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Exploring the potential of buckwheat hull-based biosorbents for efficient water pollutant removal

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ABSTRACT

This mini-review aims to explore the potential applications of buckwheat hulls as adsorbents for the removal of pollutants from water. With the global demand for clean water, steadily increasing and water pollution ranking among the most pressing environmental challenges, the development of efficient water purification techniques is of paramount importance. Among these, adsorption using activated carbon has proven to be one of the most effective methods. However, the production of commercial activated carbon predominantly relies on non-renewable fossil fuels, leading to significant environmental concerns and high operational costs. Commercially activated carbon and zeolites are the most commonly used adsorbents for water and wastewater treatment due to their high surface area and effective contaminant removal capabilities; however, alternative adsorbents such as lignocellulosic materials and biochars derived from agricultural waste offer advantages like lower cost, eco-friendliness, and potential for regeneration, making them attractive for sustainable wastewater management solutions. Buckwheat hulls, a by-product of buckwheat processing, present a viable option due to their availability, cost-effectiveness, and potential utility as raw materials for both energy and environmental applications. This mini-review provides an overview of the physicochemical properties of buckwheat hulls and their applications in water treatment. It highlights the use of both native (unmodified) and chemically or physically modified buckwheat hulls in adsorption processes to remove a range of waterborne pollutants, including heavy metals and synthetic dyes. Based on the existing body of literature, it is evident that buckwheat hulls, in their various forms, represent a sustainable and efficient alternative to conventional non-renewable adsorbents. Their utilization not only offers an environmentally friendly solution for water purification but also contributes to the valorisation of agri-industrial by-products/waste, aligning with the principles of a circular economy.

KEYWORDS
adsorption; buckwheat hulls; food industry by-products; biosorbents; water pollutants removal

KEY CONTRIBUTION
Buckwheat hulls, an agri-food by-product, have potential as cost-effective and sustainable adsorbents for water pollutant removal.
Buckwheat hulls offer an eco-friendly and efficient alternative to non-renewable, fossil fuel-based activated carbon.
Utilizing buckwheat hulls addresses environmental concerns related to conventional activated carbon production while promoting the valorisation of agri-industrial waste (thus aligning with circular economy principles).

Introduction

Water pollution remains one of the most pressing global challenges, as water sources are increasingly contaminated with pollutants such as heavy metals, dyes, pesticides, surfactants, personal care products, and other substances from agricultural, municipal, and industrial activities. With rising water consumption and the limited availability of freshwater suitable for human use, significant research efforts have been devoted to developing efficient wastewater treatment technologies. These methods encompass physical (e.g. adsorption, membrane filtration, flocculation), chemical (e.g. coagulation, advanced oxidation processes, ozonation), and biological approaches (e.g. enzymes, microorganisms).
Among these, adsorption is recognized as one of the most effective techniques for removing heavy metals, dyes, and organic pollutants from wastewater (Rashid et al., 2021). This is due to its high removal efficiency, established technical reliability, broad applicability, cost-effectiveness, simple operating conditions, environmental friendliness, and low reusability costs (Al-Ghouti et al., 2023). The adsorption process is considered a surface phenomenon, in which ions, molecules, or atoms from a gas, liquid, or dissolved solid move from the gas or liquid phase to a solid or solid-liquid phase. There, they form a mono- or multilayer by adhering to the active sites of the adsorbent (Alaqarbeh, 2020). The process is driven by interactions between the pollutant molecules and the oppositely charged functional groups on the sorbent surface (Chai et al., 2021). The adsorption process can be divided into two major categories: physical adsorption, and chemical adsorption (Al-Ghouti et al., 2023). In physisorption, weak van der Waals forces govern the interactions, resulting in the physical attraction of solute molecules to the sorbent surface. Chemisorption, by contrast, involves the formation of chemical bonds, typically producing a single molecular layer and offering stronger, less reversible binding (De Gisi et al., 2016). To quantify adsorption efficiency, models such as the Langmuir and Freundlich isotherms are frequently employed (Rashid et al., 2021).
Activated carbon, a carbon-based adsorbent, is the most commonly used material due to its large surface area, well-developed pore structure (macro-, meso-, and micropores), and abundance of functional groups (e.g. carboxyl, carbonyl, phenol, lactone, quinone) that enhance pollutant adsorption. However, its application is often constrained by high production costs, limited regeneration capacity, and disposal challenges (De Gisi et al., 2016; Gautam et al., 2014). Activated carbon is produced from various precursors, such as charcoal and agricultural waste. Commercially produced activated carbon, which is non-renewable, tends to be more expensive than its non-commercial counterpart (Neme et al., 2022). Additionally, the reliance on fossil fuel-derived raw materials for commercial

