–π interaction, π–π electron donor–acceptor interaction, π-stacking interaction, and physisorption. For antibiotic removal hydrogen bonding, π–π interaction, cation–π interaction, electrostatic attraction, electron-π donor–acceptor interaction, and amidation reactions were the possible mechanisms.

Coating on nanoparticles surface could improve the properties of adsorbents like increased active sites, large surface area, and improved removal efficiency. It has been observed that the coating of graphene on biochar attributed to the adsorption of organic pollutants through π–π interactions (Tang et al. 2015; Zhang et al. 2012). Both hydrophobic and π–π interaction may operate between the carbon nanotubes loaded bagasse biomass derived biochar and organic contaminant sulfapyridine (Inyang et al. 2015). Redox reaction and surface complexation were involved mechanisms for As^{3+} adsorption onto cerium modified chitosan ultrafine nanobiosorbent (Zhang et al. 2016a). The monodentate and bidentate complexes formation mechanism involved between the hydroxyl groups of nanoadsorbent and As^{3+} followed by oxidation of As^{3+} to As^{6+}. Other mechanisms of adsorption like pore filling, partitioning, and electron donor-acceptor were also studied for the interaction of water contaminants with biochar-based materials. Zheng et al. (2013) found redox reaction between electron donor biochar and electron acceptor sulfamethoxazole. The functional groups like carboxylate and hydroxyl groups present onto the surface nanoadsorbents are responsible for interactions (ion exchange and electrostatic attraction) with inorganic contaminants like metal ions. Incorporation of nanosized material into adsorbent like biochar increases the surface active sites and surface area. For example, a nanocomposite biochar/AlOOH adsorbed arsenic and phosphate ions from the solution more effectively than pristine biochar (Zhang and Gao 2013).

11.3.4 Adsorbent Selection and Regeneration

The selection of a treatment method involves economic, technical, and social considerations (Kumar et al. 2019). In terms of socio-economic aspect, an adsorbent should be cost-effective, readily available, developed from locally available materials, requires least technical expertise and should be easily applicable in large scale. For an adsorbent to be successful and sustainable in technical aspects include high sorption properties, high selectivity, high applicability in a wide range of contaminants concentration, easy applicability in vast ranges of matrices, and high reusability. Technical aspect of adsorbent selection can be evaluated through a variety of experimental assessment (Kumar et al. 2019; Patel et al. 2019; Ateia et al. 2020;

Mudhoo et al. 2021). For the better selection of an adsorbent, its physicochemical, morphological, and structural properties as well as contaminants removal capacity must be properly characterized (Patel et al. 2019). Both batch and dynamic sorption studies must be conducted followed by adsorbent regeneration studies. Batch sorption studies help in the optimization of adsorbent properties during its developmental stage (Choudhary et al. 2020; Patel et al. 2021), while dynamic studies simulate the real-world scenarios of the adsorbent applicability. Thus, agricultural residue-derived nanoadsorbent with minimum chemical utilization, low cost, easy preparation and wide applicability would be the adsorbent of choice.

Regeneration of nanoadsorbents leads to the applications such as reusability of nanoadsorbent and recovery of valuable metal species. Regeneration of exhausted adsorbent is essential to revive its adsorption capacity. It involved the stripping off the adsorbed metals or other contaminants so that the adsorbent can be used again and again. Due to this stripped metals can be recycled back to the process of origin, it makes the adsorption method economically viable. In the several regeneration cycles, the adsorption capacity decreased to some extent due to decrease in surface area and active sites. For the recovery of metal ions mainly dilute acids (HNO_3, H_2SO_4, and HCl) are used. Hu et al. (2020) synthesized a cheap adsorbent (Zr@MCS) for phosphate removal by incorporation of nanosized Zr^{4+} oxide onto amino modified corn straw. Zr@MCS successfully adsorbed the phosphate ions and this loaded Zr@MCS regenerated using 5% NaOH–NaCl solution. After the first regeneration it was found that the removal efficiency decreased from 70% to 65% and after 2–8 runs the efficiency decreased only up to 63%. Further, phosphate was regenerated from phosphate-rich desorption solution by struvite crystallization method and used as phosphate fertilizer in soil. 0.5 M NaOH solution was used for Cr^{6+} desorption from β-cyclodextrin–chitosan modified biochar by Huang et al. (2016) and it was analyzed that after the five adsorption-desorption cycles the removal capacity decreased up to 56%. Nanobiochar from artichoke leaves was synthesized and modified with NaOH to adsorb antidiabetic drug Metformin hydrochloride (MFH) from the solution (Mahmoud et al. 2020). MFH loaded Artich-Bch-NaOH then regenerated using 0.1 M HCl. For this, first of all Artich-Bch-NaOH-bounded-MFH dried at 70 °C and treated with 0.1 M HCl for 40–45 min, filtered and dried at 70 °C. The regenerated adsorbent was then used about 4–5 times and it was estimated that even after 5 cycles the adsorption capability was in the range 78.5–82.0%. So, for the economic reasons it should be ensured that prepared adsorbent can be used several times.

