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Journal

Carbon Research, 1(1)

ISSN

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Publication Date

2022-12-01

DOI

Peer reviewed

REVIEW

Modification of agricultural wastes to improve sorption capacities for pollutant removal from water – a review

Guofei Liu[1,2], Zhongmin Dai[1,2], Xingmei Liu[1,2], Randy A. Dahlgren[3] and Jianming Xu[1,2*]

Abstract

Water pollution is a great risk to aquatic ecosystems and human health. Among water pollution remediation strategies, adsorption mechanisms provide strong efficacy for a wide variety of pollutants. Several recent efforts examined the development of low cost adsorbents utilizing commonly available agricultural wastes. However, raw (i.e., unaltered) agricultural wastes typically exhibit low sorption capacity for pollutants due to their non-reactive structural/composition properties. Hence, modifications of raw agricultural wastes to enhance their sorption capacities for various aquatic pollutants are necessary to optimize their performance for pollutant removal. Numerous modification techniques are effective in altering agricultural wastes for improved sorption performance. This paper reviews the development of modified agricultural waste materials for pollutant removal from water. We compiled an extensive inventory of modification techniques applied to agricultural wastes to enhance their adsorption capacities for removal of a wide range of pollutants. Modification strategies and their effects on sorption properties were rigorously examined to highlight key advancements in the preparation of adsorbents from agricultural wastes. Finally, the costs of these materials were examined, along with the benefits and drawbacks concerning their use. This review provides a thorough assessment for advancing the utilization of agricultural wastes for preparing adsorbents for water treatment.

Highlights

1. Modification methods and their effects on adsorption performance are summarized.

2. The roles of introduced functional groups and their retention mechanisms are investigated.

3. Benefits and drawbacks of low-cost agricultural waste adsorbents are assessed.

Keywords: Water pollution, Modification, Adsorption mechanisms, Agricultural wastes, Cost estimation

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Graphical Abstract
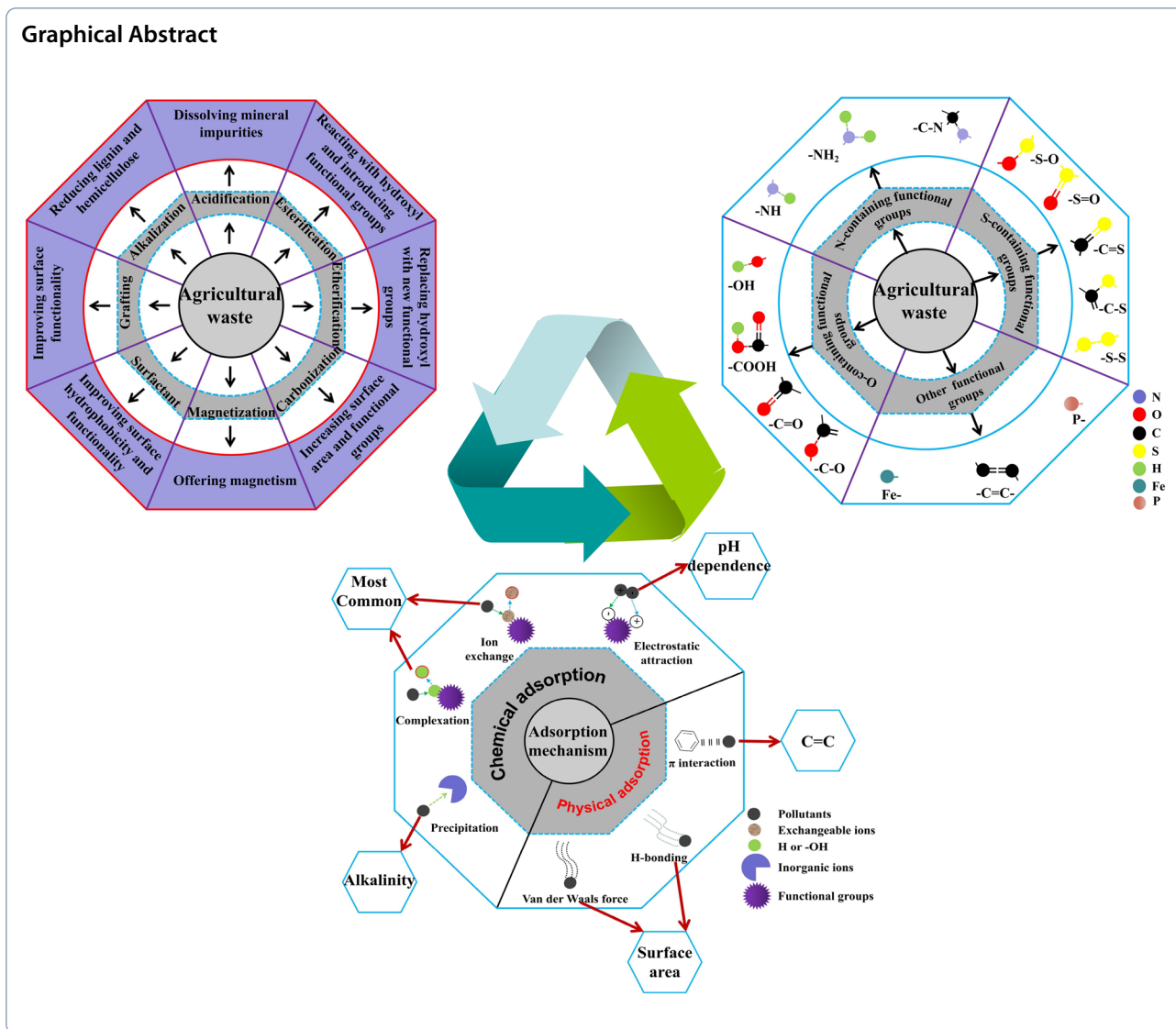
1 Introduction

Developments in industry and agriculture have greatly improved people's living standards, but they often cause negative impacts on environmental health. Water pollution caused by human activities is a progressively growing threat, especially in rapidly developing countries (Mo et al. 2018). A wide variety of pollutants (e.g., nutrients, heavy metals, dyes, phenols, antibiotic, pesticides) are released into natural waters where they pose a serious threat to drinking water safety, human health and aquatic ecosystems (Abdolali et al. 2014; Ling et al. 2006). These pollutants may be further transmitted from the water to soils when the polluted water is used for agricultural irrigation, thereby entering plants and threatening food safety (Afroze and Sen 2018). Accordingly, the treatments for remediation of contaminated wastewaters are necessary to protect human and ecosystem health. Various techniques have been developed for pollutants removal, including adsorption, biodegradation, coagulation/flocculation, oxidation, membrane filtration etc. (Qu et al. 2022a; Rashid et al. 2021). Among the various methods applied to water purification/remediation in recent decades, sorption techniques display strong efficacy due to their high adsorption capability for selected compounds and their ease of preparation and operation (Mo et al. 2018).

Commercial sorbents demonstrate high removal rates for selected pollutants from wastewater, however, their high production cost, intricate design and complex operational conditions often limit widespread application.

Hence, there is a distinct need for low-cost and effective adsorption materials to remove pollutants from waters (Abdolali et al. 2014). Nowadays, there is considerable interest in utilization of cheap alternatives based on the sorption potential of agricultural wastes, which provide favorable economic and eco-friendly (i.e., green chemistry) options (Kwon et al. 2020; Yang et al. 2019). Widespread agricultural and industrial activities generate large amounts of solid wastes. Some of these materials are reused, whereas other materials find no commercial utilization resulting in their ultimate disposal, which often causes environmental damage (Shi et al. 2020; Wang et al. 2013). Agricultural wastes are ubiquitous and nearly free of cost under most circumstances. Thus, conversion of these waste materials into low-cost adsorbents for water pollutant remediation is a compelling alternative that also solves a solid-waste disposal problem. There are now several examples of the utilization of raw agricultural wastes to successfully remove a myriad of water contaminants (Bhatnagar et al. 2015).

Raw (unaltered) agricultural wastes usually do not have high adsorption capacity for pollutants due to their inherent chemical structure/composition (Kaçakgil et al. 2021). The intermingled chemical structures comprising agricultural wastes and the low specific surface area of industrial wastes limit their physical and chemical interactions with many pollutants (Liu et al. 2020a). Consequently, several studies have investigated modification of agricultural wastes to enhance their adsorption capacity for various contaminants (Ding et al. 2014). Modification processes alter several physicochemical properties of agricultural wastes, such as their hydrophilic/hydrophobic characteristics, surface area and porosity, reactive functional groups, resistance to microbiological attack and thermal stability, thereby improving the adsorption performance for pollutant removal (Abdolali et al. 2014).

To date, a limited number of reviews exist on the use of agricultural wastes to adsorb pollutants and most of them take a holistic look at a variety of pollutants by focusing on either adsorbate-specific or adsorbent-specific applications (Bhatnagar et al. 2015; Dai et al. 2018). Notably, there are currently no systematic and comprehensive syntheses exploring the use and modification of agricultural wastes for pollutant abatement. Thus, in this review, we compiled and evaluated the various methods used to prepare agricultural waste adsorbents. Further, we compiled the literature on the extensive use and efficiency of these modified adsorbents for removal of various pollutants. The primary goals of this review were to: (i) present a comprehensive summary on the use of modified agricultural wastes as adsorbents in water pollution treatment; (ii) examine the myriad of mechanisms enabling pollutant removal; (iii) compile adsorption efficiency metrics for typical agricultural wastes; and (iv) provide perspectives on future applications and research needs to facilitate the efficient use of agricultural wastes in water pollution remediation.

2 Agricultural waste materials and their modification

Agricultural wastes, particularly those containing cellulose, are a by-product of agricultural and forestry production and mainly composed of lignin, cellulose and hemicellulose (Bhatnagar et al. 2015). These components contain several functional groups (e.g., alcohols, aldehydes, ketones, ether groups, and aromatic rings) in their molecular structures that can adsorb pollutants (Dai et al. 2018). The type of functional groups and chemical components comprising different agricultural wastes are similar, but occur in appreciably contrasting amounts. Some functional groups are shielded or sterically hindered inside the bulk structure of the organic matrix rendering them inaccessible to interact with pollutants directly, thereby hindering adsorption performance.

Modification alters the nature of surface functional groups, with the specific modification methods selected to optimize products for the intended application and chemical characteristics of the targeted contaminants. Modification methods for agricultural wastes can be classified into physical and chemical modifications. Chemical modification usually creates better physicochemical properties (functional group and surface area) for adsorbents, which enhance the adsorption performance more than that of physical modification techniques (Aryee et al. 2021). Thus, chemical modification is the most common way to modify agricultural wastes. Various chemical methods have been used to modify agricultural wastes in recent decades. Among these methods, alkalization, acidification, esterification, etherification, carbonization and magnetization are common modification procedures for agricultural wastes, along with surfactant modification and grafting (Fig. 1). The following discussion provides an overview of the common modification treatments employed to alter the physicochemical properties of agricultural wastes along with a synthesis of supporting studies demonstrating the efficacy of these modified products for pollutant retention/removal.

2.1 Alkalization
Conventionally, alkaline treatment for modification of agricultural wastes is performed by reaction with NaOH or KOH (Dai et al. 2018). The treatment reduces the content of amorphous constituents, such as lignin and hemicellulose, thereby increasing the surface area and exposing additional functional groups within the treated agricultural wastes (Kovacova et al. 2020; Liu
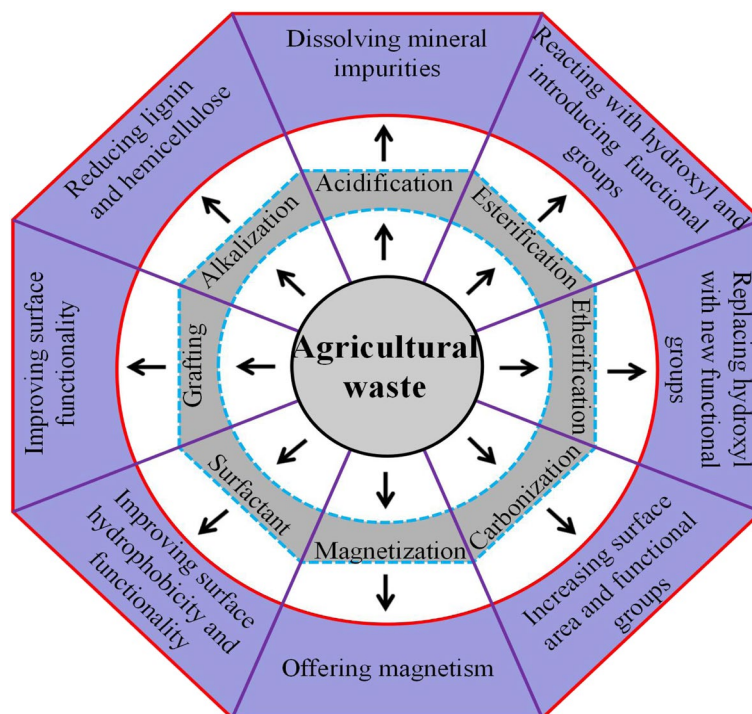
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Fig. 1 Classification of modification techniques for agricultural wastes

et al. 2020a). After alkaline modification, the mechanical properties and thermal stability of agricultural wastes are also improved, further facilitating enhanced pollutant removal (Sahu and Gupta 2020).

Asadi et al. (2008) demonstrated increased BET surface area of rice hulls following NaOH treatment from 0.7 to 4.3 m^2g^{-1}, which played an important role in increasing interactions between adsorbent and adsorbates. Some studies demonstrated that modified agricultural waste surfaces have augmented pores compared to the virgin feedstock (Ding et al. 2014), which increased pollutant adsorption through improved diffusion into pores. For example, KOH alkalization appears to unblock some pores resulting in the generation of more visible pores than the untreated material, which strengthens the retenion ciprofloxacin and tetracycline on the surface of adsorbent through hydrophobic interactions, H-bonding or van der Waals forces (Egbedina et al. 2021). Moreover, hydroxyl groups are generated in new adsorbents after NaOH treatment via hydrolysis of carbonyl groups and dissolution of lignin and hemicellulose, which enhance chemical reactivity for pollutants (Zafar et al. 2020). Furthermore, alkaline treatment releases cations (e.g., K^+, Ca^{2+}) from the treated residues that increase the ion exchange capacity contributing to increased retention of cationic pollutants (Azzaz et al. 2017). As a result, NaOH treated

rice husk showed strong complexation, ionic exchange and H-bonding interactions with Cu^{2+} due to increased hydroxyl groups content, cation exchange capacity and porosity.

Notably, NaOH treatment may confer differing effects for different types of agricultural wastes. For example, sawdust generated from poplar and fir wood displayed similar adsorption capacities for Zn^{2+}, while the adsorption capacity for Zn^{2+} increased by approximately 17 and 13 times for poplar and fir sawdust after NaOH treatment (Sciban et al. 2006). The contrasting sorption capacities induced by NaOH treatment were attributed to differences in the anatomical structure and chemical composition of the contrasting woody materials.