activated carbon production underscores the need for environmentally sustainable and cost-effective alternatives (Ai et al., 2020; Karagöz et al., 2008).

The disposal of agri-food production residues, including by-products, poses significant environmental challenges due to their physical characteristics, large volumes, and, in some cases, potential toxicity. Utilizing these materials, particularly lignocellulosic substances, as low-cost adsorbents offers a dual environmental benefit: reducing waste volume and mitigating water pollution. For a low-cost adsorbent to be effective, it must demonstrate high adsorption capacity, rapid adsorption rates, and selectivity across varying pollutant concentrations (De Gisi et al., 2016; Grassi et al., 2012).

The functional groups present in the components of lignocellulosic materials - such as hemicellulose, lignin, lipids, proteins, sugars, hydrocarbons, and starch - play a pivotal role in adsorption processes (De Gisi et al., 2016; Bhatnagar et al., 2015; Bhatnagar and Sillanpää, 2010). Adsorbents derived from biological or organic materials are commonly referred to as biosorbents, as biosorption, a subcategory of adsorption, specifically involves materials of biological origin (Michalak et al, 2013). Biosorbents can be categorized into several groups, including algae, microbial, and agricultural waste-based adsorbents. Using biomass, such as agricultural waste, offers several advantages, including low operational costs, reduced energy requirements, and a decrease in waste production (Varghese et al., 2019). Due to its simplicity, effectiveness, similarity to conventional ion exchange processes, and availability of biomass, biosorption has emerged as a promising biotechnological method for removing pollutants from solutions (Rusu et al., 2021). However, its industrial application remains limited, even in hybrid technologies designed to complement traditional pollutant treatment methods.

Building on the promising potential of agro-industrial biomass, buckwheat hulls stand out as a particularly viable resource for developing low-cost and sustainable adsorbents (Ai et al., 2020). These hulls are rich in amino acids featuring amino ($-NH_2$) and carboxyl (-COOH) functional groups, along with other functional moieties, which actively facilitate the adsorption of pollutants from aqueous solutions (Shaikhiev et al., 2020; Shaikhiev et al., 2017). The unique amino acid composition of buckwheat hulls underscores their suitability as a cost-effective biosorbent, as these functional groups enable selective interaction with various types of pollutants, depending on the characteristics of the adsorbate (Reljić et al., 2022).

This review explores the feasibility of leveraging buckwheat hulls as an economical and eco-friendly solution for wastewater treatment, offering a sustainable alternative to conventional activated carbon. By addressing both water pollution and waste management challenges, the utilization of buckwheat hulls exemplifies the dual environmental benefits associated with repurposing agro-industrial residues.

Characteristics of buckwheat hulls

Buckwheat

Buckwheat (*Fagopyrum*) is a herbaceous plant belonging to the *Polygonaceae* family. It exists as either an annual or perennial species, typically growing to heights between 10 and 100 cm. The plant is characterized by its upright, branched, and evenly leafy growth. Originally native to the mountain slopes of southern China, buckwheat is now cultivated across diverse ecological zones worldwide, including Asia, Europe, and the United States (Huda et al., 2021; Ji et al., 2019; Sinkovič et al., 2020).