11.4 Conclusion and Recommendations

Adsorption is an easy to use and economic wastewater treatment unit process. However, the design and development of an effective, cheap and specific adsorbent is a challenge. The conventional adsorbents (for example, clay, lime stone, silica, soil, zeolite, activated charcoal, activated alumina) have certain challenges associated with them like high cost, difficulty in surface modification, regeneration, exhaustion, and low pollutants removal efficiency. Nanoadsorbents prepared using low-cost and abundantly available agricultural residue may help to deal with the above said constraints associated with the conventional adsorbents. Agricultural residue-based nanoadsorbents (silica, cellulose, lignin, biochar) might be ideal candidates being cost-effective, eco-friendly and effective for conventional emerging pollutants removal from (waste)water. These adsorbents must be made more smart through surface functionalization, composite formation and improving their reusability for emerging pollutants removal in aqueous phase. Future studies must focus on exploring mechanistic aspects of wastewater remediation using novel agri-residue-based nanoadsorbent. Agricultural residue-derived nanoadsorbents are expected to have a great future in the wastewater purification sector.

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References

Afkhami, A., Saber-Tehrani, M. and Bagheri, H., 2010. Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2, 4-dinitrophenylhydrazine. *Journal of Hazardous Materials*, *181*(1-3), pp. 836-844.

Ahamad, A., Madhav, S., Singh, A.K., Kumar, A. and Singh, P., 2020. Types of water pollutants: conventional and emerging. In *Sensors in Water Pollutants Monitoring: Role of Material* (pp. 21-41). Springer, Singapore.

Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry*, *40*(3-4), pp. 997-1026.

Ali, I. and Gupta, V.K., 2006. Advances in water treatment by adsorption technology. *Nature Protocols*, *1*(6), pp. 2661-2667.

Ali, I., 2012. New generation adsorbents for water treatment. *Chemical Reviews*, *112*(10), pp. 5073-5091.

Ali, I., Asim, M. and Khan, T.A., 2012. Low cost adsorbents for the removal of organic pollutants from wastewater. *Journal of Environmental Management*, *113*, pp. 170-183.

Ali, M., Almohana, A.I., Alali, A.F., Kamal, M.A., Khursheed, A., Khursheed, A. and Kazmi, A.A., 2021 Common effluent treatment plants monitoring and process augmentation options to conform non-potable reuse. *Frontiers in Environmental Science*, p. 598.

Ali, M.E., Hoque, M.E., Safdar Hossain, S.K. and Biswas, M.C., 2020. Nanoadsorbents for wastewater treatment: next generation biotechnological solution. *International Journal of Environmental Science and Technology*, *17*, pp. 4095-4132.

Ali, S.M., 2018. Fabrication of a nanocomposite from an agricultural waste and its application as a biosorbent for organic pollutants. *International Journal of Environmental Science and Technology*, *15*(6), pp. 1169-1178.

Ateia, M., Helbling, D. E., &Dichtel, W. R. (2020). Best practices for evaluating new materials as adsorbents for water treatment. *ACS Materials Letters*, *2(11),* 1532-1544.

Azimvand, J., Didehban, K. and Mirshokraie, S.A., 2018. Preparation and characterization of nano-lignin biomaterial to remove basic red 2 dye from aqueous solutions. *Pollution, 4(3),* pp. 395-415.

Aziz, H.A., Adlan, M.N. and Ariffin, K.S., 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: post treatment by high quality limestone. *Bioresource technology*, *99*(6), pp. 1578-1583.