Alkaline treatment is an efficient methodology for exposing/generating functional groups on organic materials. The removal rate of Cu^{2+} by NaOH-thermal treated wheat straw increased to 21.9% (288 K), 25.8% (298 K), and 28.3% (308 K) compared with raw wheat straw (Guo et al. 2016). An increased intensity of the -C-O- group and Cu^{2+}-complexed functional groups in the FTIR spectrum of the treated wheat straw indicated that an increase of -C-O- functional groups was the main reason for enhanced Cu^{2+} adsorption. Similarly, NaOH treatment increased the removal rate of UO_2^{2+} by wheat straw from 32.64% to 84.45% due to an increase of -OH

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and C=O groups (Xiao-Teng et al. 2019). Moreover, the alkaline treatment exposed more Si=O and P-O on the treated surface, which further promoted UO_2^{2+} adsorption (Xiao-Teng et al. 2019).

Structural changes to alkali modified agricultural wastes promote pollutant retention. Table 1 summarizes the effects of alkalization on the removal of pollutants by modified adsorbents in terms of their maximum adsorption capacities, specific functional groups and adsorption mechanisms. NaOH modified rice straw exhibited excellent adsorption capacity for ciprofloxacin (Huang et al. 2020). Adsorption equilibrium with ciprofloxacin was achieved at ~35 min for NaOH modified rice straw and the maximum adsorption capacity was 93.5 $mg\,g^{-1}$. The sorption improvements were attributed to NaOH breaking down the lignin encapsulating cellulose or hemicellulose, thereby increasing the exposure of cellulose for reaction. Creation of tiny fissures on the treated rice straw surfaces enlarged the surface area, thereby increasing ciprofloxacin retention via physical adsorption. In an analogous study, NaOH treatment of wheat straw increased sulfonylurea herbicide retention resulting in a maximum adsorption capacity as high as 337.22 $mg\,g^{-1}$ (Cara et al. 2017). Alkaline treatment increased both the surface roughness and functional surface activity (carboxyl and hydroxyl groups) due to hydrolysis of esters. These changes strengthened the interactions between the alkaline-treated straw and chlorsulfuron through H-bonding, ion exchange and complexation reactions. Notably, alkali treatment is operationally straightforward; however, excessive alkali concentrations should be avoided as excess alkali can degrade the functional group content as demonstrated for wheat straw (Guo et al. 2016).

2.2 Acidification
Acidification is a wet oxidation process that can remove mineral impurities from agricultural wastes and further improves the acidic behavior and hydrophilic nature of the adsorbent surface (Yanyan et al. 2018). Common reagents for acid modification include H_3PO_4, HCl, HNO_3 and H_2SO_4. During treatment, acids dissolve constituents reducing the tortuosity of the porous structure and increase the O content of the material. In particular, acid treatment promotes cellulose hydrolysis of agricultural wastes creating a more reactive material (Yoon et al. 2014).

Thevannan et al. (2011) demonstrated that HCl reduced the mineral content of barley straw; Al, P, Mn, Cu and Zn concentrations decreased by 2.28%~9.80% after acid treatment. This reduction of mineral content contributed to increased adsorption of Ni^{2+} from solution due to decreasing competition among cations for adsorption sites. Generally, lignocellulosic adsorbents

Table 1 Sorption performance of alkali modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Adsorption capacity	Functional groups	Sorption mechanism	Reference
Alkalization	NaOH modified rice hull	Cu^{2+}	0.92 $mg\,g^{-1}$	-OH	Electrostatic attraction, H-bonding	Asadi et al. 2008
	NaOH modified rice stem	U^{6+} (UO_2^{2+})	18.97 $mg\,g^{-1}$	-OH, −COOH, −Si=O, −P-O	Ion exchange, complexation and H-bonding	Xiao-Teng et al. 2019
	NaOH modified peanut hulls	Pb^{2+}	19.7 $mg\,g^{-1}$	—	H-bonding	Ding et al. 2014
		Methylene blue	49.6 $mg\,g^{-1}$			
	NaOH modified wheat straw	Cu^{2+}	10.05 $mg\,g^{-1}$	-C-O	Complexation	Guo et al. 2016
	NaOH modified rice husk	Cu^{2+}	$9.1 \times 10^{-5}\,mol\,g^{-1}$	-OH, −NH, −Si-O	Electrostatic attraction	Zafar et al. 2020
	NaOH modified rice husk	Hg^{2+}	118.0 $mg\,g^{-1}$	-OH, −NH, −Si-O	Complexation and electrostatic attraction	Song et al. 2014
	NaOH modified straw	Ciprofloxacin	93.51 $mg\,g^{-1}$	-OH	Electrostatic attraction	Huang et al. 2020
	NaOH modified straw	Sulfonylurea	337.22 $mg\,g^{-1}$	-C-O-C-, −OH, −COOH	H-bonding, ion exchange and complexation	Cara et al. 2017
	NaOH modified orange tree sawdust	Methylene blue	226.35 $mg\,g^{-1}$	$-OH^-$, $−COO^-$, −C-O	Complexation and ion exchange	Azzaz et al. 2017
	NaOH modified poplar	Cu^{2+}	0.040 $mmol\,g^{-1}$	$-OH^-$, −OH	Ion exchange and precipitation	Sciban et al. 2006
		Zn^{2+}	0.015 $mmol\,g^{-1}$			
	NaOH modified fir	Cu^{2+}	0.037 $mmol\,g^{-1}$			
		Zn^{2+}	0.015 $mmol\,g^{-1}$			

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have low adsorption capacities for anionic pollutants due to their negatively charged surfaces. However, case studies have demonstrated that acidification can improve the adsorption performance for anionic pollutants (Acid Red 111) as well (Ayan et al. 2012). They ascribed this phenomenon to HNO_3 treatment promoting non-electrostatic interactions between adsorbent and adsorbate, such as van der Waals and H-bonding mechanisms.

Dilute acids increase the amount of C-H, O-H and C-O groups on agricultural wastes. The main functional groups in modified rice straw after HCl treatment were O-H and C-O groups, which facilitated the adsorption of 2-chlorophenol (Balarak et al. 2017). Concentrated acids can effectively convert hydroxyl and aldehyde groups to more oxidized groups, such as the carboxyl moiety. H_2SO_4-oxidized coconut shell had relatively high C (51.90%) and O (44.63%) contents due to the release of volatile compounds during acid oxidation (i.e., conversion of organic matter to carbonaceous compounds through destructive distillation) (Jawad et al. 2020). The surface of the treated material was surrounded by COO^- and SO_3^- groups, which were highly effective for the adsorption of methylene blue. Further, the O content

of HCl- and HNO_3-treated agave bagasse increased by 4.9% compared with the raw material due to an increase of carboxyl groups (Velazquez-Jimenez et al. 2013). Carboxyl groups are highly effective in the adsorption of heavy metals (Cd^{2+}, Pb^{2+} and Zn^{2+}) through formation of strong bridging complexes. Notably, concentrated acid oxidation was shown to decrease the surface area of oxidized coconut shell due to strong corrosion, which may reduce the porosity and efficacy of the adsorbent material for retention of some pollutants (Jawad et al. 2020).

Several studies have demonstrated the efficacy of acid-treated agricultural wastes for heavy metal ions, such as Zn^{2+}, Pb^{2+} and Cr^{6+} ($Cr_2O_7^{2-}$) (Argun et al. 2007; Velazquez-Jimenez et al. 2013). Acid treatment alters functional groups and several surface area/porosity characteristics to enhance adsorption performance (Table 2). The adsorption capacity of natural corncob for Cd^{2+} increased from 4.7 to 19.3 mg g^{-1} when the material was acidified by HNO_3 (Leyvaramos et al. 2005). The Cd^{2+} was adsorbed mainly by the carboxylic sites through ion exchange and the adsorption capacity increased directly proportional to the concentration of carboxylic sites. The glycosidic bonds of cellulose and hemicellulose are

Table 2 Sorption performance of acidification modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Adsorption capacity	Functional groups	Sorption mechanism	Reference
Acidification	HCl modified corn stalk	Cu^{2+}	0.325 mmol g^{-1}	-OH, −C-O-C-	Ion exchange	Vafakhah et al. 2014
	HCl modified agave bagasse	Cd^{2+}	12.50 mg g^{-1}	-OH, −COOH	Complexation	Velazquez-Jimenez et al. 2013
		Pb^{2+}	42.31 mg g^{-1}			
		Zn^{2+}	12.40 mg g^{-1}			
	HNO_3 modified agave bagasse	Cd^{2+}	13.50 mg g^{-1}			
		Pb^{2+}	54.29 mg g^{-1}			
		Zn^{2+}	14.43 mg g^{-1}			
	HNO_3 modified oreganum stalks	Basic Red 18	272.92 mg g^{-1}	-OH, −COOH	Electrostatic interaction	Ayan et al. 2012
		Methylene blue	142.86 mg g^{-1}			
		Acid Red 111	112.36 mg g^{-1}	—	H-bonding	
	H_3PO_4 modified oreganum stalks	Basic Red 18	280.73 mg g^{-1}	-OH, −COOH	Electrostatic interaction	
		Methylene blue	147.06 mg g^{-1}			
	HCl modified mango seed	Victazol Orange 3R dye	63.3 mg g^{-1}	-OH, −C=O, −COOH	Electrostatic interaction and H-bonding	Alencar et al. 2012
	HNO_3 modified corncob	Cd^{2+}	19.3 mg g^{-1}	-COO$^-$	Ion exchange	Leyvaramos et al. 2005
	HCl modified sugar beet pulp	Cu^{2+}	30.9 mg g^{-1}	-COO$^-$	Ion exchange	Pehlivan et al. 2006
		Zn^{2+}	35.6 mg g^{-1}			
	H_2SO_4 modified coconut shell	Methylene blue	50.6 mg g^{-1}	-OH, −COOH, −C=O, −C=C, −S=O, −S-O	Electrostatic attraction, H-bonding and π-π interactions	Jawad et al. 2020
	Acid N_2O_4 modified softwood pulp	Cd^{2+}	30.86 mg g^{-1}	-COOH	Ion exchange	Foglarova et al. 2009
		Ni^{2+}	9.58 mg g^{-1}			
		Zn^{2+}	18.69 mg g^{-1}			

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broken down to produce aldehyde groups and eventually carboxylic groups during acidic modification. Similarly, the maximum Cu^{2+} sorption capacity of HNO_3-treated corn cob ($0.325\,mmol\,g^{-1}$) was 3-fold higher than that of the raw corn stalk ($0.113\,mmol\,g^{-1}$) (Vafakhah et al. 2014). The pH_{PZC} (i.e., point of zero charge) for modified corn stalk was 3.3, which was lower than that of untreated material due to the increase of O-containing groups. The acid-modified adsorbent also showed a lower separation factor ($R_L = 0.224$) than raw corn stalk (0.716), further contributing to enhanced adsorption properties.

Acid-treated agricultural wastes are also effective for removal of several organic pollutants. Attainment of adsorption equilibrium for Basic Red 18 and methylene blue by HNO_3- and H_3PO_4-modified oreganum stalks was much shorter (2 h) than that of the corresponding non-treated stalks (4 h). The more rapid kinetics were ascribed to increased surface area and reactive functional groups after acid treatment, which created enhanced electrostatic and hydrophobic interactions between adsorbents and adsorbates (Ayan et al. 2012). The results showed that the maximum adsorption of Victazol orange 3R dye to dilute HCl-treated mango seed increased from 36.9 to $63.3\,mg\,g^{-1}$ with much faster sorption kinetics than the untreated seeds owing to increased BET surface area ($8.5 \rightarrow 11.5\,m^2\,g^{-1}$) and average pore diameter ($4.31 \rightarrow 5.78\,nm$). Overall, acid treatment contributes greater functional group reactivity and structural properties (e.g., surface area, porosity) to enhance adsorption performance.

2.3 Esterification

Esters are generated from the esterification of free hydroxyl groups in cellulose by reacting with one or more carboxyl groups (anhydrides), whereby cellulose reacts as a trivalent polymeric alcohol (Hokkanen et al. 2016). Succinic anhydride, EDTA (Ethylenediaminetetraacetic acid) dianhydride, citric acid anhydride and maleic anhydride are widely used for esterification reactions, thereby adding functional groups to the surface of agricultural wastes. In addition, the hydrophobicity and mechanical strength of adsorbents are improved by esterification as well (Pang et al. 2019). These beneficial changes from esterification contribute to enhanced adsorption performance of agricultural wastes for application in remediation of aqueous systems.

Crop straws are widely used as a feedstock for esterification treatment. For instance, soybean straw and citric acid (0.6 M) were mixed at a solid:liquid ratio of 1:10 (w/v) and reacted at 50 °C for 24 h and 120 °C for 90 min to prepare an esterified adsorbent (Zhu et al. 2008). After modification, a strong stretching vibration at $1742\,cm^{-1}$ (assigned to $C=O$) occurred in the FTIR spectrum, indicating a successful esterification process (Zhu et al. 2008). The -OH of cellulose reacted with citric acid to form ester linkages and imparted carboxyl groups onto the straw surface. With regard to the adsorption mechanisms, the carboxyl groups introduced by citric acid reacted with Cu^{2+} via a complexation reaction. Similarly, the etherification procedure was adopted to prepare esterified rice straw using EDTA as a modifying agent. The EDTA etherification processes generated both amino groups and carboxyl groups as adsorbents (Moyo et al. 2017). The relative peak shifts and signal strength alterations of FTIR spectrums revealed the combined actions of carboxyl, ester and amine groups of the grafted EDTA in Pb^{2+} binding. Additionally, some studies determined that the carboxyl esterification not only introduced more carboxyl groups on wheat straw, but also roughened the surface, thereby increasing surface area and porosity (Han et al. 2010). As a result, the increased $-COO^-$ content and porous surface properties enhanced methylene blue sorption through improved ion exchange and intraparticle diffusion.

The type of esterification reagent strongly affects the adsorption properties of agricultural wastes. For example, citric acid modified sesame straw fixed more methylene blue than that formed by tartaric acid modification (Feng et al. 2017). The contrasting effects of these two reagents were attributed to differences in their molecular structures. Citric acid possesses more carboxyl groups than tartaric acid, which resulted in generation of more adsorption sites following citric acid treatment (72.61 cmol kg^{-1}) than for tartaric acid treatment (17.46 cmol kg^{-1}). The FTIR spectrum of the modified materials confirmed a large increase in the intensity of the $C=O$ stretching peak resulting from citric acid treatment. Catalyst addition could further promote the esterification efficiency during modification. The esterification between citric acid and hydroxyl groups achieved in high efficiency using a mild catalyst ($NaH_2PO_2 \cdot H_2O$) in a N, N-dimethylformamide medium (Li et al. 2010), $NaH_2PO_2 \cdot H_2O$, as a catalyst, increased the speed of the esterification reaction and allowed for a simplified procedure compared to traditional methods without catalyst. The catalyzed process created ester linkages within the spent grain complex and increased carboxylic acid groups on the adsorbent surface.