The two most widely cultivated and consumed species of buckwheat are common buckwheat (*Fagopyrum esculentum* Moench) and Tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn) (Huda et al., 2021; Ahmed et al., 2013). In recent years, buckwheat has gained increased popularity due

to its health-promoting properties, which are attributed to its rich nutritional and bioactive composition (Huda et al., 2021; Ge and Wang, 2020).
Its seeds are a significant ingredient in the production of baked goods and confectionery, contributing to its expanding global utilization (Huda et al., 2021; Mohajan et al., 2019).
The industrial processing of buckwheat groats involves several stages, including cleaning, roasting, sizing, hulling, sorting, and the separating of the waste and by-products. Among the notable by-products of this technological process, are buckwheat straws and hulls, which are generated in significant quantities (Hęś et al., 2012; Dziedzic et al., 2010).
These by-products, particularly buckwheat hulls, are of growing interest for their potential applications in sustainable industries, including their use as low-cost adsorbents for wastewater treatment. Their composition and functional properties offer a compelling case for repurposing agricultural residues, aligning with global efforts to reduce waste and promote environmental sustainability.

Composition of the buckwheat hulls
Expanding on the viability of buckwheat hulls as cost-effective adsorbents, their chemical composition and structural characteristics further reinforce their suitability for environmental applications. The nutrient composition of buckwheat hulls, according to Zhang et al. (2023), is shown in Table 1. More than 30% of buckwheat hulls' composition consists of insoluble non-starch polysaccharides (NSPs). The total amino acid content in BHs is 25.67 mg/g, which includes essential amino acids (EAAs) at 1.04% and non-essential amino acids (non-EAAs) at 1.53%, covering all individual EAAs (Table 1). The three most abundant individual amino acids are the non-EAA glutamic acid (0.33%), aspartic acid (0.25%), and cysteic acid (0.23%). The content of individual EAAs is less than 2 mg/g. These results are consistent with the study conducted by Matseychik et al. (2021).
The physical structure of buckwheat hulls also plays a crucial role in their adsorption capabilities. The surface features a well-developed microrelief with micropores measuring up to 0.1 µm, which enhances the surface area available for pollutant interaction and adsorption (Shaikhiev et al., 2020).

Table 1. Nutrient composition and amino acid composition of buckwheat hulls (% w/w). The values are expressed as g/100 g dry weight ± SD (standard deviation) (Zhang et al., 2023)

		Amino Acid Composition			
Nutrient composition	**Content (%)**	**EAA**	**Content (%)**	**Non-EEA**	**Content (%)**
Moisture	10.8±0.0	Leucine	0.19	Glutamic acid	0.33
Ash	1.7±0.0	Tryptophan	0.15	Aspartic acid	0.25
Protein	4.05±0.05	Threonine	0.14	Cysteic acid	0.23
Total fat	0.1±0.0	Valine	0.13	Glycine	0.16
Total starch	2.55±0.0	Phenylalanine	0.11	Serine	0.15
Resistant starch	n.d.	Histidine	0.11	Proline	0.14
Total NSPs		Isoleucine	0.11	Alanine	0.13
-Insoluble	31.1±0.2	Lysine	0.09	Arginine	0.1
-Soluble	0.30±0.05	Methionine	0.02	Tyrosine	0.04
				Cystine	n.d.

Utilisation of buckwheat hulls as a sustainable biosorbent for water treatment applications

Figure 1. Physical appearance of unmodified buckwheat hulls alongside biochar derived from buckwheat hulls

Table 2. Overview of buckwheat hull-based biosorbents for water pollutants and other adsorbates

Biosorbens	Adsorbate/Pollutant	q_{max} (mg/g)	Modification	Reference
Unmodified buckwheat hulls	Hg (II), (Zn(II), Cd(II))	244.0 (35 °C)	-	Wang et al., 2013
	Zn(II), Cd(II), Co(II), Cu(II), Ni(II))	0.4 -0.8	-	Tomczak et al., 2013
	Au(III)	425.53 (35 °C)	-	Deng et al., 2014
	Cr(VI)	63.61 (35 °C)	-	Li et al., 2014
Chemically modified buckwheat hulls	Au(III)	450.45 (35 °C)	1-hydroxylethylidene diphosphonic acid	Yin et al., 2012
	Au(III)	390.11	organophosphonic acid	Yin et al., 2013
	Au(III)	456.16	organodiphosphonic acid	Xu et al., 2013
	Cu(II)	50.0	5% (w/v) NaOH	Tomczak and Kaminski, 2021
	dye Reactive Black 5	85.18	epichlorohydrin and ammonia water	Jóźwiak et al., 2021
	pesticide 2,4-dichlorophenoxyacetic acid	161.1 (25 °C)	sulfuric acid	Franco et al., 2021
	ketoprofen	194.1	sulfuric acid	Franco et al., 2022
Thermally modified buckwheat hulls (biochar and activated carbon)	Zn(II) and tetracycline	Tetracycline 106.38 Zn(II) 151.52 (single-component) Tetracycline 126.58 Zn(II) 357.14 (competitive)	biochar modified with ammonium chloride solution (2 g/L) and magnetite (Fe_3O_4) (mass ratio 6.5:2)	Ai et al., 2020
	Co(II)	24.0 (35 °C)	biochar immobilised in 1.5 wt% Na-alginate + 1% (w/v) $CaCl_2$	Lim et al., 2022
	P-PO_4	75.26	biochar modified with $CaCl_2$	Pan et al., 2024