Aziz, S.Q. and Ali, S.M., 2016. Performance of biological filtration process for wastewater treatment: a review. *ZANCO Journal of Pure and Applied Sciences*, *28*(2), pp. 554-563.

Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, *4*(4), pp. 361-377.

Belessi, V., Romanos, G., Boukos, N., Lambropoulou, D. and Trapalis, C., 2009. Removal of reactive red 195 from aqueous solutions by adsorption on the surface of TiO2 nanoparticles. *Journal of Hazardous Materials*, *170*(2-3), pp. 836-844.

Bhatnagar, A., Hogland, W., Marques, M. and Sillanpää, M., 2013. An overview of the modification methods of activated carbon for its water treatment applications. *Chemical Engineering Journal*, *219*, pp. 499-511.

Biswas, M.C., Tiimob, B.J., Abdela, W., Jeelani, S. and Rangari, V.K., 2019. Nano silica-carbon-silver ternary hybrid induced antimicrobial composite films for food packaging application. *Food Packaging and Shelf Life*, *19*, pp. 104-113.

Browne, M.A., Underwood, A.J., Chapman, M.G., Williams, R., Thompson, R.C. and van Franeker, J.A., 2015. Linking effects of anthropogenic debris to ecological impacts. *Proceedings of the Royal Society B: Biological Sciences*, *282*(1807), p. 20142929.

Caliman, F.A. and Gavrilescu, M., 2009. Pharmaceuticals, personal care products and endocrine disrupting agents in the environment – a review. *Clean-Soil, Air, Water, 37(4-5),* pp. 277–303.

Choudhary, V., Patel, M., Pittman Jr, C.U. and Mohan, D., 2020. Batch and continuous fixed-bed lead removal using himalayan pine needle biochar: isotherm and kinetic studies. *ACS Omega*, *5*(27), pp. 16366-16378.

Chu, J., Ma, H., Zhang, L. and Wang, Z., 2021. Biomass-derived paper-based nanolignin/palladium nanoparticle composite film for catalytic reduction of hexavalent chromium. *Industrial Crops and Products*, *165*, p. 113439.

Comstock, S.E. and Boyer, T.H., 2014. Combined magnetic ion exchange and cation exchange for removal of DOC and hardness. *Chemical Engineering Journal*, *241*, pp. 366-375.

Crane, R.A. and Scott, T.B., 2012. Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *Journal of Hazardous Materials*, *211*, pp. 112-125.

Crini, G., 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, *30*(1), pp. 38-70.

Crini, G. and Lichtfouse, E., 2019. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, *17*(1), pp. 145-155.

Dawood, S. and Sen, T., 2014. Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents. *Journal of Chemical and Process Engineering*, *1*(104), pp. 1-11.

Dhaka, S., Kumar, R., Khan, M.A., Paeng, K.J., Kurade, M.B., Kim, S.J. and Jeon, B.H., 2017. Aqueous phase degradation of methyl paraben using UV-activated persulfate method. *Chemical Engineering Journal*, *321*, pp. 11-19.

El-Sayed, M.E., 2020. Nanoadsorbents for water and wastewater remediation. *Science of the Total Environment*, *739*, p. 139903.

Akhayere, E., Essien, E.A. and Kavaz, D., 2019. Effective and reusable nano-silica synthesized from barley and wheat grass for the removal of nickel from agricultural wastewater. *Environmental Science and Pollution Research*, *26*(25), pp. 25802-25813.

Fakhrian, S. and Baseri, H., 2020.Production of a magnetic biosorbent for removing pharmaceutical impurities. *Korean Journal of Chemical Engineering*, *37*(9), pp. 1541-1551.

Fu, F. and Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management*, *92*(3), pp. 407-418.

Gan, C., Liu, Y., Tan, X., Wang, S., Zeng, G., Zheng, B., Li, T., Jiang, Z. and Liu, W., 2015. Effect of porous zinc–biochar nanocomposites on Cr (VI) adsorption from aqueous solution. *RSC Advances*, *5*(44), pp. 35107-35115.

García-Montaño, J., Ruiz, N., Munoz, I., Domenech, X., García-Hortal, J.A., Torrades, F. and Peral, J., 2006. Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal. *Journal of hazardous materials*, *138*(2), pp. 218-225.

