

A Review on Utilising Combined Agricultural Waste Adsorbents for Ammonia Nitrogen Removal: Insights into Bamboo Biochar and Empty Fruit Bunch

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Abstract: This review highlights the effectiveness of bamboo biochar and empty fruit bunch (EFB) fibres as low-cost adsorbents for ammonia nitrogen removal from wastewater. Both materials are highlighted for their abundant availability and substantial adsorption capabilities. Bamboo biochar, derived from pyrolysed bamboo, benefits from its high surface area and porosity, enhanced further through chemical activation that increases its functional groups and pore structure. This modification significantly improves its efficiency in adsorbing ammonia nitrogen. Similarly, EFB, a by-product of palm oil production, is treated through carbonisation and activation, which enhances its adsorption properties. The review also discusses the potential for combining bamboo biochar and EFB, as their complementary properties could offer a more effective solution for wastewater treatment. The paper emphasises the advantages of these materials in addressing environmental challenges and highlights the need for further research into their combined use, as well as their potential for reuse and regeneration to promote sustainability. This review provides insights into optimising adsorbent modifications and exploring practical applications in wastewater treatment.

Keywords: Bamboo biochar; Modified empty fruit bunch; Combined adsorbent; Ammonia nitrogen Adsorption; Wastewater

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1. Introduction

Wastewater is considered one of the primary contributors to water pollution. Human activities have led to the unavoidable production of waste, and a portion of this waste ends up as wastewater. The amount and type of waste produced vary depending on people's lifestyle, behaviour, and surrounding condition. The design of the sewer system plays a notable role in the composition of wastewater [1]. The urban drainage system is made up of a series of sewer networks that transport urban wastewater and rainwater to one or more terminal sites. Some of the wastewater discharged from the combined systems is released into local water bodies, sometimes without treatment [1]. Moreover, urbanization is rapidly increasing in many cities, leading to more frequent storm events due to climate change. Consequently, existing combined sewer systems in these cities are often unable to transport all rainwater and wastewater to treatment plants during periods of high-intensity rainfall. As a result, certain areas experience flooding, and combined sewer overflows (CSOs) leak untreated water into the environment [2]. This has heightened societal concern about environmental protection,

particularly water management in metropolitan areas, and growing the demand for access to clean drinking water [3-4].

There are many constituents that can be found in wastewater including debris, grease and grit, bacteria, nitrogen, ammonia, and metals [1]. When these contaminants are released into the environment through wastewater discharge, they can have harmful effects on both the environment and human health. Ammonia is an essential component in biological wastewater treatment because bacteria need it to create proteins, including enzymes for breaking down food and producing energy. However, in drainage system, the concentration of ammonia nitrogen should not be high due to various ecological problems [5]. Despite this, waste discharged from urban housing into urban drainage systems often contains high levels of ammonia, which is concerning as it can be released into rivers or other waterways. Excessive amount of ammonia nitrogen in water bodies can lead to environmental disruption, including the depletion of dissolved oxygen, eutrophication and toxicity to aquatic life [6]. Therefore, effective ways to remove ammonia nitrogen in water need to be developed, to improve the quality and sustainability of the environment.

Wastewater can be treated using various methods such as chemical precipitation, membrane filtration, reverse osmosis, ion exchange, and adsorption [7]. However, some of these approaches are considered limiting due to their significant capital and operational expenses, as well as the generation of secondary wastes that pose additional treatment challenges. Currently, researchers have studied several methods, both traditional and conventional, to remove ammonia nitrogen contamination from water, including chemical precipitation [8], biological treatment [9], air stripping [10-11], ion exchange [12-13], breakpoint chlorination [14], biological nitrification-denitrification [15-16] and adsorption [9]. Biological treatments are a classic way of eliminating ammonia from wastewater, but they have various drawbacks, such as being rapidly inhibited by toxic shock, pH shifts, low dissolved oxygen, and low temperature. Kinidi et al. (2018) reported that ammonia removal through air stripping can remove up to 95.4% of the ammonia from wastewater [17]. However, the ammonia stripping has several disadvantages, including high operating and maintenance costs, fouling issues, sludge generation, and the emission of ammonia gas into the environment. Viotti et al. (2015) reported that the stripper efficiency decreases from 98% to 80% over six months of usage [18]. Hence, among all the mentioned techniques, adsorption has been proven to be the best treatment method based on previous studies as it is cost-effective, simple to operate and eco-friendly. The adsorption process occurs when a solute in phase of gas or liquid accumulates on the surface of the adsorbent, forming an atomic or molecular film known as adsorbate. Purification, catalytic reaction and bulk separation processes benefit the most from adsorption due to its high efficiency of separation and mild operating conditions [19].