Several studies demonstrated improved adsorption performance for pollutants following esterification of agricultural wastes (Table 3). Adsorption of Cu^{2+} by citric acid modified soybean straw was rapid during the first 10 min and reached a maximum adsorption capacity of 0.69 to $0.76\,mmol\,g^{-1}$ based on a Langmuir model (Zhu et al. 2008). The adsorption mechanism also changed due to the increase of functional groups. The

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Table 3 Sorption performance of esterification modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Adsorption capacity	Functional groups	Sorption mechanism	Reference
Esterification	Citric acid modified spent grain	Pb^{2+}	$293.30\,mg\,g^{-1}$	-COOH	Ion exchange	Li et al. 2010
		Cu^{2+}	$104.13\,mg\,g^{-1}$			
		Zn^{2+}	$232.10\,mg\,g^{-1}$			
		Cd^{2+}	$296.61\,mg\,g^{-1}$			
		Ag^{+}	$205.80\,mg\,g^{-1}$			
	Citric acid modified corncob	Cd^{2+}	$42.90\,mg\,g^{-1}$	-OH, —COOH	Ion exchange	Leyva-Ramos et al. 2012
	Citric acid modified soybean straw	Cu^{2+}	$0.76\,mmol\,g^{-1}$	-COOH	Complexation	Zhu et al. 2008
	Citric acid modified barley straw	Cu^{2+}	$37.71\,mg\,g^{-1}$	-COOH	Ion exchange, electrostatic attractions and chelatation	Pehlivan et al. 2012
	Citric acid modified wheat straw	Methylene blue	$396.9\,mg\,g^{-1}$	-COO^{-}	Ion exchange	Han et al. 2010
	Citric acid modified sesame straw	Methylene blue	$650\,mg\,g^{-1}$	-C=O, —COO^{-}	Complexation	Feng et al. 2017
	Tartaric acid modified sesame straw		$280\,mg\,g^{-1}$			
	N-isopropylacrylamide and citric acid modified rice husk	Cu^{2+}	$84.67\,mg\,g^{-1}$	-C=O, —COOH, —NH	Chelation and ion exchange	Kumar and Sharma 2019
		Pb^{2+}	$118.3\,mg\,g^{-1}$			
		Ni^{2+}	$79.87\,mg\,g^{-1}$			
	Succinic anhydride modified cotton	Pb^{2+}	$465.1\,mg\,g^{-1}$	-C-O, —COO^{-}	Complexation and ion exchange	Yu et al. 2013
		Cd^{2+}	$344.8\,mg\,g^{-1}$			

biosorption energy of citric acid modified barley straw for Cu^{2+} adsorption was $8.513\,kJ\,mol^{-1}$, indicating a chemical adsorption mechanism, as opposed to a physical adsorption mechanism for the raw biomass (Pehlivan et al. 2012). Similarly, Pb^{2+} adsorption capacity increased from $125.84\,mg\,g^{-1}$ (raw grain) to $293.30\,mg\,g^{-1}$ (citric acid esterified grain) due to the formation of both ester linkages and grafting of carboxyl groups (Pehlivan et al. 2012). For organic pollutants, the intensity of chemisorption was closely related to the number of functional groups. Methylene blue adsorption capacity increased from $170\,mg\,g^{-1}$ (raw biomass) to $650\,mg\,g^{-1}$ (citric acid treatment) and $280\,mg\,g^{-1}$ (tartaric acid treatment) (Feng et al. 2017). The larger methylene blue adsorption capacity for the citric acid treatment was due to a larger increase of C=O in carboxyl groups, which interacted with methylene blue via complexation. In general, carboxyl and amino functional groups are the most common groups introduced onto adsorbents by esterification, which consequently improve adsorption performance through complexation reactions.

2.4 Etherification

Ethers are synthesized through etherification, whereby -OH groups on agricultural wastes are substituted by other functional groups (Hokkanen et al. 2016). Reaction of -OH groups with ethylene oxide or other epoxides is a typical etherification reaction yielding several reactive sites for further functionalization to introduce adsorption groups. Triethyleneteramine, diethylenetriamine and ethylenediamine are usually used to generate amine groups for adsorbents during the functionalization process. Generally, carboxyl, thio and amino functional groups are introduced to the biomass surfaces by the etherification process (Kong et al. 2018; Wang et al. 2017).

Etherification may generate positively-charged functional groups to augment sorption sites for retention of anions, such as PO_4^{3-}, NO_3^{-} and SO_4^{2-} (de Lima et al. 2012; Keranen et al. 2015; Qiao et al. 2019). The interaction between epichlorohydrin and -OH groups of agricultural wastes is a common etherification process to generate new functional groups. For example, epoxy and amino groups were introduced onto raw rice straw by reaction between epichlorohydrin and trimethylamine (Cao et al. 2011). An FTIR peak associated with the C-N bond at $1470\,cm^{-1}$ and a peak for quaternary ammonium salt at $1062\,cm^{-1}$ appeared on the surface of rice straw following modification, thereby indicating generation of positively charged amino groups. This etherification process increased the total exchange capacity of the adsorbent from 0.32 to $1.64\,mEq\,g^{-1}$ and rapid adsorption of

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sulfate via an ion exchange mechanism. Similarly, ethylenediamine-cross-linked wheat straw was utilized to introduce amine groups for use in removing $HCrO_4^-$ and $H_2PO_4^-$ from solutions (Xu et al. 2011). Although the BET surface area of the modified biomass decreased from 6.5 to $5.3\,m^2\,g^{-1}$, the modification process increased the quantity of positive charge. After modification, the zeta potential of the modified wheat straw was in the range of $+39.3 \sim -7.0\,mV$ compared with $+5.2 \sim -45.8\,mV$ for the raw wheat straw. The higher zeta potential for the modified material was attributed to the presence of $-CN^+$, which possessed a stronger electrostatic attraction for anionic pollutants. Several studies have documented the efficacy of etherification for increasing the reactivity of agricultural wastes for retention of anionic pollutants through electrostatic interactions (Chen et al. 2011; Wu et al. 2016).

Etherification processes are also utilized to improve the removal rate of cationic pollutants by introducing amino groups for modified adsorbents. Kong et al. (2018) introduced amino and carboxyl groups on the surface of wheat straw to investigate Cu^{2+} sorption behavior. They found that the introduced $-NH_2$ groups shared their lone pair of electrons to form $R\text{-}NH_2Cu^{2+}$ complexes as the adsorption mechanism. Moreover, the introduced -COOH groups facilitated charge transfer to the O to attract the Cu^{2+}, thereby further promoting Cu^{2+} retention. Etherification can also generate thio groups on adsorbents to attach cationic pollutants. Moreover, ethylenediamine and CS_2 treatment generated S-containing functional groups on sugarcane bagasse, which played an important role in adsorbing Pb^{2+}, Cu^{2+} and Zn^{2+} (Wang et al. 2017). Characterization of the etherification product indicated formation of $-S=$metal bonds formed through coordination bonds with the S atom in the biosorbent owing to the lone pair of S electrons sharing a bond with the metal.

A summary of etherification modified agricultural wastes as adsorbents for the removal of pollutants from aqueous solution were presented in Table 4. The maximum Cu^{2+} sorption capacity of etherified wheat straw cellulose reached up to $130\,mg\,g^{-1}$, which were attributed to complexation reactions of Cu^{2+} with the amino and carboxyl groups generated by etherification (Kong et al. 2018). Additionally, adding an activated bond of -CN (acrylonitrile) to the cellulose -OH groups greatly improves Cd^{2+} adsorption performance (Zheng et al. 2010a). The Langmuir sorption model provided a better fit to the Cd^{2+} adsorption equilibrium data than a Freundlich model, and determined a maximum uptake of $12.73\,mg\,g^{-1}$ for modified corn stalks, compared to $3.39\,mg\,g^{-1}$ for raw corn stalks. With respect to anionic retention, etherification of rice straw increased the maximum adsorption capacity of sulfate from 11.68 to $74.76\,mg\,g^{-1}$ by introducing amino groups (Cao et al. 2011). Generation of positively charge, $-C\text{-}N^+$ moieties, was responsible for the removal of sulfate by electrostatic

Table 4 Sorption performance of etherification modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Adsorption capacity	Functional groups	Sorption mechanism	Reference
Etherification	Ethylenediamine and CS_2 modified sugarcane bagasse	Pb^{2+}	$558.9\,mg\,g^{-1}$	-CS, $-N\text{-}H$, $-OH$, $-C\text{-}O$	Complexation and ion exchange	Wang et al. 2017
		Cu^{2+}	$446.2\,mg\,g^{-1}$			
		Zn^{2+}	$363.3\,mg\,g^{-1}$			
	Acrylonitrile modified corn stalk	Cd^{2+}	$12.73\,mg\,g^{-1}$	-C-N, $-OH$, $-C\text{-}O$	Complexation	Zheng et al. 2010b
	Trimethylamine modified rice straw	SO_4^{2-}	$74.76\,mg\,g^{-1}$	$-C\text{-}N^+$	Ion exchange	Cao et al. 2011
	Triethylamine modified wheat straw	Cr^{6+} ($Cr_2O_7^{2-}$)	$5.68\,mmol\,g^{-1}$	$-C\text{-}N^+$, $-COOH$	Complexation and electrostatic attraction	Xu et al. 2011
		PO_4^{3-}	$1.71\,mmol\,g^{-1}$	$-C\text{-}N^+$	Electrostatic attraction	
	Triethylamine modified rice straw	Cr^{6+} ($Cr_2O_7^{2-}$)	$15.82\,mg\,g^{-1}$	$-NH_3^+$	Electrostatic attraction	Wu et al. 2016
		Ni^{2+}	$3.95\,mg\,g^{-1}$	$-NH_2$	Complexation	
	Diethylenetriamine modified corn stalks	Cr^{6+} ($Cr_2O_7^{2-}$)	$200.00\,mg\,g^{-1}$	$-C\text{-}N^+$	Electrostatic attraction	Chen et al. 2011
	2-hydroxypropyltrimethyl ammonium chloride modified coconut shell fiber	NO_3^-	$33.74\,mg\,g^{-1}$	$-C\text{-}N^+$	Electrostatic attraction	de Lima et al. 2012
		SO_4^{2-}	$31.22\,mg\,g^{-1}$			
		PO_4^{3-}	$200.57\,mg\,g^{-1}$			
	Amine cross-linked tea leaves	NO_3^-	$136.43\,mg\,g^{-1}$	$-C\text{-}N^+$, $-C\text{-}Cl$	Electrostatic attraction and ion-exchange	Qiao et al. 2019
		PO_4^{3-}	$98.72\,mg\,g^{-1}$			
		Crystal violet	$159.24\,mg\,g^{-1}$			

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interactions. Furthermore, triethylamine-etherification significantly accelerated the adsorption rate of wheat straw for anionic constituents (Xu et al. 2011). Adsorption equilibrium was achieved in 35 min for $HCrO_4^-$ and 15 min for $H_2PO_4^-$, compared with 3 hr for the unaltered biomass. Accordingly, the adsorption capacity of modified wheat straw for $HCrO_4^-$ and $H_2PO_4^-$ were 0.98 and 1.15 mmol g^{-1}, respectively. Electrostatic attraction, complexation and ion exchange mechanisms were the most prominent sorption mechanisms contributing to cationic and anionic retention by etherified adsorbents.

2.5 Carbonization

Carbonization is a thermal decomposition process of organic materials resulting in the production of a carbonaceous residue with a concomitant removal of distillates. Conversion of agricultural wastes into biochar (a heterogeneous charcoal material) is a common carbonization process that has been extensively studied (Jung et al. 2015; Yang et al. 2019). Biochar products have a larger specific surface area, greater porosity and more functional groups than the raw agricultural wastes from which they were formed (Divband Hafshejani et al. 2016). The alkaline nature (causd by the formation of alkaline carbonate during the pyrolysis) and the existence of mineral constituents on biochar surfaces also promote the formation of metal precipitates on the biochar surface (Liu et al. 2020b; Wu et al. 2018; Dai et al. 2014). The fixation ability of original biochar for pollutants is relatively limited and many studies have explored altering pyrolysis conditions (e.g., temperature, feedstock, chemical amendments) to generate activated biochars with altered functional groups and rougher surfaces to enhance sorption capacities for various pollutants.

Carbonization temperature has an especially strong effect on the properties of biochar generated from agricultural waste (Qiu et al. 2021). In general, biochar produced at lower temperatures (< 500 °C) contains a greater functional group content, whereas those produced at higher temperatures (500 ~ 700 °C) have a more porous surface and overall porosity (Oliveira et al. 2017). For example, aldehyde and ketone functionalities formed at ~ 200 °C and became dominant at 300 ~ 500 °C, increasing the adsorption capacity for various pollutants (Zhang et al. 2020). However, the drastic fusion of the ring structures in biochar occurred from 550 to 650 °C, which decreased the content of functional groups and weakened the chemical fixation for pollutants. The influence of feedstock source (i.e., type of biomass material) is also an important factor determining the efficiency of pollutant removal by agricultural waste-derived biochars. The type of functional groups and chemical components comprising various agricultural wastes are different, thereby

significantly affecting the adsorption performance. The most important of these properties in relation to the adsorption capacity were the O/C ratio, the P content and the ash content (Arán et al. 2016). The capacity of the biochar to retain Cu present in solution depended on the size of the inorganic fraction and varied in the following order: rice biochar > chicken manure biochar > olive mill waste biochar > acacia biochar > eucalyptus biochar > corn cob biochar.

The addition of chemical amendments to the biomass feedstock has an appreciable effect on biochar characteristics and the adsorption performance of the biochar material. The selective introduction of functional groups, heteroatoms, metal atoms into biochar can improve its specific properties. In-situ synthesis of biochar refers to the preparation of modified biochar in only one step by simultaneously pyrolyzing reagents and agriculture wastes. As a result, the modified biochar has the optimized physicochemical structures and properties. Post-optimization of biochar is useful to further enhance its potential value after pyrolysis, a special biochar could be designed via the further surface modification and pore regulation.

Addition of acidic reagents has been shown to markedly increase functional group content. For example, H_2SO_4 addition during carbonization generated excellent sorption performance for methylene blue, brilliant green, crystal violet and orange G by formation of -SO_3 groups on the biochar surface that increased the chemical affinity for pollutants through covalent bonding (Goswami and Phukan 2017). Similarly, HNO_3 addition to the feedstock generated N-containing functional groups on biochar, with the positive $\equiv N^+$ group interacting with the negative -$O\equiv$, $N=C$ and heterocycle N-C groups on methylene blue to facilitate adsorption (Yu et al. 2018). In addition, the weakly acidic $FeCl_3$ would be transformed to Fe_2O_3 during the preparation process of biochar, increasing the Fe-O functional groups strongly on the surface of biochar (Qu et al. 2022b). The peaks of Fe $2p_{1/2}$ and Fe $2p_{3/2}$ shifted after the stabilization of Cd, suggesting that the iron-bound functional groups participated in the Cd retention actively.

The addition of alkaline reagents was shown to increase both surface area and functional group content of biochars. Activation of orange peel biochar with $CO(NH_2)_2$ and KOH strongly altered several physicochemical properties (Xiao et al. 2020). During pyrolysis, $CO(NH_2)_2$ reacted with K_2CO_3 (an intermediate of KOH activation) to generate NH_3 and create a more porous structure with increased N-containing groups, which correspondingly increased the retention of methylene blue. Addition of oxidizing agents is a common technique for generating higher concentrations of oxygenated functional groups

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on biochar surfaces (Yang et al. 2019). Co-pyrolyzed peanut hulls with H_2O_2 resulted in an increase in the O content (16.4 ➔ 22.3%) and surface carboxyl functional groups, improving chemical adsorption (Xue et al. 2012). As another example of oxidation effects, a $KMnO_4$-treated hickory wood biochar surface was covered with ultrafine MnO_x particles exhibiting a surface enrichment of O-containing functional groups and a higher surface area (Wang et al. 2015). Metal retention by this engineered biochar mainly resulted from surface adsorption mechanisms involving both the surface MnO_x particles and O-containing functional groups.