Garcia-Segura, S., Salazar, R. and Brillas, E., 2013. Mineralization of phthalic acid by solar photoelectro-Fenton with a stirred boron-doped diamond/air-diffusion tank reactor: Influence of Fe3+ and Cu2+ catalysts and identification of oxidation products. *Electrochimica Acta*, *113*, pp. 609-619.

Gunatilake, S.K., 2015. Methods of removing heavy metals from industrial wastewater. *Journal of Multidisciplinary Engineering Science Studies*, *1*(1), p. 14.

Gupta, V.K., Ali, I., Saleh, T.A., Nayak, A. and Agarwal, S., 2012. Chemical treatment technologies for waste-water recycling—an overview. *RSC Advances*, *2*(16), pp. 6380-6388.

Han, L., Xue, S., Zhao, S., Yan, J., Qian, L. and Chen, M., 2015. Biochar supported nanoscale iron particles for the efficient removal of methyl orange dye in aqueous solutions. *PloS One*, *10*(7), p. e0132067.

Hassan, M.M. and Carr, C.M., 2021. Biomass-derived porous carbonaceous materials and their composites as adsorbents for cationic and anionic dyes: A review. *Chemosphere*, *265*, p. 129087.

Hernández, F., Sancho, J.V., Ibáñez, M. and Guerrero, C., 2007. Antibiotic residue determination in environmental waters by LC-MS. *Trends in Analytical Chemistry*, *26*(6), pp. 466-485.

Hoque, M.E. and Philip, O.J., 2011. Biotechnological recovery of heavy metals from secondary sources—An overview. *Materials Science and Engineering C*, *31*(2), pp. 57-66.

Hu, Y., Du, Y., Nie, G., Zhu, T., Ding, Z., Wang, H., Zhang, L. and Xu, Y., 2020. Selective and efficient sequestration of phosphate from waters using reusable nano-Zr (IV) oxide impregnated agricultural residue anion exchanger. *Science of the Total Environment*, *700*, p. 134999.

Huang, X., Liu, Y., Liu, S., Tan, X., Ding, Y., Zeng, G., Zhou, Y., Zhang, M., Wang, S. and Zheng, B., 2016. Effective removal of Cr (VI) using β-cyclodextrin–chitosan modified biochars with adsorption/reduction bifunctional roles. *RSC Advances*, *6*(1), pp. 94-104.

Hurt, R.H., Monthioux, M. and Kane, A., 2006. Toxicology of carbon nanomaterials: status, trends, and perspectives on the special issue. *Carbon*, *44*(6), pp. 1028-1033.

Ilisz, I., Dombi, A., Mogyorósi, K. and Dékány, I., 2003. Photocatalytic water treatment with different TiO_2 nanoparticles and hydrophilic/hydrophobic layer silicate adsorbents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *230*(1-3), pp. 89-97.

Inyang, M., Gao, B., Zimmerman, A., Zhou, Y. and Cao, X., 2015. Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars. *Environmental Science and Pollution Research*, *22*(3), pp. 1868-1876.

Joseph, L., Jun, B.M., Jang, M., Park, C.M., Muñoz-Senmache, J.C., Hernández-Maldonado, A.J., Heyden, A., Yu, M. and Yoon, Y., 2019. Removal of contaminants of emerging concern by metal-organic framework nanoadsorbents: A review. *Chemical Engineering Journal*, *369*, pp. 928-946.

Kakavandi, B., Bahari, N., Kalantary, R.R. and Fard, E.D., 2019. Enhanced sono-photocatalysis of tetracycline antibiotic using TiO_2 decorated on magnetic activated carbon (MAC@ T) coupled with US and UV: a new hybrid system. *Ultrasonics Sonochemistry*, *55*, pp. 75-85.

Kaliannan, D., Palaninaicker, S., Palanivel, V., Mahadeo, M.A., Ravindra, B.N. and Jae-Jin, S., 2019. A novel approach to preparation of nano-adsorbent from agricultural wastes (*Saccharum officinarum leaves*) and its environmental application. *Environmental Science and Pollution Research*, *26*(6), pp. 5305-5314.

Kardam, A., Rajawat, D.S., Kanwar, S. and M., 2017. Enhanced removal of cationic dye methylene blue from aqueous solution using nanocellulose prepared from agricultural waste sugarcane bagasse. In *Recent Trends in Materials and Devices* (pp. 29-36). Springer, Cham.