As previously highlighted, the unique combination of rich chemical composition, diverse functional groups, and favourable physical properties make buckwheat hulls a promising candidate for wastewater treatment applications. However, despite their potential, the body of literature on the utilisation of buckwheat hulls as a biosorbent remains limited. Table 2 provides an overview of some of the pollutants that have been successfully removed using buckwheat hulls as a biosorbent. Additionally, Figure 1 illustrates the physical appearance of unmodified buckwheat hulls alongside biochar derived from buckwheat hulls, showcasing the transformation through thermal modification and its impact on material morphology. A more detailed examination of specific studies is presented in the following sections of the manuscript.

Unmodified buckwheat hulls as biosorbent

In their unmodified form, buckwheat hulls have been studied as biosorbents for the removal of various metal ions.

Wang et al. (2013) explored the capacity of buckwheat hulls to adsorb Hg(II) ions in the presence of Zn(II) and Cd(II) ions. The results confirmed that buckwheat hulls effectively remove Hg(II) from aqueous media, achieving a maximum adsorption capacity of 244 mg/g, as determined by the Langmuir isotherm model at 35 °C. Furthermore, buckwheat hulls exhibited 100% selectivity for Hg(II) over other metal ions, underscoring the significant role of functional groups such as carboxyl, hydroxyl, and amino groups. The carboxyl groups facilitate coordination with Hg(II) ions, while the electron-donating properties of the hydroxyl and amino groups further enhance the interaction.

In another study, Tomczak et al. (2013) investigated the adsorption of various heavy metal ions (Zn(II), Cd(II), Co(II), Cu(II), Ni(II)) from aqueous solutions using buckwheat hulls. The adsorption experiments, conducted at an initial ion concentration of 10-50 mg/L, pH 5-6, and 25 °C, revealed the highest adsorption capacity for Co(II) ions and the lowest for Cu(II) ions.

Deng et al. (2014) examined the use of buckwheat hull residues (BHJC) for the adsorption of Au(III). The study found that BHJC demonstrated both a high adsorption capacity and selectivity for Au(III), positioning it as a potential biosorbent for gold ion removal from aqueous solutions. The experimental data were best described by the Langmuir isotherm model, indicating single-layer coverage and chemical adsorption of Au(III) on the BHJC surface. The maximum adsorption capacity for Au(III) was determined to be 425.53 mg/g at 35 °C, a high value attributed to the presence of surface functional groups, such as hydroxyl and carboxyl groups, which have a strong affinity for gold ions.

Li et al. (2014) reported that the adsorption of Cr(VI) by buckwheat hulls followed the Langmuir isotherm, with a maximum capacity of 63.61 mg/g at 45 °C. The removal mechanism involved interactions with carboxyl and amino groups, along with the chemical reduction of Cr(VI) to Cr(III).

Collectively, these studies demonstrate that buckwheat hulls are a versatile and effective biosorbent for the removal of a broad range of heavy metal ions from water. The adsorption capacities are influenced by the presence of specific functional groups and the characteristics of the involved metal ions.

Chemically modified buckwheat hulls as biosorbent

The modification of different materials, including lignocellulosic materials such as buckwheat hulls aims to enhance their adsorption properties, making them more effective in treating wastewater. The following studies explore the adsorption capacity and performance of modified buckwheat hulls for various pollutants.