A myriad of studies have demonstrated the efficacy of carbonization as an effective method for improving the adsorption performance of agricultural wastes, especially for modified biochar adsorbents (Table 5). The total adsorption capacity for Cd^{2+} increased due to the introduction of C-S complexes on biochar that facilitated the retention of Cd^{2+} through a strong bond with S (Tajar et al. 2009). Wang et al. (2018) showed that maximum acid red 18 dye sorption capacities for

NH_4Cl/CH_3COONH_4-modified adsorbents were 1.41 and 1.18 times higher than for non-N-doped biochar. The enhanced sorption affinity was mainly attributed to π-π EDA (electron donor-acceptor) interactions between pyridine-N groups and acid red 18. The N functional groups enhanced the surface polarity, thereby increasing interactions with adsorbates, such as acid red 18. In addition, the amino functional group ($-NH_2$) greatly improved the adsorption behavior of Cr^{6+} ($Cr_2O_7{}^{2-}$) by polyethylenimine-treated rice husk biochar (Ma et al. 2014). A pseudo-second-order kinetic model indicated a maximum Cr^{6+} ($Cr_2O_7{}^{2-}$) adsorption capacity of $435.7\,mg\,g^{-1}$ compared to only $23.09\,mg\,g^{-1}$ for natural biochar. Moreover, this new material exhibited excellent cyclic adsorption ability (recycled use) making it a low-cost, ecofriendly adsorbent.

In summary, carbonized agricultural wastes are an economical and effective approach for pollutant removal from water owing to their intrinsic physicochemical characteristics. Abundant functional groups, high surface area and a porous structure allow biochars to rapidly

Table 5 Sorption performance of carbonization modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Adsorption capacity	Functional groups	Sorption mechanism	Reference
Carbonization	H_2O_2 modified peanut hull biochar	Pb^{2+}	$22.82\,mg\,g^{-1}$	-COOH	Complexation	Xue et al. 2012
	H_3PO_4 modified corn straw biochar	Triazine	$79.6\,mg\,g^{-1}$	-C=O, $-$C-O, $-$COOH, $-PO_3$	Electrostatic interaction	Suo et al. 2019
	KOH modified rice straw biochar	Cd^{2+}	$41.9\,mg\,g^{-1}$	OH^-	Ion exchange and precipitation	Bashir et al. 2018
	$KMnO_4$ modified hickory wood biochar	Pb^{2+}	$153.1\,mg\,g^{-1}$	-C=O-O, $-$C-O	Complexation and electron attraction	Wang et al. 2015
		Cu^{2+}	$34.2\,mg\,g^{-1}$			
		Cd^{2+}	$28.1\,mg\,g^{-1}$			
	$CO(NH_2)_2$ and KOH modified orange peel biochar	Toluene	$724.0\,mg\,g^{-1}$	-C=C, $-$OH, $-$NH	Complexation and H-bonding	Xiao et al. 2020
		Iodine	$2252.0\,mg\,g^{-1}$			
	Banana peels derived hierarchically porous carbons	Methylene blue	$1303.54\,mg\,g^{-1}$	-C=C, $-$OH, $-$COOH, $-COO^-$, $\equiv N^+$	Electrostatic interaction, π-π stacking and H-bonding	Yu et al. 2018
		Co^{2+}	$122.39\,mg\,g^{-1}$		Complexation and ion exchange	
	NH_4Cl modified *Phragmites australis* biochar	Acid red 18	$115.94\,mg\,g^{-1}$	-C=C, $-$C-N	π-π EDA interaction	Wang et al. 2018
	CH_3COONH_4 modified *Phragmites australis* biochar		$134.17\,mg\,g^{-1}$			
	H_2SO_4 modified tea leaf derived carbon	Orange G	$105.7\,mg\,g^{-1}$	-S=O, $-$S-O, $-$OH	Complexation and electrostatic interactions	Goswami and Phukan 2017
		Rhodamine B	$757.6\,mg\,g^{-1}$			
	SO_2 modified nut shell biochar	Cd^{2+}	$142.86\,mg\,g^{-1}$	-COOH, $-$C=C, $-$C=S, $-$OH	Complexation	Tajar et al. 2009
	SO_2 and H_2S modified bagasse pith biochar	Hg^{2+}	$188.68\,mg\,g^{-1}$	-S-O, $-$S-S, $-$C=S	Complexation	Krishnan and Anirudhan 2002

interact with pollutants through a variety of adsorption mechanisms (e.g., complexation, ion exchange, covalent bonding, π-π interactions, H-bonding and precipitation). Furthermore, introduction of chemical amendments (e.g., acids, bases, oxidizers, metals) to the carbonization process can generate specific chemical moieties that selectively target the removal of specific pollutants.

2.6 Magnetization

Magnetization of modified agricultural wastes, such as biochar, is a strategy to introduce transition metals or their oxides into the organic matrix to create a material (e.g., $FeCl_3$, Fe_3O_4, Fe_2O_3 and zero-valent iron nanoparticles) that is easily separable with an external magnet. Importantly, magnetic adsorbents can be easily removed making them highly effective for the removal of pollutants from aqueous solutions. Moreover, the doping of metals or metal oxides onto the surface of agricultural wastes can target specific functionalities to enhance adsorption properties, such as the modification of lignocellulose by magnetic materials to improve sorption of chloramphenicol while simultaneously allowing easy recovery and reuse of the material during adsorption applications (Dai et al. 2016).

Nanoscale-zero-valent, iron-coated wheat straw exhibited better adsorption performance for removal of Cu^{2+} than the raw adsorbent (Shao et al. 2020). A portion of the Cu^{2+} was directly adsorbed by the wheat straw, whereas another fraction of the Cu^{2+} was first reduced to zero-valent Cu and Cu_2O, which were subsequently attached to the surface of the material as part of the crystalline Fe-oxide structure. Further, doping agricultural wastes with Fe oxides was shown to promote the removal of anionic As^{5+} ($H_2AsO_4^-$) due to enhanced surface interactions associated with the Fe oxides (Pehlivan et al. 2013). The Fe-oxide modified sugarcane bagasse rapidly removed $H_2AsO_4^-$ oxyanions by electrostatic interactions, ligand exchange and chelation reactions between the positively charged surface $\equiv FeOH^{2+}$ group and the negatively charged $H_2AsO_4^-$.

Loading Fe_3O_4 (magnetite) on the surface of organic materials is a common technique for magnetization that can be achieved by ferrofluids, microwave assisted and mechanochemical techniques (Safarik et al. 2020; Safarik and Safarikova 2014). Co-precipitation is also widely adopted to synthesize and load Fe_3O_4 on material surfaces, the changes for -OH and Fe-O groups in Fe_3O_4-modified straw resulting from the combination of O in the straw with the Fe of Fe_3O_4 (Haghighat and Ameri 2016). The modification further increased the BET surface area from 3.37 to 23.56 $m^2 g^{-1}$. Pb^{2+} was retained on the Fe_3O_4-modified straw through diffusion adsorption and chemical fixation with O-containing functional groups. Similarly, Khandanlou et al. (2015) demonstrated an increase in the pore volume and BET surface area by 12 and 22 times after Fe_3O_4 modification, respectively. The enhanced porosity and functional group activation prominently promoted the adsorption of Cu^{2+} and Pb^{2+}. Further, a Fe_3O_4_doped organic adsorbent (sugarcane bagasse) exhibited excellent sorption capacity for Cd^{2+} and Pb^{2+}, with Fe-OH groups playing an important role in the adsorption mechanism (Liu et al. 2020a). The modified adsorbent also had a more robust regeneration efficacy than the raw bagasse as the Fe_3O_4 stabilized the surface properties. The effect of SnO_2/Fe_3O_4 doping on the adsorption affinity of reactive blue 4 and crystal violet by treated rice bran was investigated by Ma et al. (2020a). They found that pore size was increased by $2 \sim 4$ nm and the FTIR peaks for Sn-O and Fe-O strengthened upon doping with SnO_2/Fe_3O_4. The numerous -OH groups associated with the SnO_2/Fe_3O_4-adsorbent interacted with the reactive blue 4 and crystal violet to effectively remove these polluting dyes from solution.

The removal efficiencies of magnetic biosorbents for pollutants are listed in Table 6. Magnetization of wheat straw increased the adsorption capacity for Pb^{2+} by 23%, with an optimal contact time of 30 min facilitating rapid processing (Haghighat and Ameri 2016). Baldikova et al. (2016) found that magnetized barley straw increased adsorption of methylene blue and crystal violet by 16.7% and 54.9%, respectively, due to creation of a larger surface area. Further, the SnO_2/Fe_3O_4-doped rice bran showed a high adsorption affinity for reactive blue 4 and crystal violet with sorption capacities of 218.8 and 159.2 $mg g^{-1}$, respectively (Ma et al. 2020a). Characterization of the SnO_2/Fe_3O_4-absorbent indicated that the surface was covered with abundant -OH functional groups, which played an important role in increasing the adsorption capacity through strong electron attraction. Moreover, Fe oxide-modified sugarcane bagasse showed a superior potential for $H_2AsO_4^-$ removal (up to 22.1 $mg g^{-1}$) compared to several other modification methods (Pehlivan et al. 2013). Positively charged $\equiv FeOH_2^+$ and negatively charged $H_2AsO_4^-$ rapidly interacted through electrostatic interactions and ligand exchange reactions. Overall, magnetic adsorbents have demonstrated the capacity to efficiently remove heavy metals, anionic constituents, antibiotics and various dyes from water. The most prominent feature of magnetic modification is that a product can be easily recovered and reused, with improved the utilization efficiency and reduces production/use costs.

2.7 Surfactants

Surfactants are compounds that consist of hydrophilic heads and hydrophobic tails, which can reduce the

Table 6 Sorption performance of magnetization modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Adsorption capacity	Functional groups	Sorption mechanism	Reference
Magnetization	Citric acid and Fe_3O_4 modified sugarcane bagasse	Cd^{2+}	$118.3\,mg\,g^{-1}$	-C=C, −COOH, −COO$^-$, −OH, −Fe-O	Complexation, ion exchange and cation-π	Liu et al. 2020a
		Pb^{2+}	$34.5\,mg\,g^{-1}$			
	Fe_3O_4 modified rice straw	Cu^{2+}	$16.31\,mg\,g^{-1}$	—	H-bonding	Khandanlou et al. 2015
		Pb^{2+}	$19.45\,mg\,g^{-1}$			
	Fe oxides modified sugarcane bagasse	As^{5+} (AsO_4^{3-})	$22.1\,mg\,g^{-1}$	$\equiv$Fe-OH$_2^+$	Surface precipitation, ion exchange and complexation	Pehlivan et al. 2013
	Nanoscale zero-valent iron modified wheat straw	Chlortetracycline	$1280.80\,mg\,g^{-1}$	-OH	Complexation and degradation	Shao et al. 2020
		Cu^{2+}	$376.4\,mg\,g^{-1}$		Complexation	
	SnO_2/Fe_3O_4 modified rice bran nanoparticles	Reactive blue 4	$218.82\,mg\,g^{-1}$	-NH$_2$, −COOH, −OH	Electron attraction	Ma et al. 2020a
		Crystal violet	$159.24\,mg\,g^{-1}$			

surface tension between different media when used as detergents and dispersing agents (Lee et al. 2018). The charge characteristics of the hydrophilic head classify the surfactants as ionic and non-ionic surfactant groups (Abrankó-Rideg et al. 2015). Various functional groups (e.g., phosphates, sulphonates and quaternary ammonium salts) occur in the structure of ionic surfactants, favoring the selective adsorption of various pollutants in solutions. Thus, surfactant modifications improve the surface hydrophobic/hydrophilic properties and enrich the variety and quantity of functional groups comprising agricultural wastes. Linear alkyl benzene sulphonates, secondary alkane sulphonates, alkyl trimethyl ammonium halides and quaternary ammonium-based compounds are common surfactants with widespread applications (Ying 2006).

Cationic surfactant treated agricultural wastes demonstrate a good potential for removal of anionic pollutants. Cetyl trimethyl ammonium bromide modified wheat straw obtained higher N (0.44%), C (46.32%) and H (6.49%) contents than that of the origin wheat straw (0.22% N, 42.34% C, and 5.81% H) due to the loading of the surfactant (Zhang et al. 2014). FTIR spectra indicated that the -CH$_2$ peak strengthened while the -NH$_2$ and -OH bands broadened in wheat straw after modification. Changes in these characteristics indicated that modification increased the number of ammonia functional groups, which combined with Congo red dye through ionic interactions. Moreover, the adsorption results indicated that π-π dispersion interactions between the surfactant and dye played an important role in the removal of the Congo red dye. Furthermore, Thamilarasi et al. (2018) found that cetyl trimethyl ammonium bromide formed a surfactant bilayer containing anion exchange properties due to reaction with acidic functional groups on palm fruit husk surfaces. The surfactant loading on the surface of the palm fruit husk surface reached a maximum at a cetyl trimethyl ammonium bromide concentration of 1.0% in solution. The cationic surfactants created numerous positive charges on the adsorbent surface, which increased its retention of negatively charged VO_4^{3-} in solution. Notably, some studies showed that surfactant modification decreased the BET surface area of adsorbents. For example, tetradecyl trimethyl ammonium bromide treated corn straw had a lower BET surface area ($4.21\,m^2\,g^{-1}$) than that of the original straw ($7.29\,m^2\,g^{-1}$) (Soldatkina and Zavrichko 2019). This phenomenon might be caused by the blockage of pores and loss of access to internal surface area; however, the loss of surface area did not affect the enhanced adsorption performance of the modified agricultural waste for acid red, acid orange and VO_4^{3-} due to a concomitant increase in the number of positive sites.

Sodium dodecyl sulfate is a common anionic surfactant used to improve the adsorbent performance for positively charged pollutants. Pirbazari et al. (2016) determined that surfactant molecules created aggregates on the surface of rice straw, which promoted the formation of a porous adsorbent structure during the modification. SEM characterization showed that the surface of modified straw was rougher with a specific surface area of 150 $m^2\,g^{-1}$ compared with 58 $m^2\,g^{-1}$ for the original straw, which provided an enhanced adsorption capacity for methylene blue. In addition, a -SO$_3$ group was attached to the surface of the modified straw further increasing the adsorption capacity. Similarly, studies have demonstrated that sodium dodecyl sulfate treated peanut husk exhibited a high removal efficiency for rhodamine B dye in solution (Fatimah

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et al. 2018). Kinetic studies demonstrated that the adsorption of rhodamine B by the modified peanut husk was best described with a pseudo-second-order kinetic model, indicating that chemical interactions played a dominant role in the retention of the rhodamine B dye.

Surfactant-modified agricultural waste products for the removal of a diverse range of aquatic pollutants are summarized in Table 7. The maximum adsorption capacity of sodium dodecyl sulfate treated peanut husks for rhodamine B was 240.0 mg g^{-1}, which was about a 100-fold increase compared to the pristine husks (Fatimah et al. 2018). Pollutant adsorption onto the modified adsorbent was mainly controlled by a hydrophobic interaction mechanism, along with a considerable contribution from a cation exchange mechanism (Pirbazari et al. 2016). In addition, cetyl trimethyl ammonium bromide strengthened π-π interactions for organic pollutants due to the increasing role of benzene rings in the adsorption process (Zhang et al. 2014). As a result, the adsorption performance of modified wheat straw for Congo red dye was about a factor of two times higher than for the untreated straw. Although a decrease in BET surface area may occur in surfactant-modified adsorbents due to the constriction of pore channels by attachment of surfactant moieties, the overall adsorption performance for several pollutants increased due to an increased number of positively charged surface sites (Thamilarasi et al. 2018). Overall, surfactant modification is a feasible method for improving adsorption performance due to significant changes in surface properties of the adsorbent, such as the hydrophobicity, hydrophilicity and functional groups.