In adsorption, adsorbents are used to help remove the pollutants from wastewater. Many adsorbents effective in removing contaminants from wastewater system, including carbons, zeolites, aluminas, and silica gels [20]. However, the cost of these conventional adsorbent is high, which limits the usage of adsorption in wastewater treatment applications. Consequently, research to identify effective and affordable adsorbents have been gradually increasing, as these are more economically feasible, readily available, and environmentally friendly (20-21). One alternative adsorbent that is gaining attention among researchers is the

use of agricultural waste and natural materials as adsorbents [22-23]. Ali et al. (2012) reported that the removal of various organic pollutants by the natural materials and agricultural waste as adsorbent ranges from 80% to 99.9% [24]. Bamboo charcoal, with its outstanding features such as high surface area, high porosity, and enriched surface functional groups, have shown enormous potential for various applications [25]. It also has considerable capability for removing pollutants from wastewater [26]. In addition, EFB fibres have been reported to be effective adsorbents for the removal of ammonia nitrogen, colour, and nutrients [6,27]. Demirak et al. (2015) observed that modifying agricultural waste can break the lignin structure, leading to increase in ammonia nitrogen removal [28]. A multi-adsorbent systems has also been gaining attention as it is reported to exhibit higher adsorption rates [29]. Based on previous research, no studies currently report that these systems have a lower adsorption rate compared to single adsorbent systems. The adsorbents in multi-adsorbent systems are either combined, mixed or hybridised, depending on the physical characteristics of the adsorbent used.

1.1 Types of adsorbent

Adsorbent are materials that adsorbs other substances through adsorption. There are two types of adsorbents: natural and synthetic [30]. Natural adsorbents are generally inexpensive, abundant, and offer great flexibility for modification and improvement to enhance their adsorption capabilities [31]. Synthetic adsorbents, on the other hand, are typically prepared from various types of waste materials [31]. Each adsorbent has unique characteristics that aid in removal of the contaminants. Adsorbents can also be derived from agricultural waste, including shells and stones of nuts and fruits, as well as waste from food industry processing, such as rice husks, sugarcane and bagasse [32-35]. In recent decades, agricultural waste has increasingly been used as an adsorbent in water treatment procedures, utilising materials like fruit shells and stones and waste from cereal production [36-39]. These materials can be used in their natural state or modified physically and chemically [40]. To enhance the adsorption effectiveness of adsorbates, these adsorbents can be blended, mixed, or hybridised.

Hammanini et al. (2007) reported that the physicochemical properties of adsorbents can be affected by the characteristics of the solution in which they are used [41]. Factors such as pH, concentration, ionic strength, the presence of anions, and other variables all play a role in the adsorption process [41-43]. Thus, this method is particularly convenient for immobilising ions in dilute solutions, such as wastewater [44]. Nevertheless, the most important property of an efficient adsorbent for pollutant removal is its porous structure. Good porous structure equates to high surface area, which results in high adsorption rate. Additionally, the time required to reach adsorption equilibrium should be as short as possible, allowing the adsorbent to remove contaminants quickly [45]. Furthermore, the capacity of the adsorbents to accumulate pollutants within the given time frame is also important.

Given the diverse range of adsorbents available, the cost-effectiveness and environmental impact of these materials are critical considerations. This has led to a growing interest in low-cost adsorbents derived from natural and waste materials, which offer a sustainable alternative for wastewater treatment.