Yin et al. (2012) functionalized buckwheat hulls with 1-hydroxylethylidene diphosphonic acid (HEDP-BH) to improve their adsorption capacity for metal ions. The introduction of HEDP groups, containing both hydroxyl (OH) and phosphonate (PO_3) functional groups, significantly enhanced the coordination properties of the biosorbent. These groups facilitated the formation of strong chelate structures, which contributed to the high adsorption capacity and selectivity of HEDP-BH for various metal ions. The study demonstrated that HEDP-BH successfully adsorbed Au(III), Hg(II), Cu(II), Co(II), Cd(II), Cr(III), Zn(II), and Ni(II) ions from simulated wastewater, with a maximum adsorption capacity for Au(III) of 450.45 mg/g at 35 °C. The functionalized hulls exhibited almost 100% selectivity for Au(III), particularly in the presence of Zn(II) and Co(II). The regeneration of HEDP-BH was also evaluated, with results showing a decrease in adsorption capacity after two cycles, even though thiourea and HCl effectively facilitated desorption.

In a similar study, Yin et al. (2013) functionalized spent buckwheat hulls with organophosphonic acid (OPA-BH) to enhance their adsorption capacity for Au(III) ions from gold-containing wastewater. Esterification of buckwheat hulls improved their coordination properties, leading to better adsorption performance. The results showed that OPA-BH exhibited a higher adsorption capacity for Au(III) than unmodified buckwheat hulls, with a maximum adsorption capacity of 390.11 mg/g, as determined by the Langmuir isotherm. Desorption experiments with HCl and thiourea revealed a slight reduction in adsorption capacity after two cycles, indicating the good reproducibility of OPA-BH for Au(III) removal.

Xu et al. (2013) explored the modification of buckwheat hulls with organodiphosphonic acid (ODPA-BH) for the adsorption of Au(III) ions from spiked and industrial wastewater. The powdered buckwheat hull biomass underwent surface modification by agitation in a 20.0% 1-hydroxylethylidenediphosphonic acid solution at 60 °C for 24 hours. After filtration and drying, the treated biomass was subjected to a thermochemical reaction at 120 °C for 4 hours. The thermochemical modification process created negatively charged oxygen and hydroxyl groups that contributed to the binding of metal ions. The adsorption capacity for Au(III) was determined to be 456.16 mg/g at 35 °C, as indicated by the Langmuir isotherm, demonstrating the effectiveness of ODPA-BH as an adsorbent for gold ions in wastewater.

Tomczak and Kaminski (2021) studied the adsorption of Cu(II), Zn(II), and Ni(II) ions from multicomponent aqueous solutions using modified buckwheat hulls. The hulls were pre-treated with 5% (w/v) NaOH at 25 °C and demonstrated better adsorption performance compared to raw buckwheat hulls. The modification process contributed to ion exchange, where Na^+ ions replaced metal cations such as Cu^{2+}, Ni^{2+}, and Zn^{2+}. The study revealed a maximum adsorption capacity of 50 mg/g for Cu(II), while Ni(II) and Zn(II) ions had lower adsorption capacities of 5.9 mg/g and 5.6 mg/g, respectively. This study confirmed that pre-treated buckwheat hulls can effectively remove metal ions from multicomponent wastewater systems.