2.8 Grafting

Grafting of polymers onto the surface of agricultural wastes is an important technique for selectively imparting the chemical characteristics of the polymer to the waste structure. Therein, the backbone of a polymer is linked to a side chain of lignocellulose in agricultural waste to form a branched copolymer (Hokkanen et al. 2016). Grafting-to, grafting-from and grafting-through are the three main linkage types, which are based on the type of polymer. Grafting-from is the most common method for introducing polymers onto agricultural waste surfaces. The process involves the addition of monomer units to form copolymers on the adsorbent surface, which transforms the surface functionality (Carlmark. 2013). Usually, grafting-from treatment occurs in an aqueous environment and a suitable initiator is required to induce the modification reaction. Chemical, radiation and photochemical processes are the main techniques employed to initiate the grafting process. For example, a chemical initiator generates free radicals to react with -OH groups on lignocellulose and is widely used due to its ease of operation and low cost. Potassium permanganate ($KMnO_4$), potassium persulfate ($K_2S_2O_8$) and ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$) are common initiators for polymerization of monomers on agricultural wastes (Li et al. 2012; Zheng et al. 2010b). Many monomeric species, such as acrylic acid, acrylamide, acrylonitrile and aniline, are used for the synthesis of a polymeric adsorbent surface (Kumar et al. 2018). These monomers usually contain acidic ($-COOH$, $-SO_3H$, $-COONa$, $-SO_3Na$) or basic ($-NH_2$) functional groups.

Corn stalk was modified with an acrylonitrile monomer in the presence of $KMnO_4$ as the initiator (Zheng

Table 7 Sorption performance of surfactant modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Sorption capacity	Functional groups	Sorption mechanism	Reference
Surfactant modification	Sodium dodecyl sulfate modified rice straw	Methylene blue	296 mg g^{-1}	-SO$_4$Na	Hydrophobic interaction and cationic exchange	Pirbazari et al. 2016
	Cetyltrimethyl ammonium bromide modified wheat straw	Congo red dye	665 mg g^{-1}	-C=C	π-π interaction	Zhang et al. 2014
	Sodium dodecyl sulfate-modified peanut shel	Rhodamine B	236.699 meq g^{-1}	-SO$_4$Na	Complexation	Fatimah et al. 2018
	Hexadecylpyridinium bromide modified peanut husk	Light green	146.2 mg g^{-1}	-COOH and -C=C	Electrostatic attraction and π-π interaction	Zhao et al. 2017
	Epichlorohydrin and triethylenetetramine modified peanut husk	Cr^{6+}(Cr$_2$O$_7^{2-}$)	138.34 mg g^{-1}	-OH, −COOH and -C-N	Ion exchange	Yue et al. 2013

et al. 2010b), resulting in the -OH groups of cellulose reacting with the monomer to form copolymers on the surface. A FTIR spectrum indicated the presence of -CN functional groups and the N content of the corn stalk increased from 1.11% to 4.02%. The grafted material sorbed Cd^{2+} yielding an activation energy (E_α) of $9.43\,kJ\,mol^{-1}$, indicating that the Cd^{2+} retention mechanism was a chemical process. Further, the adsorption behaviors of Indosol orange RSN and Indosol black NF by polyethyleneimine-grafted peanut husks were studied by Sadaf et al. (2015). The -NH and -C=O functional groups were introduced by the modification process and the adsorbent surface became rougher (i.e., more porous) as determined by FTIR and SEM analyses, respectively. As a result, the Indosol dyes reacted with the carboxylic and carbonyl functional groups leading to their efficient removal. Additionally, Fotsing et al. (2020) demonstrated that polyethyleneimine-grafted cocoa shell was an effective material for the removal of NO_3^- and Cr^{6+} ($Cr_2O_7^{2-}$) from solutions. The pH_{pzc} value of modified cocoa shell was 9.3, much higher than untreated adsorbent (3.4) due to the large number of amino groups grafted on the material surface. Amino groups on the surface of the modified adsorbent reacted with H^+ during acidic treatment, producing a surficial-NH_3^+ moiety, which subsequently adsorbed NO_3^- and Cr^{6+} ($Cr_2O_7^{2-}$) through electrostatic attraction.

Polyaniline grafting to agricultural wastes strongly alters their physiochemical properties, which in turn strongly alters adsorption performance for various pollutants. For instance, Soldatkina and Zavrichko (2017) prepared a new composite by chemical polymerization of aniline on the surface of corn stalks using ammonium persulfate $(NH_4)_2S_2O_8$ as an oxidation agent and H_3PO_4 as a dopant. H-bonding and π-π interactions between aniline and cellulose in the corn stalk structure anchored aniline firmly to the surface of the material. Moreover, the specific surface area of the adsorbent increased from

15.1 to $46.9\,m^2\,g^{-1}$ after modification, facilitating physical adsorption of acid red and acid orange dyes. In addition, π-π interactions between aniline and the two dyes promoted chemical adsorption. Some reagents can also exhibit excellent adsorption performance for pollutants without changing adsorbents surface structure srongly due to the unique properties of reagents. For instance, β-cyclodextrin has a well-developed three-dimensional structure (cavity) and numerous -OH, which made modified rice husk adsorb Pb and bisphenol A quite effectively (Liu et al. 2022). β-cyclodextrin grafting accomplished synergetic Pb and bisphenol A elimination through averting their competitive behaviors owing to diverse capture mechanisms for Pb (ion exchange, complexation and electrostatic attraction) and bisphenol A (hydrogen bonding and host-guest inclusion).

Grafting treatment improves agricultural waste adsorption for several pollutants as summarized in Table 8. The adsorption capacity of Congo red dye by polyphenolic tannin treated jute fiber was much higher than for the untreated fibers (Roy et al. 2013). The N atoms in -N=N- and -NH_2 and S and O atoms in the -SO_3^- moiety of the modified adsorbent participated in removal of Congo red dye via formation of intermolecular hydrogen bonds with the -OH moiety of the dye. Further, aniline modified corn stalk exhibited high adsorption capacity and efficiency for acid red and acid orange compared with unmodified corn stalk (Soldatkina and Zavrichko 2017). Adsorption equilibrium occurred within 120–150 min and the adsorption capacity of the modified corn stalk was ~2 times more than that of raw stalk (Soldatkina and Zavrichko 2017).

Grafting treatment of agricultural wastes has also been shown to enhance adsorption performance for inorganic pollutants. Acrylonitrile-modified corn stalk showed a maximum Cd^{2+} uptake of $12.7\,mg\,g^{-1}$ compared with $3.4\,mg\,g^{-1}$ for raw corn stalk, owing to an increase of -CN groups that promoted metal complexation (Zheng et al. 2010b). Similarly, polyethyleneimine-modified

Table 8 Sorption performance of grafing modified agricultural wastes as adsorbents for pollutant removal from water

Modification	Adsorbent	Adsorbate	Sorption capacity	Functional groups	Sorption mechanism	Reference
Grafing	Acrylic acid grafted cellulosic *Luffa cylindrical* fiber	Methylene blue	$62.15\,mg\,g^{-1}$	-COOH	Electrostatic attraction and Van der Waals forces	Gupta et al. 2013
	Methyl acrylate/acrylamide modified *Luffa cylindrica* fiber	Congo red	$17.39\,mg\,g^{-1}$	-C=O	Complexation	Gupta et al. 2014
	Epichlorohydrin modified pine needles	Congo red	$34.7\,mg\,g^{-1}$	-C=O	Complexation	Kumari et al. 2016
	Polyethyleneimine modified peanut shell	$Cr^{6+}(Cr_2O_7^{2-})$	$32.0\,mg\,g^{-1}$	-NH_3^+	Electrostatic attraction	Ma et al. 2020b
	Ethylenediamine modified peanut shell	Hg^{2+}	$30.72\,mg\,g^{-1}$	-NH	Electrostatic attraction	Liu et al. 2010

peanut shells increased the number of positive charges on the modified surface, thereby strengthening electron attraction for Cr^{6+} ($Cr_2O_7^{2-}$) in the pH range of 2.0–11.0 (Ma et al. 2020b). Sorption of Cr^{6+} ($Cr_2O_7^{2-}$) followed 2nd-order kinetics and a Freundlich-type isotherm, with a maximum adsorption capacity of $24.8\,mg\,g^{-1}$. Overall, the primary adsorption mechanisms for grafted adsorbents were complex formation and electrostatic attraction between the grafted functional groups and pollutants in the solution.

3 Functional groups and their roles on adsorption mechanisms

3.1 O-containing functional groups

O-containing functional groups play a predominant role in surface reactions, hydrophobic/hydrophilic characteristics and electrical properties of adsorbents (Yang et al. 2019). The -OH and -COOH moieties are among the most abundant functional groups and participate in a wide range of adsorption mechanisms with various types of pollutants (Kurup 2012; Zafar et al. 2020) (Fig. 2). The adsorption of heavy metals (Cd^{2+}, Pb^{2+} and Zn^{2+}) and dyes (basic red 18, methylene blue, and acid red 111) by HNO_3 modified agave bagasse and oreganum stalks increased due to generation of -OH and -COOH on the surface of the modified materials (Velazquez-Jimenez et al. 2013). The -OH and -COOH groups may dissociate

to form of $-O^-$ and $-COO^-$ upon interaction with water (Azzaz et al. 2017; Han et al. 2010) (Fig. 2). These acid ionic functional groups can interact with cationic pollutants through ion exchange or electron attraction mechanisms.

The -C=O and -C-O groups are commonly associated with modified agricultural waste products (Li et al. 2010; Ogata et al. 2015; Wang et al. 2017) (Fig. 2). For example, NaOH treatment increased the -C-O- content of wheat straw, which enhanced Cu^{2+} adsorption (Guo et al. 2016). The Cu^{2+} adsorption occurred primarily through a complexation interaction between -C-O- and the metal (Yu et al. 2013). Given the multifunctionality of modified agricultural wastes, most complexation reactions involve interactions between the pollutant and multiple functional groups, such as -OH, −COOH, −C=O and -C-O. For instance, NaOH-modified orange tree sawdust resulted in generation of -OH-, −COO- and -C-O groups, thereby promoting the retention of methylene blue through complexation reactions with each of the different functional groups (Azzaz et al. 2017). Similarly, −C=O, −C-O and -COOH groups in corn straw biochar interacted with triazine via electrostatic interactions resulting in effective removal of triazine from solutions (Suo et al. 2019). In summary, modification of agricultural wastes to generate additional O-containing functional groups increases pollutant adsorption, primarily
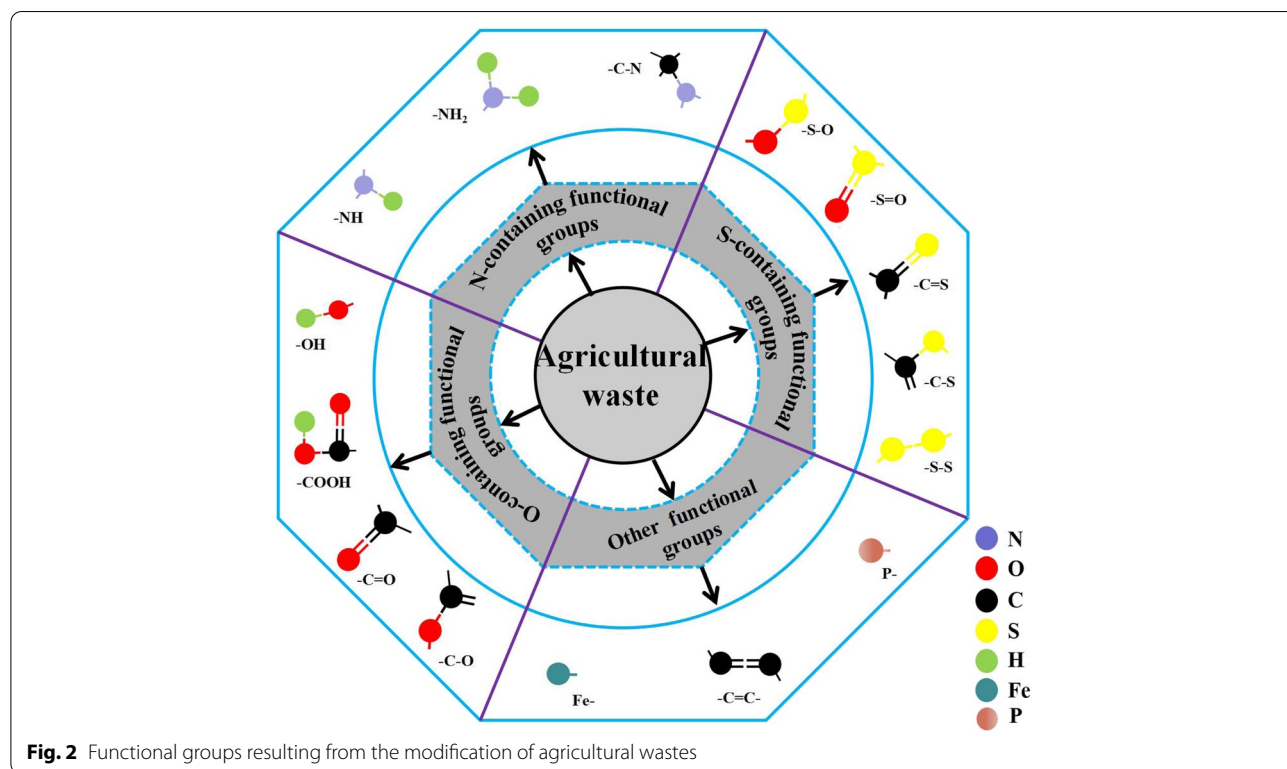

Fig. 2 Functional groups resulting from the modification of agricultural wastes

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through complexation reactions, hydrogen bonding, Van der Waals interactions and electrostatic interactions.

3.2 N-containing functional groups

N-containing functional groups are introduced to the surface of the agricultural material through etherification modification resulting in generation of -NH$_2$, −NH and -C-N (Fig. 2). The N atom has a lone pair of electrons that serves as an activation site to trigger interactions with pollutants. Qu et al. (2022c) showed that N doping introduced graphitic/pyridinic N on adsorbents for serving as reactive sites during the reaction, Pyridine N could transfer electrons from phenol to persulfate, while graphite N trigger nucleophilic addition of persulfate to generate $^1O_2$ to degradate phenol further. In general, the N-containing functional groups on modified agricultural wastes increase the basic properties of adsorbents, thereby generating negatively charged surfaces to enhance the sorption of cationic pollutants (de Lima et al. 2012; Keranen et al. 2015; Qiao et al. 2019). For example, NaOH treatment exposed more -NH groups on the adsorbent surface, which strengthened the material's affinity for Hg^{2+} and Cu^{2+} through complexation and electrostatic attraction (Song et al. 2014; Zafar et al. 2020). Similarly, modification with triethylamine increased -NH$_2$ concentration on modified adsorbents resulting in enhanced Ni^{2+} retention via electron sharing with the N atom (Wu et al. 2016).