Kaur, M., Kumari, S. and Sharma, P., 2020. Removal of Pb (II) from aqueous solution using nano-adsorbent of *Oryza sativa* husk: Isotherm, kinetic and thermodynamic studies. *Biotechnology Reports*, *25*, p. e00410.

Khajeh, M., Laurent, S. and Dastafkan, K., 2013. Nanoadsorbents: classification, preparation, and applications (with emphasis on aqueous media). *Chemical Reviews*, *113*(10), pp. 7728-7768.

Krstić, V., Urošević, T. and Pešovski, B., 2018. A review on adsorbents for treatment of water and wastewaters containing copper ions. *Chemical Engineering Science*, *192*, pp. 273-287.

Kumar, E., Bhatnagar, A., Hogland, W., Marques, M. and Sillanpää, M., 2014. Interaction of anionic pollutants with Al-based adsorbents in aqueous media–A review. *Chemical Engineering Journal*, *241*, pp. 443-456.

Kumar, R., Kang, C.U., Mohan, D., Khan, M.A., Lee, J.H., Lee, S.S. and Jeon, B.H., 2020. Waste sludge derived adsorbents for arsenate removal from water. *Chemosphere*, *239*, p. 124832.

Kumar, R., Kim, S.J., Kim, K.H., Kurade, M.B., Lee, S.H., Oh, S.E., Roh, H.S. and Jeon, B.H., 2018. Development of hybrid adsorbent for effective aqueous phase sorptive removal of copper. *Surface and Interface Analysis*, *50*(4), pp. 480-487.

Kumar, R., Patel, M., Singh, P., Bundschuh, J., Pittman Jr, C.U., Trakal, L. and Mohan, D., 2019. Emerging technologies for arsenic removal from drinking water in rural and peri-urban areas: Methods, experience from, and options for Latin America. *Science of the Total Environment*, *694*, p. 133427.

Kurniawan, T.A., Chan, G.Y., Lo, W.H. and Babel, S., 2006. Physico–chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, *118*(1-2), pp. 83-98.

Kwon, O.H., Kim, J.O., Cho, D.W., Kumar, R., Baek, S.H., Kurade, M.B. and Jeon, B.H., 2016. Adsorption of As (III), As (V) and Cu (II) on zirconium oxide immobilized alginate beads in aqueous phase. *Chemosphere*, *160*, pp. 126-133.

Leiknes, T., 2009. The effect of coupling coagulation and flocculation with membrane filtration in water treatment: A review. *Journal of Environmental Sciences*, *21*(1), pp. 8-12.

Li, G., Zhao, Z., Liu, J. and Jiang, G., 2011. Effective heavy metal removal from aqueous systems by thiol functionalized magnetic mesoporous silica. *Journal of Hazardous Materials*, *192*(1), pp. 277-283.

Li, R., Zhang, Y., Deng, H., Zhang, Z., Wang, J.J., Shaheen, S.M., Xiao, R., Rinklebe, J., Xi, B., He, X. and Du, J., 2020. Removing tetracycline and Hg (II) with ball-milled magnetic nanobiochar and its potential on polluted irrigation water reclamation. *Journal of Hazardous Materials, 384*, p. 121095.

Li, Z., Chen, J. and Ge, Y., 2017. Removal of lead ion and oil droplet from aqueous solution by lignin-grafted carbon nanotubes. *Chemical Engineering Journal*, *308*, pp. 809-817.

Mahamuni, N.N. and Adewuyi, Y.G., 2010. Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation. *Ultrasonics Sonochemistry*, *17*(6), pp. 990-1003.

Mahmoud, M.E., El-Ghanam, A.M., Saad, S.R. and Mohamed, R.H.A., 2020. Promoted removal of metformin hydrochloride anti-diabetic drug from water by fabricated and modified nanobiochar from artichoke leaves. *Sustainable Chemistry and Pharmacy*, *18*, p. 100336.

Makeswari, M. and Santhi, T., 2013. Optimization of preparation of activated carbon from *Ricinus communis* leaves by microwave-assisted zinc chloride chemical activation: competitive adsorption of Ni^{2+} ions from aqueous solution. *Journal of Chemistry*, *2013*.