Jóźwiak et al. (2021) investigated the modification of buckwheat hulls with epichlorohydrin and ammonia water for the removal of the anionic dye Reactive Black 5 (RB5). The adsorption process was conducted in two phases: a short, intensive first phase (45-60 min) and a longer, slower second phase (195-255 min). The results showed that unmodified buckwheat hulls (BH) had the shortest sorption time due to their compact structure and lower number of functional groups. However, buckwheat hulls modified with ammonia and epichlorohydrin (BH-E-A) exhibited longer sorption times, likely due to electrostatic interactions between the aminated polysaccharide chains. According to Jóźwiak et al. (2020), the modification of the sorbent surface structure during ammonization likely caused the swelling of external layers. The acidic amine groups (pH 3) incorporated into the polysaccharide chains underwent protonation, resulting in repulsion between the positively charged cellulose/hemicellulose chains. This created larger gaps on the surface of the buckwheat husks, allowing RB5 to penetrate deeper layers. Swelling was not immediate upon introducing the sorbent into an acidic solution, and the sorption centres, previously inaccessible to RB5, were gradually exposed, extending the time needed to reach sorption equilibrium. The longer equilibrium time of BH-E, compared to BH, could be due to the presence of epoxide groups on the sorbent's surface, which – theoretically – could bind dyes permanently. The functional groups of RB5 (vinyl sulfone, sulfone, hydroxyl, and amine ones) reacted with the epoxide groups of BH-E under conditions not optimal for chemisorption (pH 3), which made the reaction longer. The maximum sorption capacity was 85.18 mg/g for the epichlorohydrin-ammonia modified hulls, attributed to the increased number of amine functional groups in the modified structure. The RB5 dye sorption efficiency on all tested sorbents (BH, BHE, BH-A, and BH-E-A) was highest at the initial sorption pH (pH 3) and decreased as the pH increased. The high sorption effectiveness of RB5 at low pH (pH 3) was attributed to the protonation of the sorbent's functional groups (–OH, $-NH_2$). At low pH, the positively charged surface of the sorbent electrostatically attracted the anionic dye, enhancing its sorption. The hydroxyl functional groups of polysaccharides are easily protonated in a strongly acidic environment. This explains the notable reduction in RB5 binding efficiency on BH and BH-E at pH values greater than 3.

In the study by Franco et al. (2021), buckwheat hulls were modified with sulfuric acid to enhance their adsorption capacity for the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions. Characterisation of the modified material revealed significant improvements in its adsorptive properties. The optimal conditions for adsorption were found at pH 2, where the maximum adsorption capacity reached 161.1 mg g^{-1} at 25 °C. Kinetic and equilibrium data indicated that the adsorption process involved electrostatic interactions, with the Avrami-fractional order and Liu model best fitting the experimental data. Furthermore, modified material proved efficient in removing 2,4-D from river water samples, achieving removal rates of 76% for both the "Conceição" and "Jacuí" rivers simulated effluent.

In a subsequent study, Franco et al. (2022) investigated the use of acid-modified buckwheat hulls for the adsorption of ketoprofen in batch experiments. Characterisation results revealed that acid treatment induced a more irregular surface with additional porous spaces. The adsorption process was most effective at an acidic pH of 3. Kinetic studies followed a pseudo-second-order model, with a maximum adsorption capacity of 74.3 mg g^{-1} for a 200 mg L^{-1} ketoprofen solution. The adsorption capacity decreased with increasing temperature, reaching a maximum of 194.1 mg g^{-1}. Thermodynamic analysis confirmed that the process was exothermic, indicating that physical forces were likely involved. Furthermore, the modified buckwheat husks demonstrated high efficiency, achieving a 71.2% removal rate when applied to synthetic effluents containing various drugs and salts.

These studies demonstrate that modifications to buckwheat hulls, including functionalization with organic acids and alkali treatment, significantly enhance their adsorption capacity for various metal ions, but also for dyes, pesticides, and pharmaceuticals.

Thermally modified buckwheat hulls as biosorbent: biochar and activated carbon

Common feedstocks for commercial activated carbon include fossil oil residues, wood, peat, lignite, and coal (Altenor et al., 2009), all of which are typically expensive, with some being non-renewable (Ahmedna et al., 2000; Tan et al., 2008). Due to these limitations, there has been growing interest in using agricultural by-products as sustainable, cost-effective alternatives. These materials can be transformed into biochar or activated carbon through thermal processes with or without chemical activation (Yahya et al., 2015). While both biochar and activated carbon are carbon-rich materials derived from biomass, they differ in terms of their production processes and applications. Biochar is typically produced through a pyrolysis process at lower temperatures and is primarily used for soil enhancement and carbon sequestration. It is characterized by a relatively lower surface area and porosity compared to activated carbon. On the other hand, activated carbon is produced through higher-temperature pyrolysis or chemical activation processes, resulting in a material with a highly developed surface area and extensive porosity. This makes activated carbon particularly effective for adsorption applications, such as water treatment and air purification, due to its higher adsorption capacity for various pollutants.