N-containing functional groups can also form positive charges to attract anionic pollutants following protonation of the -C-N group in acidic environments to form -C-N$^+$. For instance, a modified coconut shell fiber with increased -C-N group content exhibited strong attraction for nitrate, sulfate and phosphate with maximum adsorption capacities of 33.7, 31.2 and 200.6 mg g^{-1}, respectively (de Lima et al. 2012; Keranen et al. 2015). Similarly, −NH$_2$ can be converted to -NH$_3^+$ upon acidification, which effectively retained Cr^{6+} (Cr$_2$O$_7^{2-}$) through electrostatic attraction (Wu et al. 2016). Thus, N-containing functional groups provide modified adsorbents with the capacity to retain both cationic and anionic pollutants depending on the pH of the reaction environment. Additionally, N-containing functional groups often interact synergistically with O-containing functional groups for retention of pollutants, such as toluene, methylene blue and acid red 18 (Xiao et al. 2020; Yu et al. 2018).

3.3 S-containing functional groups

S-containing functional groups (e.g., −S-O, −S=O, −C-S, −C=S, −S-S) on modified agricultural wastes can enhance the sorption capacity for several pollutants (Fig. 2). Sulfur is loaded onto waste materials through a sulfuration treatment, such as solution infiltration (H$_2$SO$_4$) or gas activation (SO$_2$, H$_2$S) (Tajar et al. 2009; Jawad et al. 2020). The sulfuration process introduces -S=O and -S-O moieties to the modified surface to enhance pollutant adsorption. For example, H$_2$SO$_4$-treated coconut shell generated numerous -S=O and -S-O functional groups that substantially increased the adsorption of methylene blue through electrostatic attractions, H-bonding interaction, and π-π interaction (Tajar et al. 2009; Jawad et al. 2020). Further chlorosulfonic acid activation of matured tea leaf biochar generated additional -S=O and -S-O functional groups, which participated in retention of Rhodamine B and orange G through complexation and electrostatic interactions (Goswami and Phukan 2017). Grafting of -C-S, −C=S and -S-S to adsorbent surfaces has also been used to improve adsorption properties. For example, sugarcane bagasse reacted with ethylenediamine and CS$_2$ produced a material with exceptionally high adsorption capacities for heavy metals (Pb^{2+}, Cu^{2+} and Zn^{2+}), with -C-S functional groups participating in the metal complexation reaction (Wang et al. 2017). Similarly, SO$_2$ or H$_2$S gas modified agricultural wastes biochars produced -C=S and -S-S groups, which formed strong complexes with Cd^{2+} and Hg^{2+} (Tajar et al. 2009; Krishnan and Anirudhan 2002).

Depending on experimental conditions, methods to introduce S-containing functional groups can either increase or decrease specific surface area and pore volume of carbonaceous adsorbents (Tajar et al. 2009; Yang et al. 2019); however, any reduction in sorption capacity associated with the loss of surface area and porosity is generally offset by the increased S-containing functional groups. Sulfur-functional groups also interact with other functional group types (e.g., O-containing or N-containing groups) in synergist adsorption mechanisms. When -COO-, −NH and -C-S were co-introduced to the surface of sugarcane bagasse during modification procedures, these groups interacted to retain metals (Pb^{2+}, Cu^{2+} and Zn^{2+}) through ion exchange and complexation reactions (Wang et al. 2017). The interactions among these functional groups greatly improved the overall sorption capacity for many environmental pollutants.

3.4 Other functional groups

While O-, N- and S-containing functional groups are the predominant reactive groups controlling adsorption performance, other functional groups (e.g., −C=C, Fe-O and -P-O) may also enhance the adsorption performance of agricultural waste products (Tables 1, 2, 3, 4, 5, 6, 7 and 8, Fig. 2). Most of the -C=C groups exist in benzene rings and react with pollutants through π-π interactions. Aniline addition modification enhanced the -C=C content of corn stalk and strengthened π-π interactions between

adsorbent and adsorbates, thereby increasing the adsorption capacity for acid red and acid orange dyes (Soldatkina and Zavrichko 2017).

Fe-containing functional groups are typically introduced onto agricultural waste materials to prepare magnetic adsorbents, especially in the preparation of biochar. Doping with magnetic materials (e.g., Fe_3O_4, Fe_2O_3) creates an adsorbent that can be easily separated from solution to remove biochar-bound pollutants. These Fe oxides were highly efficient for the removal of As^{3+} (AsO_2^-) and As^{5+} (AsO_4^{3-}) through specific sorption reactions (Wu et al. 2018). Additionally, Fe_3O_4 reacts with H_2O creating a polar structure that can retain pollutants by hydrogen bonding.

P-containing functional groups (e.g., $-P-O$) are generated on adsorbents by H_3PO_4 modification and are capable of retaining pollutants primarily by ion exchange mechanisms. Tang et al. (2019) demonstrated the presence of a large number of -P-O functional groups on corn stalks after H_3PO_4 treatment. The -P-O group was effective in retention of methylene blue through ion exchange. Additionally, the -P-O group efficiently retained U^{6+} (UO_2^{2+}) from solution via ion exchange (Xiao-Teng et al. 2019). Adsorption of uranium changed the morphology and the structural characteristics by decreasing the distributed interstices, voids and crystal structure in the surface of the modified rice stem through interaction with -P-O.

3.5 Effects of functional groups on adsorption mechanisms

Adsorption mechanisms are primarily affected by specific surface area, pore volume/connectivity and the amount/type of surface functional groups. Physical adsorption takes place by weak Van der Waals' attraction forces and H-bonding, whereas chemisorption occurs through stronger chemical bonding between adsorbates and adsorbents. Chemisorption (e.g., ion exchange, complexation, electrostatic interaction, precipitation) generally plays a more prominent role in pollutant removal from aqueous solution than physisorption for modified agricultural adsorbents (Tables 1, 2, 3, 4, 5, 6, 7 and 8). Notably, although no functional groups or chemical bonds take part in the fixation of pollutants during the precipitation process, chemical reaction occurs during the formation of the solid products casused by the adsorbents. The retention of pollutants through precipitation is still a chemisorption process. Many O-, N- and S-containing functional groups are suitable for the removal of cationic pollutants, whereas O- and N-containing groups are more suitable for adsorption of anionic pollutants. Fe- and
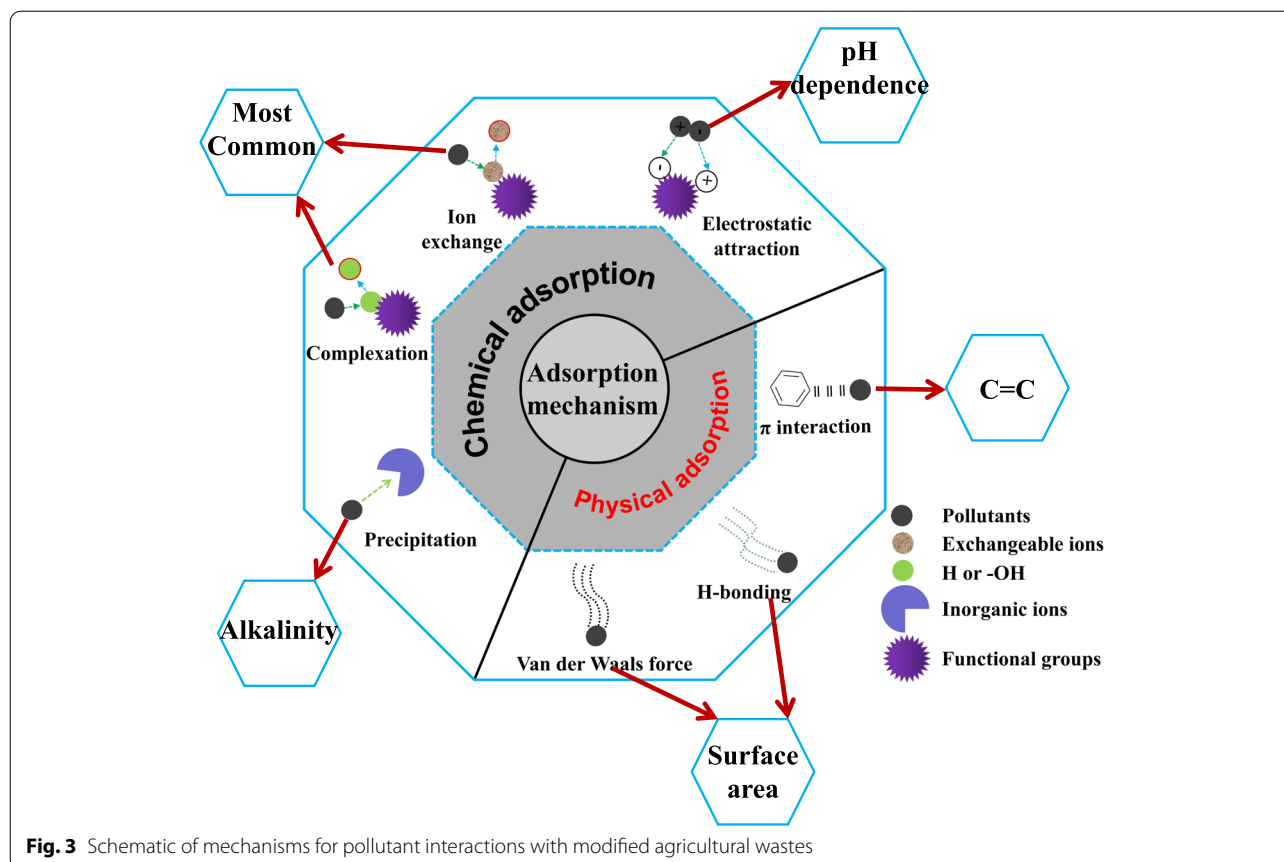
S-containing functional groups often coexist with modified adsorbents surface and were used to binding divalent cationic heavy metals via complexation (Qu et al. 2022b). Moreover, chemical precipitation usually occurred as well for the pollutants retention due to the formation of stable crystal structures.

Complexation and ion exchange are the main adsorption mechanisms for O-containing groups (Azzaz et al. 2017; Li et al. 2010; Qiao et al. 2019; Song et al. 2014), whereas N- and S-containing functional groups interact with pollutants primarily through complexation (Goswami and Phukan 2017; Yang et al. 2019). Studies involving modifications to increase O- and N-functionality of agricultural wastes are much more common than those addressing enhancement of S-functionality, due to the prominence of O- and N-functional groups and their higher adsorption affinity compared to S-functional groups, especially for anionic pollutants.

The main mechanisms for pollutant interactions with modified agricultural wastes are portrayed in Fig. 3. Complexation and ion exchange are often the most important adsorption mechanisms for interactions between functional groups and various pollutants. These chelate-forming or electron-donating functional groups readily react with pollutants to form complexes. Electrostatic attraction is a prominent adsorption process, especially under acidic or alkaline conditions where dissociation/ionization of functional groups initiates interaction with oppositely charged pollutant compounds. For carbonization-treated agricultural wastes, π-π interactions with organic pollutants and alkaline precipitation mechanisms are improved due to the increased C=C content and high alkalinity (leading to decreased metal solubility) after modification (Bashir et al. 2018; Wang and Wang 2019). Moreover, carbonization generally increases the specific surface area of the modified materials, which favors physical adsorption (Chen et al. 2008), H-bonding and van der Waals' attraction. Given the multi-functionality of most modified adsorbents, the overall adsorption process will involve a combination of several mechanisms.

4 Cost analysis

Cost is an important consideration when selecting an agricultural waste and modification treatment. Currently, few studies have assessed cost estimates of modified adsorbent, thereby limiting an evaluation of material and processing costs. A few studies demonstrated that modified agricultural wastes showed a good price advantage compared with commercial adsorbents. For example, the cost of citric acid modified sugarcane bagasse was 4.76 $ kg^{-1} (Gupta et al. 2018), much lower than commercial activated carbon

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Fig. 3 Schematic of mechanisms for pollutant interactions with modified agricultural wastes

($56.06 \$ \ kg^{-1}$). Further, Kannan and Sundaram (2001) determined that the price of carbonised adsorbents prepared from rice husk or straw was ~5 times cheaper than commercial activated carbon. In addition, some modified adsorbent materials exhibited excellent pollutant removal efficiency over at least three reaction/recovery cycles (Huang et al. 2020; Liu et al. 2020a; Xu et al. 2019), allowing for reuse potential that further reduces their lifetime costs. Moreover, many feedstocks for bio-adsorbents originate from agricultural wastes that would otherwise be discarded. Hence, the reuse of these solid waste materials is beneficial for utilization of waste materials as well as reducing waste disposal costs, which is often a more substantial cost than the modification costs. Other studies demonstrated that biochar preparation could generate energy (bio-oil and biogas), thereby offsetting production costs partly (Frank et al. 2020). Based on the available studies, almost all cost-benefit analyses indicated that agricultural waste modification provides a low-cost option for preparation of bio-adsorbents for environmental remediation.

Most studies of bio-adsorbent preparation were limited to laboratory evaluations of synthesis costs, which do not account for several associated costs. The costs of raw materials, transportation, modification chemicals and energy are the main factors determining the final preparation cost. Many of these costs are site and time (i.e., inflation) specific making it difficult to produce a universal cost estimate (Gkika et al. 2019). For example, Salam et al. (2011) calculated that the total cost (transportation, handling, chemicals, electrical, energy, drying, etc.) of HCl-modified peanut husk was L.E. $5000 t^{-1}$ (about $\$ 838.55 t^{-1}$ in 2011), a factor of two lower than commercial activated carbon (L.E. $10,000 t^{-1}$, about $\$ 1679.10 t^{-1}$ at 2011) at that time. Additionally, bio-adsorbents will have variable efficiencies for retention of a given pollutant, wherein a higher cost, but higher efficiency product will actually have a lower application cost per unit of pollutant removal. More research is required to assess the costs of modified agricultural waste materials, not only for their production costs, but also for the cost per unit of pollutant removal (including recycling/reuse of materials) and including a complete life-cycle analysis that accounts for externalities, such as greenhouse gas impacts.

5 Future perspectives

The main purpose of current modification procedures is to alter the physical (e.g., surface area, porosity) and chemical (e.g., O-, N- and S- functional groups) characteristics on the surface of agricultural wastes to enhance pollutant adsorption. Future studies will undoubtedly devise new techniques to improve the efficiency and selectivity of the modified adsorbents for targeted applications. In addition, some adsorbent modification processes generate a series of potentially toxic by-products that must be addressed to minimize negative environmental impacts. Thus, optimization studies are required to generate low-cost adsorbents that are tunable for efficient and selective retention of targeted pollutants using green-chemistry principals. This will require systematic studies followed by physicochemical characterization of the modified materials and finally testing of their efficacy for retention of various pollutants under a wide range of environmental water conditions. Rigorous physicochemical characterization is a critical intermediate step in this overall process. First, characterization provides the details for how various modification steps affect the physicochemical properties of the modified products. Second, understanding the physicochemical properties of the modified products is critical for mechanistically understanding the materials ability to retain various pollutants. Once sufficient characterization data has been systematically compiled, it will serve as a toolbox for fine-tuning modification techniques to optimize materials for efficient and selective retention of specific pollutants.