Manyangadze, M., Chikuruwo, N.H.M., Chakra, C.S., Narsaiah, T.B., Radhakumari, M. and Danha, G., 2020. Enhancing adsorption capacity of nano-adsorbents via surface modification: A review. *South African Journal of Chemical Engineering*, *31*(1), pp. 25-32.

Mohan, S.V., Babu, V.L. and Sarma, P.N., 2007. Anaerobic biohydrogen production from dairy wastewater treatment in sequencing batch reactor (AnSBR): effect of organic loading rate. *Enzyme and Microbial Technology*, *41*(4), pp. 506-515.

Moharrami, P. and Motamedi, E., 2020. Application of cellulose nanocrystals prepared from agricultural wastes for synthesis of starch-based hydrogel nanocomposites: Efficient and selective nanoadsorbent for removal of cationic dyes from water. *Bioresource Technology*, *313*, p. 123661.

Moliner-Martínez, Y., Ribera, A., Coronado, E. and Campíns-Falcó, P., 2011. Preconcentration of emerging contaminants in environmental water samples by using silica supported Fe_3O_4 magnetic nanoparticles for improving mass detection in capillary liquid chromatography. *Journal of Chromatography A*, *1218*(16), pp. 2276-2283.

Moncayo-Lasso, A., Sanabria, J., Pulgarin, C. and Benítez, N., 2009. Simultaneous *E. coli* inactivation and NOM degradation in river water via photo-Fenton process at natural *p*H in solar CPC reactor. A new way for enhancing solar disinfection of natural water. *Chemosphere*, *77*(2), pp. 296-300.

Mudhoo, A., Mohan, D., Pittman Jr, C. U., Sharma, G., &Sillanpää, M. (2021). Adsorbents for real-scale water remediation: Gaps and the road forward. Journal of Environmental Chemical Engineering, 9(4), 105380.

Muhd Julkapli, N., Bagheri, S. and Bee Abd Hamid, S., 2014. Recent advances in heterogeneous photocatalytic decolorization of synthetic dyes. *The Scientific World Journal*, *2014*.

Naghdi, M., Taheran, M., Pulicharla, R., Rouissi, T., Brar, S.K., Verma, M. and Surampalli, R.Y., 2019. Pine-wood derived nanobiochar for removal of carbamazepine from aqueous media: Adsorption behavior and influential parameters. *Arabian Journal of Chemistry*, *12*(8), pp. 5292-5301.

Nemati, M., Hosseini, S.M. and Shabanian, M., 2017. Novel electrodialysis cation exchange membrane prepared by 2-acrylamido-2-methylpropane sulfonic acid; heavy metal ions removal. *Journal of Hazardous Materials*, *337*, pp. 90-104.

Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman Jr, C. U. and Mohan, D. 2019. Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods. *Chemical Reviews, 119(6)*, 3510-3673.

Patel, M., Kumar, R., Pittman Jr, C. U. and Mohan, D., 2021. Ciprofloxacin and Acetaminophen sorption onto banana peel biochars: Environmental and process parameter influences. *Environmental Research,* 111218.

Pei, A., Butchosa, N., Berglund, L.A. and Zhou, Q., 2013. Surface quaternized cellulose nanofibrils with high water absorbency and adsorption capacity for anionic dyes. *Soft Matter*, *9*(6), pp. 2047-2055.

Peng, H. and Guo, J., 2020. Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review. *Environmental Chemistry Letters*, pp. 1-14.

Pham, T.D., Bui, T.T., Nguyen, V.T., Bui, T.K.V., Tran, T.T., Phan, Q.C., Pham, T.D. and Hoang, T.H., 2018. Adsorption of polyelectrolyte onto nanosilica synthesized from rice husk: characteristics, mechanisms, and application for antibiotic removal. *Polymers*, *10*(2), p. 220.

Pham, T.D., Bui, T.T., Truong, T.T.T., Hoang, T.H., Le, T.S., Duong, V.D., Yamaguchi, A., Kobayashi, M. and Adachi, Y., 2020. Adsorption characteristics of beta-lactam cefixime onto nanosilica fabricated from rice husk with surface modification by polyelectrolyte. *Journal of Molecular Liquids*, *298*, p. 111981.

Preda, C., Ungureanu, M.C. and Vulpoi, C., 2012. Endocrine disruptors in the environment and their impact on human health. *Environmental Engineering & Management Journal*, *11*(9).