Materials with high carbon content and low inorganic impurities are especially suited as precursors for activated carbon production (Ioannidou and Zabaniotou, 2007; Yahya et al., 2015). Its classification is typically based on the source material, which plays a pivotal role in determining the carbon's quality and characteristics (Mozammel et al., 2002). Several factors influence the properties of activated carbon, including the choice of an activating agent (Hirunpraditkoon et al., 2011; Hervy et al., 2018), activation time (Gliścińska and Babeł, 2013), impregnation conditions, processing temperature (Amaya et al., 2005), and the presence of inorganic impurities (Yahya et al., 2015). The selection of raw materials for activated carbon production depends on their cost, purity, activation potential, and the reliability of supply (Hernandez et al., 2007).

Activated carbon can be produced from buckwheat hulls using either physical or chemical activation methods. In physical activation, the raw material is first carbonized and then activated using steam, CO_2, air, or a gas-steam mixture, a process known as "dry oxidation" (Yahya et al., 2015). CO_2 activation typically results in activated carbon with higher carbon content and lower ash, as well as increased microporosity (89%) compared to steam activation (61%), yielding larger surface areas (Pena et al., 2020). Carbonization occurs at temperatures between 400 and 850 °C, while activation takes place between 600 and 900 °C (Ioannidou and Zabaniotou, 2007). Carbonization reduces volatile substances and increases carbon content, creating initial porosity, but not sufficient surface area. Chemical activation, or "wet oxidation," involves impregnating the raw material with a chemical agent before heating, typically at temperatures between 450 and 600 °C (Bello and Ahmad, 2011). Common activating agents include $ZnCl_2$ and H_3PO_4 (Donald and Ohtsuka, 2011; Cruz et al., 2012) H_2SO_4, K_2S, KCNS (Demiral et al, 2008), HNO_3, H_2O_2, $KMnO_4$ (Al-Qodah and Shawabkah, 2009), NaOH, KOH (Zhengrong and Xiaomin, 2013), and K_2CO_3 (Hayashi et al., 2002, Adinata and Daud, 2007). This method produces higher surface areas in a shorter time and allows better control over porosity, though it is more expensive and environmentally harmful compared to physical activation (Pena et al., 2020). Both methods require a washing step to remove excess chemicals, typically using acid or alkali, followed by a water rinse to prevent blockage of the carbon's porosity. Key factors influencing carbon activation include pore structure, surface oxygen groups, the carbonate matrix, and active sites formed by inherent alkaline and alkaline-earth species (Hervy et al., 2018; Pena et al., 2020).

To date, only a few studies have explored the use of buckwheat hull biochar and activated carbon in water treatment applications. Existing research includes the removal of zinc (Zn) and tetracycline from wastewater (Ai et al., 2020), the removal of cobalt from aqueous solutions (Lim et al., 2022), and phosphorus removal using calcium chloride-modified buckwheat hull biochar (Pan et al., 2024). While these studies are limited, they demonstrate the potential of buckwheat hull-based materials in addressing water contamination. Additionally, buckwheat hull biochar and activated carbon have been applied in other fields, such as toluene adsorption from air (Takada et al., 2022), synthesis gas purification (Pena et al., 2020), and as materials for lithium-ion batteries (Yu et al., 2021) and supercapacitor electrodes (Zhang et al., 2022).

The study of Ai et al (2020) investigated the single-component and competitive adsorption of antibiotic tetracycline (TC) and Zn(II) using a magnetic biochar derived from buckwheat peel powder (NH_4Cl-BHP-char/Fe_3O_4) in batch experiments. The new material exhibited a high surface area

(1119.097 m^2/g) and pore volume (0.139 cm^3/g). The adsorption process was found to be endothermic, spontaneous, and highly pH-dependent. For single-component adsorption, the maximum adsorption capacities were 106.38 mg/g for TC and 151.52 mg/g for Zn(II), with both following monolayer adsorption. In competitive adsorption, the maximum capacities increased to 126.58 mg/g for TC and 357.14 mg/g for Zn(II), with both film diffusion and intra-particle diffusion contributing to the adsorption process. The study also highlighted that TC and Zn(II) enhanced each other's adsorption. The biochar also demonstrated good reusability.