Although the modification methods discussed above are effective to improve the adsorption performance of agricultural wastes, there are some drawbacks that need attention. High alkali concentration may cause an excess elimination of covering materials from the cellulose surface and delignify the fibre extremely due to the hydrolysis, which can negatively affect the strength of the fibre. Concentrated acid oxidation has strong corrosiveness and was shown to decrease the surface area of oxidized adsorbent, which may reduce the porosity and efficacy of the adsorbent material for retention of some pollutants. Esterification and etherification creat high cost of the organic solvents used, the catalyst would also need to be recovered after modification. Carbonization not only consumes a lot of electricity, but also reduces the content functional groups of adsorbent at a high temperature. Magnetization can reduce surface area due to the block of magnetic particles in the pore of adsorbent. Surfactant and grafting have strict requirements for preparing environment and are prone to produce formation of undesirable block co-polymers. In all, the effectiveness of the treatment depends not only on the adsorption environment, but also on various preparation conditions.

The conditions (i.e., temperature, atmosphere, reagent, reaction time, concentration, etc.) for the production of low-cost adsorbents after surface modification for higher uptake of pollutants need to be optimized further. Therefore, we still need to refine these modification methods to reduce their shortcomings and make them exhibit greater potential in preparing agricultural waste based adsorbents.

Although modified agricultural wastes have been proven effective in retention of various pollutants in water, remediation actions that leave the pollutant-adsorbent compounds in the water environment have not been fully investigated. Over time, pollutants retained by bio-adsorbents and accumulated in aquatic sediments may be released back to the water column upon changes in pH, temperature, ionic strength, redox conditions and bio-adsorbent degradation. Thus, bio-adsorbents that can be effectively extracted from the water environment, such as magnetic compounds, will provide a more permanent solution for pollutant retention and extraction from environmental waters.

While modified agricultural wastes show great potential for the removal of various pollutants under laboratory conditions, far fewer studies have demonstrated their efficacy in real-world environmental waters, such as industrial/municipal wastewaters. The composition of wastewaters is much more complicated than that of synthetic wastewaters used in many laboratory studies, which undoubtedly will affect the adsorption performance of the bio-adsorbents. Testing common bio-adsorbents across a wide range of environmental waters (e.g., industrial wastewater, municipal wastewaters, aquaculture tailwaters, urban storm runoff, livestock waste runoff) will provide fundamental knowledge to optimize applications for real-world use.

Finally, most previous studies focused on the single adsorbent-adsorbate system, while there is a paucity of studies evaluating simultaneous use of multiple bio-adsorbents for retention/extraction of multiple pollution types. The coexistence of different pollutants is a common scenario in environmental waters and interactions among pollutants often affect the adsorption performance of various adsorbents. Moreover, there is a distinct paucity of research on the removal of rare and emerging pollutants (e.g., endocrine disruptors, radionuclides, pharmaceuticals, antibiotic resistance genes, persistent organic pollutants), which are of considerable concern for human and aquatic ecosystem health. Finally, greater effort is required to rigorously investigate adsorption/retention mechanisms. In addition to traditional sorption isotherm and kinetic studies, the emergence of advanced analytical methods, such as spectroscopic, microscopic, isotopic and molecular techniques, offer great potential

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for advancing our understanding of adsorption mechanisms. We are currently at the cross-roads of advancing from a more trial-and-error approach to developing a cook-book approach for designing modification techniques to achieve targeted materials for selective removal of pollutants.

Abbreviations
BET: Brunauer-emmett-teller; EDTA: Ethylene diamine tetraacetic acid; FTIR: Fourier transform infrared spectroscopy; π-π EDA: π-π electron-donor-acceptor; SEM: Scanning electron microscope.

Authors' contributions
Guofei Liu: Conceptualization, Writing - original draft, Software, Validation; Zhongmin Dai: Validation, Formal analysis, Resources; Xingmei Liu: Formal analysis, Visualization; Randy A. Dahlgren: Writing - review & editing; Jianming Xu: Conceptualization, Resources, Supervision, Writing - review & editing, Project administration. The author(s) read and approved the final manuscript.

Availability of data and materials
This review article contains no research data available.

Declarations

Ethics approval and consent to participate
This work is original and is not under consideration for publication elsewhere. None of the aspects of this work has been previously published. Informed consent was obtained from all individual authors included in the study.

Consent for publication
Authors are responsible for correctness of the statements provided in the manuscript. The publication has been approved by all co-authors.

Competing interests
The authors declare that they have no known competing financial interests or personal relationships that infuence the work reported in this paper.

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References
Abdolali A, Guo WS, Ngo HH, Chen SS, Nguyen NC, Tung KL (2014) Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: a critical review. Bioresour Technol 160(SI):57–66

Abrankó-Rideg N, Horvai G, Jedlovszky P (2015) Structure of the adsorption layer of various ionic and non-ionic surfactants at the free water surface, as seen from computer simulation and ITIM analysis. J Mol Liq 205:9–15

Afroze S, Sen TK (2018) A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. Water Air Soil Pollut 229(7):225

Alencar WS, Acayanka E, Lima EC, Royer B, de Souza FE, Lameira J, Alves CN (2012) Application of Mangifera indica (mango) seeds as a biosorbent for removal of Victazol Orange 3R dye from aqueous solution and study of the biosorption mechanism. Chem Eng J 209:577–588

Amen R, Bashir H, Bibi I, Shaheen SM, Niazi NK, Shahid M, Rinklebe J (2020) A critical review on arsenic removal from water using biochar-based sorbents: the significance of modification and redox reactions. Chem Eng J 396:125195

Arán D, Antelo J, Fiol S, Macías F (2016) Influence of feedstock on the copper removal capacity of waste-derived biochars. Bioresour Technol 212:199–206

Argun ME, Dursun S, Ozdemir C, Karatas M (2007) Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. J Hazard Mater 141(1):77–85

Aryee AA, Mpatani FM, Kani AN, Dovi E, Han R, Li Z, Qu L (2021) A review on functionalized adsorbents based on peanut husk for the sequestration of pollutants in wastewater: modification methods and adsorption study. J Clean Prod 310:127502

Asadi F, Shariatmadari H, Mirghaffari N (2008) Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater. J Hazard Mater 154(1–3):451–458

Ayan EM, Secim P, Karakaya S, Yanik J (2012) Oreganum stalks as a new biosorbent to remove textile dyes from aqueous solutions. Clean-Soil Air Water 40(8):856–863

Azzaz AA, Jellali S, Souissi R, Ergaieg K, Bousselmi L (2017) Alkaline-treated sawdust as an effective material for cationic dye removal from textile effluents under dynamic conditions: breakthrough curve prediction and mechanism exploration. Environ Sci Pollut Res 24(22):18240–18256

Balarak D, Bazrafshan E, Mahdavi Y, Lalhmunsiama, Lee S (2017) Kinetic, isotherms and thermodynamic studies in the removal of 2-chlorophenol from aqueous solution using modified rice straw. Desalin Water Treat 63:203–211

Baldikova E, Politi D, Maderova Z, Pospiskova K, Sidiras D, Safarikova M, Safarik I (2016) Utilization of magnetically responsive cereal by-product for organic dye removal. J Sci Food Agric 96(6):2204–2214

Bashir S, Zhu J, Fu Q, Hu H (2018) Comparing the adsorption mechanism of cd by rice straw pristine and KOH-modified biochar. Environ Sci Pollut Res 25(12SI):11875–11883

Bhatnagar A, Sillanpaa M, Witek-Krowiak A (2015) Agricultural waste peels as versatile biomass for water purification - a review. Chem Eng J 270:244–271

Cao W, Dang Z, Zhou X, Yi X, Wu P, Zhu N, Lu G (2011) Removal of sulphate from aqueous solution using modified rice straw: preparation, characterization and adsorption performance. Carbohydr Polym 85(3):571–577

Cara I, Rusu B, Raus L, Jitareanu G (2017) Sorption potential of alkaline treated straw and a soil for sulfonylurea herbicide removal from aqueous solutions: an environmental management strategy. Chemosphere 186:360–366

Carlmark A (2013) Tailoring cellulose surfaces by controlled polymerization methods. Macromol Chem Phys 214(14):1539–1544

Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environ Sci Technol 42(14):5137–5143

Chen S, Yue Q, Gao B, Li Q, Xu X (2011) Removal of Cr(VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study. Chem Eng J 168(2):909–917

Dai J, He J, Xie A, Gao L, Pan J, Chen X, Zhou Z, Wei X, Yan Y (2016) Novel pitaya-inspired well-defined core-shell nanospheres with ultrathin surface imprinted nanofilm from magnetic mesoporous nanosilica for highly efficient chloramphenicol removal. Chem Eng J 284:812–822

Dai Y, Sun Q, Wang W, Lu L, Liu M, Li J, Yang S, Zhang K, Xu J, Zheng W, Hu Z, Yang Y, Gao Y, Chen Y, Zhang X, Gao F, Zhang Y (2018) Utilizations of agricultural waste as adsorbent for the removal of contaminants: a review. Chemosphere 211:235–253

Dai Z, Wang Y, Muhammad N, Yu X, Xiao K, Meng J, Brookes PC (2014) The effects and mechanisms of soil acidity changes, following incorporation of biochars in three soils differing in initial pH. Soil Sci Soc Am J 78(5):1606–1614

de Lima ACA, Nascimento RF, de Sousa FF, Filho JM, Oliveira AC (2012) Modified coconut shell fibers: a green and economical sorbent for the removal of anions from aqueous solutions. Chem Eng J 185:274–284

Ding Z, Hu X, Zimmerman AR, Gao B (2014) Sorption and cosorption of lead (II) and methylene blue on chemically modified biomass. Bioresour Technol 167:569–573

Divband Hafshejani L, Hooshmand A, Naseri AA, Mohammadi AS, Abbasi F, Bhatnagar A (2016) Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. Ecol Eng 95:101–111

Egbedina AO, Adebowale KO, Olu-Owolabi BI, Unuabonah EI, Adesina MO (2021) Green synthesis of ZnO coated hybrid biochar for the synchronous removal of ciprofloxacin and tetracycline in wastewater. RSC Adv 11(30):18483–18492

Fatimah I, Nabila Huda B, Lucyawati Yusuf I, Hartono B (2018) Enhanced adsorption capacity of peanut shell toward rhodamine b via sodium dodecyl sulfate modification. Rasayan J Chem 11(3):1166–1176

Feng Y, Liu Y, Xue L, Sun H, Guo Z, Zhang Y, Yang L (2017) Carboxylic acid functionalized sesame straw: a sustainable cost-effective bioadsorbent with superior dye adsorption capacity. Bioresour Technol 238:675–683

Foglarova M, Prokop J, Milichovsky M (2009) Oxidized cellulose: an application in the form of sorption filter materials. J Appl Polym Sci 112(2):669–678

Fotsing PN, Woumfo ED, Mezghich S, Mignot M, Mofaddel N, Le Derf F, Vieillard J (2020) Surface modification of biomaterials based on cocoa shell with improved nitrate and Cr(vi) removal. RSC Adv 10(34):20009–20019

Fouladi Tajar A, Kaghazchi T, Soleimani M (2009) Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells. J Hazard Mater 165(1–3):1159–1164

Frank JR, Brown TR, Malmsheimer RW, Volk TA, Ha H (2020) The financial trade-off between the production of biochar and biofuel via pyrolysis under uncertainty. Bioful Bioprod Biorefin 14(3):594–604

Gkika DA, Vordos N, Liakos EV, Magafas L, Bandekas DV, Mitropoulos AC, Kyzas GZ (2019) The impact of raw materials cost on the adsorption process. Polymers 5(11):1–14

Goswami M, Phukan P (2017) Enhanced adsorption of cationic dyes using sulfonic acid modified activated carbon. J Environ Chem Eng 5(4):3508–3517

Guo Y, Zhu W, Li G, Wang X, Zhu L (2016) Effect of alkali treatment of wheat straw on adsorption of cu(II) under acidic condition. J Chem 2016:1–10

Gupta M, Gupta H, Kharat DS (2018) Adsorption of Cu(II) by low cost adsorbents and the cost analysis. Environ Technol Innov 10:91–101

Gupta VK, Agarwal S, Singh P, Pathania D (2013) Acrylic acid grafted cellulosic Luffa cylindrical fiber for the removal of dye and metal ions. Carbohydr Polym 98(1):1214–1221

Gupta VK, Pathania D, Agarwal S, Sharma S (2014) Amputation of Congo red dye from waste water using microwave induced grafted Luffa cylindrica cellulosic fiber. Carbohydr Polym 111:556–566

Haghighat ZA, Ameri E (2016) Synthesis and characterization ofnano magnetic wheat straw for lead adsorption. Desalin Water Treat 57(21):9813–9823

Han R, Zhang L, Song C, Zhang M, Zhu H, Zhang L (2010) Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. Carbohydr Polym 79(4):1140–1149

Hokkanen S, Bhatnagar A, Sillanpää M (2016) A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. Water Res 91:156–173

Huang X, Wu S, Tang S, Huang L, Zhu D, Hu Q (2020) Photocatalytic hydrogel layer supported on alkali modified straw fibers for ciprofloxacin removal from water. J Mol Liq 317:113961

Jawad AH, Abdulhameed AS, Mastuli MS (2020) Acid-factionalized biomass material for methylene blue dye removal: a comprehensive adsorption and mechanism study. J Taibah Univ Sci 14(1):305–313

Jung KW, Hwang MJ, Ahn KH, Ok YS (2015) Kinetic study on phosphate removal from aqueous solution by biochar derived from peanut shell as renewable adsorptive media. Int J Environ Sci Technol 12(10):3363–3372

Kaçakgil E, Çetintas S (2021) Preparation and characterization of a novel functionalized agricultural waste-based adsorbent for Cu^{2+} removal evaluation of adsorption performance using response surface methodology. Sustain Chem Pharm 22:100468

Kannan N, Sundaram MM (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons - a comparative study. Dyes Pigments 51(1):25–40

Keranen A, Leiviska T, Hormi O, Tanskanen J (2015) Removal of nitrate by modified pine sawdust: effects of temperature and co-existing anions. J Environ Manag 147:46–54

Khandanlou R, Ahmad MB, Fard Masoumi HR, Shameli K, Basri M, Kalantari K (2015) Rapid adsorption of copper(II) and Lead(II) by rice straw/Fe_3O_4 nanocomposite: optimization, equilibriumisotherms, and adsorption kinetics study. PLoS One 10(3):e120264

Kong W, Li Q, Li X, Su Y, Yue Q, Zhou W, Gao B (2018) Removal of copper ions from aqueous solutions by adsorption onto wheat straw cellulose-based polymeric composites. J Appl Polym Sci 135:4668036

Kovacova Z, Demcak S, Balintova M, Pla C, Zinicovscaia I (2020) Influence of wooden sawdust treatments on Cu(II) and Zn(II) removal from water. Materials 13(16):3575

Krishnan KA, Anirudhan TS (2002) Uptake of heavy metals in batch systems by sulfurized steam activated carbon prepared from sugarcane bagasse pith. Ind Eng Chem Res 41(20):5085–5093

Kumar R, Sharma RK (2019) Synthesis and characterization of cellulose based adsorbents for removal of Ni(II), Cu(II) and Pb(II) ions from aqueous solutions. React Funct Polym 140:82–92

Kumar R, Sharma RK, Singh AP (2018) Grafted cellulose: a bio-based polymer for durable applications. Polym Bull 75(5):2213–2242

Kumari S, Mankotia D, Chauhan GS (2016) Crosslinked cellulose dialdehyde for Congo red removal from its aqueous solutions. J Environ Chem Eng 4(1):1126–1136

Kurup L (2012) Evaluation of the adsorption capacity of alkali-treated waste materials for the adsorption of sulphamethoxazole. Water Sci Technol 65(9):1531–1539