Qin, J.J., Wai, M.N., Oo, M.H. and Wong, F.S., 2002. A feasibility study on the treatment and recycling of a wastewater from metal plating. *Journal of Membrane Science*, *208*(1-2), pp. 213-221.

Qiu, H., Liang, C., Yu, J., Zhang, Q., Song, M. and Chen, F., 2017. Preferable phosphate sequestration by nano-La (III)(hydr) oxides modified wheat straw with excellent properties in regeneration. *Chemical Engineering Journal*, *315*, pp. 345-354.

Ramanayaka, S., Kumar, M., Etampawala, T. and Vithanage, M., 2020. Macro, colloidal and nanobiochar for oxytetracycline removal in synthetic hydrolyzed human urine. *Environmental Pollution*, *267*, p. 115683.

Rangari, V.K., Apalangya, V., Biswas, M. and Jeelani, S., 2017. Preparation and microscopic characterization of biobased nanoparticles from natural waste materials. *Microscopy and Microanalysis*, *23*(S1), pp. 1938-1939.

Rathi, B.S. and Kumar, P.S., 2021. Application of adsorption process for effective removal of emerging contaminants from water and wastewater. *Environmental Pollution*, *280*, p. 116995.

Sachan, D., Ramesh, A. and Das, G., 2021. Green synthesis of silica nanoparticles from leaf biomass and its application to remove heavy metals from synthetic wastewater: A comparative analysis. *Environmental Nanotechnology, Monitoring & Management*, *16*, p. 100467.

Saputra, E., Utama, P., Muhammad, S., Ang, H.M., Tade, M. and Wang, S., 2011, November. Catalytic oxidation of toxic organics in aqueous solution for wastewater treatment: a review. In *Proceedings from TIChE International Conference*.

Sharma, P.R., Chattopadhyay, A., Sharma, S.K., Geng, L., Amiralian, N., Martin, D. and Hsiao, B.S., 2018. Nanocellulose from spinifex as an effective adsorbent to remove cadmium (II) from water. *ACS Sustainable Chemistry & Engineering*, *6*(3), pp. 3279-3290.

Sharma, Y.C., Srivastava, V., Singh, V.K., Kaul, S.N. and Weng, C.H., 2009. Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environmental technology*, *30*(6), pp. 583-609.

Sohni, S., Hashim, R., Nidaullah, H., Lamaming, J. and Sulaiman, O., 2019. Chitosan/nano-lignin based composite as a new sorbent for enhanced removal of dye pollution from aqueous solutions. *International Journal of Biological Macromolecules*, *132*, pp. 1304-1317.

Singh, P., Singh, R., Borthakur, A., Madhav, S., Singh, V.K., Tiwary, D., Srivastava, V.C. and Mishra, P.K., 2018. Exploring temple floral refuse for biochar production as a closed loop perspective for environmental management. *Waste Management*, *77*, pp. 78-86.

Sun, L., Wan, S., Yu, Z., Wang, Y. and Wang, S., 2012. Anaerobic biological treatment of high strength cassava starch wastewater in a new type up-flow multistage anaerobic reactor. *Bioresource Technology*, *104*, pp. 280-288.

Sun, P., Hui, C., Khan, R.A., Du, J., Zhang, Q. and Zhao, Y.H., 2015. Efficient removal of crystal violet using Fe_3O_4-coated biochar: the role of the Fe_3O_4 nanoparticles and modeling study their adsorption behavior. *Scientific Reports*, *5*(1), pp. 1-12.

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y. and Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*, *125*, pp. 70-85.

Tang, J., Lv, H., Gong, Y. and Huang, Y., 2015. Preparation and characterization of a novel graphene/biochar composite for aqueous phenanthrene and mercury removal. *Bioresource Technology*, *196*, pp. 355-363.

Tolba, G.M., Barakat, N.A., Bastaweesy, A.M., Ashour, E.A., Abdelmoez, W., El-Newehy, M.H., Al-Deyab, S.S. and Kim, H.Y., 2015. Effective and highly recyclable nanosilica produced from the rice husk for effective removal of organic dyes. *Journal of Industrial and Engineering Chemistry*, *29*, pp. 134-145.

Vaithyanathan, V.K., Cabana, H. and Vaidyanathan, V.K., 2021. Remediation of trace organic contaminants from biosolids: Influence of various pre-treatment strategies prior to *Bacillus subtilis* aerobic digestion. *Chemical Engineering Journal*, *419*, p. 129966.