Lim et al. (2022) investigated the removal of cobalt ions (($Co(NO_3)_2$ was used for model solution preparation) from aqueous solutions using buckwheat hull biochar (BHBC) in batch and fixed-bed column experiments. The biochar was produced via pyrolysis of buckwheat hulls at varying temperatures (450 °C, 600 °C, 750 °C, and 900 °C), ground to a particle size ≤0.5 mm, and immobilized by mixing with 1.5 wt% sodium alginate. The immobilized biochar was subsequently treated with a 1 wt% calcium chloride solution. Characterisation revealed that BHBC possessed functional groups such as -COOH, -OH, and -ROH, along with a negatively charged, microporous structure with a large surface area, enabling diverse adsorption mechanisms, including monolayer adsorption, chemical interactions, electrostatic interactions, cation exchange, and complexation. Batch adsorption experiments showed the process aligned well with the Langmuir isotherm model and the pseudo-second-order kinetic model, with a maximum adsorption capacity of 24.0 mg/g at 35 °C. In fixed-bed column experiments, cobalt adsorption was best described by the Thomas and Yoon-Nelson models. These results demonstrated that BHBC is a promising, cost-effective adsorbent for removing cobalt from aqueous solutions, offering versatility in both batch and continuous treatment systems.

The study by Pan et al. (2024) explored the adsorption and desorption properties of phosphorus (KH_2PO_4 was used for model solution preparation) on $CaCl_2$-modified buckwheat hull biochar (BBC) and its subsequent application as a phosphorus-rich fertilizer. The optimal biochar was produced by pyrolyzing a 1:1 mass ratio of buckwheat hulls and $CaCl_2$ at 700 °C, achieving a maximum phosphorus adsorption capacity of 75.26 mg g^{-1} with a dosage of 2.0 g L^{-1}. Adsorption was determined to be a monolayer chemisorption process, driven by a spontaneous Ca–P chemical reaction. When applied to soil as a fertilizer, phosphorus-saturated biochar improved soil properties, including increasing phosphorus content (from 0.68 to 1.38 g kg^{-1}). It also promoted buckwheat plant growth. This dual functionality positions this new material as a sustainable solution for reducing phosphorus in water bodies and addressing phosphorus deficiencies in soils.

Given these promising applications, there is substantial potential for further research into the use of buckwheat hull biochar and activated carbon for water treatment, particularly in terms of expanding their effectiveness and exploring new contaminants for removal.

Conclusions

Buckwheat hulls, an abundant and low-cost by-product of the agri-food industry, demonstrate significant promise as biosorbents for water purification. This mini-review highlights their potential to address two pressing global challenges: water pollution and the need for sustainable waste management. Modified and unmodified buckwheat hulls have shown notable adsorption capacities for a variety of pollutants, including heavy metals, synthetic dyes, pesticides, antibiotics, and nutrients like phosphorus, proving their versatility in water treatment applications. Research has demonstrated that chemical and physical modifications enhance the adsorption efficiency of buckwheat hulls by increasing their surface area, introducing functional groups, and improving porosity. Noteworthy studies include the removal of cobalt, tetracycline, and zinc from aqueous solutions, where buckwheat hull-derived adsorbents achieved competitive adsorption capacities and demonstrated favourable kinetics, thermodynamics, and reusability. Furthermore, calcium-modified buckwheat hull biochar has shown dual functionality by effectively adsorbing phosphorus from water and subsequently serving as a slow-release phosphorus fertilizer, improving soil quality and crop growth. The ability of buckwheat hull-based adsorbents to integrate multiple environmental benefits positions them as a sustainable alternative to conventional activated carbon, whose production relies heavily on non-renewable resources and is associated with high costs and environmental burdens. By valorising agricultural residues, these adsorbents contribute to the principles of a circular economy, fostering waste reduction and resource recovery. Despite their potential, the application of buckwheat hulls in water treatment remains underexplored. Future research should focus on evaluating performance in diverse water matrices, optimizing modification techniques, and scaling up production.

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