Kwon G, Bhatnagar A, Wang H, Kwon EE, Song H (2020) A review of recent advancements in utilization of biomass and industrial wastes into engineered biochar. J Hazard Mater 400:123242

Lee W, Yoon S, Choe JK, Lee M, Choi Y (2018) Anionic surfactant modification of activated carbon for enhancing adsorption of ammonium ion from aqueous solution. Sci Total Environ 639:1432–1439

Leyvaramos R, Bernaljacome L, Acostarodriguez I (2005) Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. Sep Purif Technol 45(1):41–49

Leyva-Ramos R, Landin-Rodriguez LE, Leyva-Ramos S, Medellin-Castillo NA (2012) Modification of corncob with citric acid to enhance its capacity for adsorbing cadmium(II) from water solution. Chem Eng J 180:113–120

Li Q, Chai L, Wang Q, Yang Z, Yan H, Wang Y (2010) Fast esterification of spent grain for enhanced heavy metal ions adsorption. Bioresour Technol 101(10):3796–3799

Li Q, Ma Z, Yue Q, Gao B, Li W, Xu X (2012) Synthesis, characterization and swelling behavior of superabsorbent wheat straw graft copolymers. Bioresour Technol 118:204–209

Ling W, Xu J, Gao Y (2006) Dissolved organic matter enhances the sorption of atrazine by soil. Biol Fertil Soils 42(5):418–425

Liu G, Liao L, Dai Z, Qi Q, Wu J, Ma LQ, Tang C, Xu J (2020a) Organic adsorbents modified with citric acid and Fe_3O_4 enhance the removal of Cd and Pb in contaminated solutions. Chem Eng J 395:125108

Liu G, Meng J, Huang Y, Dai Z, Tang C, Xu J (2020b) Effects of carbide slag, lodestone and biochar on the immobilization, plant uptake and translocation of as and cd in a contaminated paddy soil. Environ Pollut 266:115194

Liu J, Zhou J, Wu Z, Tian X, An X, Zhang Y, Zhang G, Deng F, Meng X, Qu J (2022) Concurrent elimination and stepwise recovery of Pb(II) and bisphenol a from water using β–cyclodextrin modified magnetic cellulose: adsorption performance and mechanism investigation. J Hazard Mater 432:128758

Liu Y, Sun X, Li B (2010) Adsorption of Hg^{2+} and Cd^{2+} by ethylenediamine modified peanut shells. Carbohydr Polym 81(2):335–339

Ma CM, Hong GB, Wang YK (2020a) Performance evaluation and optimization of dyes removal using rice bran-based magnetic composite adsorbent. Materials 13(12):2764

Ma J, Li J, Guo Q, Han H, Zhang S, Han R (2020b) Waste peanut shell modified with polyethyleneimine for enhancement of hexavalent chromium removal from solution in batch and column modes. Bioresour Technol Rep 12:100576

Ma Y, Liu W, Zhang N, Li Y, Jiang H, Sheng G (2014) Polyethylenimine modified biochar adsorbent for hexavalent chromium removal from the aqueous solution. Bioresour Technol 169:403–408

Mo J, Yang Q, Zhang N, Zhang W, Zheng Y, Zhang Z (2018) A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment. J Environ Manag 227:395–405

Moyo M, Pakade VE, Modise SJ (2017) Biosorption of lead(II) by chemically modified Mangifera indica seed shells: adsorbent preparation, characterization and performance assessment. Process Saf Environ 111:40–51

Ogata F, Imai D, Kawasaki N (2015) Adsorption of nitrate and nitrite ions onto carbonaceous material produced from soybean in a binary solution system. J Environ Chem Eng 3(1):155–161

Oliveira FR, Patel AK, Jaisi DP, Adhikari S, Lu H, Khanal SK (2017) Environmental application of biochar: current status and perspectives. Bioresour Technol 246:110–122

Pang L, Gao Z, Feng H, Wang S, Wang Q (2019) Cellulose based materials for controlled release formulations of agrochemicals: a review of modifications and applications. J Control Release 316:105–115

Pehlivan E, Altun T, Parlayici Ş (2012) Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. Food Chem 135(4):2229–2234

Pehlivan E, Cetin S, Yanik B (2006) Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash. J Hazard Mater 135(1–3):193–199

Pehlivan E, Tran HT, Ouédraogo WKI, Schmidt C, Zachmann D, Bahadir M (2013) Sugarcane bagasse treated with hydrous ferric oxide as a potential adsorbent for the removal of As(V) from aqueous solutions. Food Chem 138(1):133–138

Pirbazari AE, Kisom BF, Khararoodi MG (2016) Anionic surfactant-modified rice straw for removal of methylene blue from aqueous solution. Desalin Water Treat 57(39):18202–18216

Qiao H, Mei L, Chen G, Liu H, Peng C, Ke F, Hou R, Wan X, Cai H (2019) Adsorption of nitrate and phosphate from aqueous solution using amine cross-linked tea wastes. Appl Surf Sci 483:114–122

Qiu B, Tao X, Wang H, Li W, Ding X, Chu H (2021) Biochar as a low-cost adsorbent for aqueous heavy metal removal: a review. J Anal Appl Pyrolysis 155:105081

Qu J, Tian X, Zhang X, Yao J, Xue J, Li K, Zhang B, Wang L, Zhang Y (2022a) Free radicals-triggered reductive and oxidative degradation of highly chlorinated compounds via regulation of heat-activated persulfate by low-molecular-weight organic acids. Appl Catal B Environ 310:121359

Qu J, Xu Y, Zhang X, Sun M, Tao Y, Zhang X, Zhang G, Ge C, Zhang Y (2022c) Ball milling-assisted preparation of N-doped biochar loaded with ferrous sulfide as persulfate activator for phenol degradation: multiple active sites-triggered radical/non-radical mechanism. Appl Catal B Environ 316:121639

Qu J, Yuan Y, Zhang X, Wang L, Tao Y, Jiang Z, Yu H, Dong M, Zhang Y (2022b) Stabilization of lead and cadmium in soil by sulfur-iron functionalized biochar: performance, mechanisms and microbial community evolution. J Hazard Mater 425:127876

Rashid R, Shafiq I, Akhter P, Iqbal MJ, Hussain M (2021) A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method. Environ Sci Pollut Res 28(8):9050–9066

Roy A, Adhikari B, Majumder SB (2013) Equilibrium, kinetic, and thermodynamic studies of azo dye adsorption from aqueous solution by chemically modified lignocellulosic jute fiber. Ind Eng Chem Res 52(19):6502–6512

Sadaf S, Bhatti HN, Arif M, Amin M, Nazar F (2015) Adsorptive removal of direct dyes by PEI-treated peanut husk biomass: Box-Behnken experimental design. Chem Ecol 31(3):252–264

Safarik I, Prochazkova J, Baldikova E, Timko M, Kopcansky P, Rajnak M, Torma N, Pospiskova K (2020) Modification of diamagnetic materials using magnetic fluids. Ukr J Phys 65(9):751–760

Safarik I, Safarikova M (2014) One-step magnetic modification of non-magnetic solid materials. Int J Mater Res 105(1):104–107

Sahu P, Gupta MK (2020) A review on the properties of natural fibres and its bio-composites: effect of alkali treatment. Proceedings of the institution of mechanical engineers. P I Mech Eng L-j Mat 234(1):198–217

Salam OE, Reiad NA, Elshafei MM (2011) A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. J Adv Res 2:297–303

Sciban M, Klasnja M, Skrbic B (2006) Modified softwood sawdust as adsorbent of heavy metal ions from water. J Hazard Mater 136(2):266–271

Shao Y, Gao Y, Yue Q, Kong W, Gao B, Wang W, Jiang W (2020) Degradation of chlortetracycline with simultaneous removal of copper (II) from aqueous solution using wheat straw-supported nanoscale zero-valent iron. Chem Eng J 379:122384

Shi W, Ren H, Huang X, Li M, Tang Y, Guo F (2020) Low cost red mud modified graphitic carbon nitride for the removal of organic pollutants in wastewater by the synergistic effect of adsorption and photocatalysis. Sep Purif Technol 237:116477

Soldatkina L, Zavrichko M (2019) Equilibrium, kinetic, and thermodynamic studies of anionic dyes adsorption on corn stalks modified by cetylpyridinium bromide. Colloids Interfaces 3(1):4

Soldatkina LM, Zavrichko MA (2017) Adsorption of anionic dys on corn stalks modified by polyaniline: kinitics and thermodynamic studies. Chem Phys Technol Surf 8(1):44–55

Song S, Saman N, Johari K, Mat H (2014) Surface chemistry modifications of rice husk toward enhancement of Hg(II) adsorption from aqueous solution. Clean Techn Environ Policy 16(8):1747–1755

Suo F, You X, Ma Y, Li Y (2019) Rapid removal of triazine pesticides by P doped biochar and the adsorption mechanism. Chemosphere 235:918–925

Tang Y, Zhao Y, Lin T, Li Y, Zhou R, Peng Y (2019) Adsorption performance and mechanism of methylene blue by H3PO4- modified corn stalks. J Environ Chem Eng 7(6):103398

Thamilarasi MJV, Anilkumar P, Theivarasu C, Sureshkumar MV (2018) Removal of vanadium from wastewater using surface-modified lignocellulosic material. Environ Sci Pollut Res 25(26):26182–26191

Thevannan A, Hill G, Niu CH (2011) Kinetics of nickel biosorption by acid-washed barley straw. Can J Chem Eng 89(1):176–182

Vafakhah S, Bahrololoom ME, Bazarganlari R, Saeedikhani M (2014) Removal of copper ions from electroplating effluent solutions with native corn cob and corn stalk and chemically modified corn stalk. J Environ Chem Eng 2(1):356–361

Velazquez-Jimenez LH, Pavlick A, Rene Rangel-Mendez J (2013) Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water. Ind Crop Prod 43:200–206

Wang F, Pan Y, Cai P, Guo T, Xiao H (2017) Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. Bioresour Technol 241:482–490

Wang H, Gao B, Wang S, Fang J, Xue Y, Yang K (2015) Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from $KMnO_4$ treated hickory wood. Bioresour Technol 197:356–362

Wang J, Wang S (2019) Preparation, modification and environmental application of biochar: a review. J Clean Prod 227:1002–1022

Wang L, Yan W, He C, Wen H, Cai Z, Wang Z, Chen Z, Liu W (2018) Microwave-assisted preparation of nitrogen-doped biochars by ammonium acetate activation for adsorption of acid red 18. Appl Surf Sci 433:222–231

Wang Y, Tang C, Wu J, Liu X, Xu J (2013) Impact of organic matter addition on pH change of paddy soils. J Soils Sediments 13(1):12–23

Wu J, Huang D, Liu X, Meng J, Tang C, Xu J (2018) Remediation of As(III) and Cd(II) co-contamination and its mechanism in aqueous systems by a novel calcium-based magnetic biochar. J Hazard Mater 348:10–19

Wu Y, Fan Y, Zhang M, Ming Z, Yang S, Arkin A, Fang P (2016) Functionalized agricultural biomass as a low-cost adsorbent: utilization of rice straw incorporated with amine groups for the adsorption of Cr(VI) and Ni(II) from single and binary systems. Biochem Eng J 105:27–35

Xiao K, Liu H, Li Y, Yang G, Wang Y, Yao H (2020) Excellent performance of porous carbon from urea-assisted hydrochar of orange peel for toluene and iodine adsorption. Chem Eng J 382:122997

Xiao-Teng Z, Dong-Mei J, Yi-Qun X, Jun-Chang C, Shuai H, Liang-Shu X (2019) Adsorption of Uranium(VI) from aqueous solution by modified rice stem. J Chem 2019:1–10

Xu J, Zhang X, Sun C, Wan J, He H, Wang F, Dai Y, Yang S, Lin Y, Zhan X (2019) Insights into removal of tetracycline by persulfate activation with peanut shell biochar coupled with amorphous Cu-doped FeOOH composite in aqueous solution. Environ Sci Pollut Res 26(3):2820–2834

Xu X, Gao B, Tan X, Yue Q, Zhong Q, Li Q (2011) Characteristics of amine-crosslinked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution. Carbohydr Polym 84(3):1054–1060

Xue Y, Gao B, Yao Y, Inyang M, Zhang M, Zimmerman AR, Ro KS (2012) Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: batch and column tests. Chem Eng J 200-202:673–680

Yang X, Wan Y, Zheng Y, He F, Yu Z, Huang J, Wang H, Ok Y, Jiang Y, Gao B (2019) Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review. Chem Eng J 366:608–621

Yanyan L, Kurniawan TA, Zhu M, Ouyang T, Avtar R, Dzarfan Othman MH, Mohammad BT, Albadarin AB (2018) Removal of acetaminophen from synthetic wastewater in a fixed-bed column adsorption using low-cost coconut shell waste pretreated with NaOH, HNO_3, ozone, and/or chitosan. J Environ Manag 226:365–376

Ying GG (2006) Fate, behavior and effects of surfactants and their degradation products in the environment. Environ Int 32(3):417–431

Yoon SY, Han SH, Shin SJ (2014) The effect of hemicelluloses and lignin on acid hydrolysis of cellulose. Energy 77(SI):19–24

Yu D, Wang L, Wu M (2018) Simultaneous removal of dye and heavy metal by banana peels derived hierarchically porous carbons. J Taiwan Inst Chem 93:543–553

Yu J, Wang L, Chi R, Zhang Y, Xu Z, Guo J (2013) Competitive adsorption of Pb^{2+} and Cd^{2+} on magnetic modified sugarcane bagasse prepared by two simple steps. Appl Surf Sci 268:163–170

Yue M, Zhang M, Liu B, Xu X, Li X, Yue Q, Ma C (2013) Characteristics of amine surfactant modified peanut shell and its sorption property for Cr(VI). Chin J Chem Eng 21(11):1260–1268

Zafar S, Khan MI, Lashari MH, Khraisheh M, Almomani F, Mirza ML, Khalid N (2020) Removal of copper ions from aqueous solution using NaOH-treated rice husk. Emergent Mater 6(3):857–870

Zhang C, Zhang Z, Zhang L, Li Q, Li C, Chen G, Zhang S, Liu Q, Hu X (2020) Evolution of the functionalities and structures of biochar in pyrolysis of poplar in a wide temperature range. Bioresour Technol 304:123002

Zhang R, Zhang J, Zhang X, Dou C, Han R (2014) Adsorption of Congo red from aqueous solutions using cationic surfactant modified wheat straw in batch mode: kinetic and equilibrium study. J Taiwan Inst Chem 45(5):2578–2583

Zhao B, Xiao W, Shang Y, Zhu H, Han R (2017) Adsorption of light green anionic dye using cationic surfactant-modified peanut husk in batch mode. Arab J Chem 10:S3595–S3602

Zheng L, Dang Z, Yi X, Zhang H (2010a) Equilibrium and kinetic studies of adsorption of Cd(II) from aqueous solution using modified corn stalk. J Hazard Mater 176(1–3):650–656

Zheng L, Dang Z, Zhu C, Yi X, Zhang H, Liu C (2010b) Removal of cadmium(II) from aqueous solution by corn stalk graft copolymers. Bioresour Technol 101(15):5820–5826

Zhu B, Fan T, Zhang D (2008) Adsorption of copper ions from aqueous solution by citric acid modified soybean straw. J Hazard Mater 153(1–2):300–308

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