Verma, S., Daverey, A. and Sharma, A., 2017. Slow sand filtration for water and wastewater treatment–a review. *Environmental Technology Reviews*, *6*(1), pp. 47-58.

Wang, S., Gao, B., Li, Y., Creamer, A.E. and He, F., 2017. Adsorptive removal of arsenate from aqueous solutions by biochar supported zero-valent iron nanocomposite: batch and continuous flow tests. *Journal of Hazardous Materials*, *322*, pp. 172-181.

Wang, T., Ai, S., Zhou, Y., Luo, Z., Dai, C., Yang, Y., Zhang, J., Huang, H., Luo, S. and Luo, L., 2018. Adsorption of agricultural wastewater contaminated with antibiotics, pesticides and toxic metals by functionalized magnetic nanoparticles. *Journal of Environmental Chemical Engineering*, *6*(5), pp. 6468-6478.

Xiao, D., Ding, W., Zhang, J., Ge, Y., Wu, Z. and Li, Z., 2019. Fabrication of a versatile lignin-based nano-trap for heavy metal ion capture and bacterial inhibition. *Chemical Engineering Journal*, *358*, pp. 310-320.

Yan, J., Han, L., Gao, W., Xue, S. and Chen, M., 2015a. Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. *Bioresource technology*, *175*, pp. 269-274.

Yan, L., Kong, L., Qu, Z., Li, L. and Shen, G., 2015b. Magnetic biochar decorated with ZnS nanocrystals for Pb (II) removal. *ACS Sustainable Chemistry & Engineering*, *3*(1), pp. 125-132.

Zamboulis, D., Pataroudi, S.I., Zouboulis, A.I. and Matis, K.A., 2004. The application of sorptive flotation for the removal of metal ions. *Desalination*, *162*, pp. 159-168.

Zazouli, M.A. and Kalankesh, L.R., 2017. Removal of precursors and disinfection by-products (DBPs) by membrane filtration from water; a review. *Journal of Environmental Health Science and Engineering*, *15*(1), pp. 1-10.

Zhan, C., Sharma, P.R., He, H., Sharma, S.K., McCauley-Pearl, A., Wang, R. and Hsiao, B.S., 2020. Rice husk based nanocellulose scaffolds for highly efficient removal of heavy metal ions from contaminated water. *Environmental Science: Water Research & Technology*, *6*(11), pp. 3080-3090.

Zhang, L., Zhu, T., Liu, X. and Zhang, W., 2016a. Simultaneous oxidation and adsorption of As (III) from water by cerium modified chitosan ultrafine nanobiosorbent. *Journal of Hazardous Materials*, *308*, pp. 1-10.

Zhang, M. and Gao, B., 2013. Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite. *Chemical Engineering Journal*, *226*, pp. 286-292.

Zhang, M., Gao, B., Yao, Y., Xue, Y. and Inyang, M., 2012. Synthesis, characterization, and environmental implications of graphene-coated biochar. *Science of the Total Environment*, *435*, pp. 567-572.

Zhang, S., Wang, Z., Zhang, Y., Pan, H. and Tao, L., 2016b. Adsorption of methylene blue on organosolv lignin from rice straw. *Procedia Environmental Sciences*, *31*, pp. 3-11.

Zheng, H., Wang, Z., Zhao, J., Herbert, S. and Xing, B., 2013. Sorption of antibiotic sulfamethoxazole varies with biochars produced at different temperatures. *Environmental Pollution*, *181*, pp. 60-67.

Zhou, M.H. and Lei, L.C., 2006. Electrochemical regeneration of activated carbon loaded with p-nitrophenol in a fluidized electrochemical reactor. *Electrochimica acta*, *51*(21), pp. 4489-4496.

Zielińska, M. and Galik, M., 2017. Use of ceramic membranes in a membrane filtration supported by coagulation for the treatment of dairy wastewater. *Water, Air, & Soil Pollution*, *228*(5), p. 173.

Zong, E., Huang, G., Liu, X., Lei, W., Jiang, S., Ma, Z., Wang, J. and Song, P., 2018. A lignin-based nano-adsorbent for superfast and highly selective removal of phosphate. *Journal of Materials Chemistry A*, *6*(21), pp. 9971-9983.