1.2 Low-cost adsorbent

As previously mentioned, the use of waste products as an adsorbent is gaining popularity, particularly in wastewater treatment, primarily due to their low cost. Natural materials such as wood or peat, wastes or by-products from the industrial, agricultural, or residential sectors, like bagasse and ash, can all be categorised as low-cost adsorbents, whether organic or inorganic in nature [44]. The availability, high efficiency, easy handling, and low cost of low-cost adsorbents make them ideal for use in large-scale industrial operations and farm waste management [46]. Many studies conducted over the last decade have found that many agricultural by-products and industrial wastes are low in price or have no economic value [44]. Waste such as rice husks, peanut skins, leaves, coffee and tea waste, onion and orange peels, and many other materials have shown potential as low-cost adsorbents [47-49]. Table 1 shows various studies and research on low-cost materials used as adsorbents, either in laboratory scale or in industry, for adsorbate removal. Most of these waste materials, which are rich in lignin, cellulose and tannin are produced in large volumes and face disposal problems. Hence, their abundance and availability make them a good source of raw material for producing activated carbon, a popular adsorbent for substance removal in wastewater treatment.

Table 1. Adsorption capacities of low-cost adsorbent from agricultural waste

Adsorbent material	Adsorbates	Adsorption / Removal capacity	Reference
Wheat bran	Cadmium	87.15%	[49]
Tea waste	Copper and lead	48 mg/g – 65 mg/g	[50]
Orange peels	Nickel	96%	[51]
Banana peel	Cadmium	35.53 mg/g	[52]
Banana peel	Cr(VI)	131.56 mg/g	[53]
Langsat Peel	Ammonia Nitrogen	28.67 %	[54]
Watermelon Rinds	Ammonia Nitrogen	4.62 mg/g	[20]
Banana Stalk	Pb (II)	13.53	[55]

While low-cost adsorbents provide an economical solution, their individual performance can sometimes be limited. To enhance their efficiency, researchers are increasingly exploring hybrid and combined adsorbent systems, which leverage the complementary properties of different materials to achieve superior adsorption results.

1.3 Hybrid and combined adsorbents in wastewater treatment

Numerous studies have focused on development and modification of adsorbents for wastewater treatment, particularly low-cost adsorbents. However, the application of mixed, combined or even hybrid forms of these low-cost adsorbents in a single system is still new and is growing among researches. This combined or hybrid adsorbent system is also known as the multi-system adsorbent, where different type of adsorbent materials are combined or hybridised to form a new class of adsorbent. The difference between hybrid and combined adsorbent is that hybrid adsorbent undergoes hybridisation where different adsorbent materials are merged into a single system, and once hybridised, the materials cannot return to

its original form. In contrast, combined adsorbent are materials that are simply combined into one system without the requirement of changing their chemical or physical originality. Hence, the materials can be easily recovered and recycled, as there is no chemical or physical attachment between them.

There are only few studies that research multi-adsorbent systems for the adsorption of pollutants and contaminants. Albadarin et al. (2014) used a mixture of tea waste and dolomite as an adsorbent to remove copper and methylene blue from aqueous solutions [56]. Tea waste (TW), dolomite (DO), and a mixture of TW-DO were used as adsorbents in six different sets of experiments. The purpose of the experiment was to see how contact time, pH, and the adsorption isotherms of the adsorbents influenced the outcomes. According to the findings, the highest adsorption capacity of tea waste with dolomite as an adsorbent was 150.4 mg/g. As a result, they discovered that tea waste and dolomite were both capable of extracting copper and methylene blue from aqueous solutions. On the other hand, Tuna et al. (2013) used hybrid apricot stone activated carbon with iron oxides to remove arsenic [58]. The hybrid was able to produce Iron-Activated Carbon (IAC) by precipitating iron salts with activated carbon [58-59]. The IAC adsorbent was then added at a mass ratio of 2:1 to a solution containing 0.3 M Fe^{3+} ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) or Fe^{2+} ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) ions. After some further mixing, washing, and drying, a hybrid IAC-Fe (II) or IAC-Fe (III) adsorbent emerged. The author highlighted in their study that hybrid adsorbents were able to achieve higher adsorption efficiency for the removal of arsenic compared to activated carbon [58].

Table 2 shows existing studies of combined or hybrid adsorbent from different agricultural wastes for the removal of different types of pollutants. It is concluded that multi-adsorbents may be more efficient at removing pollutants or contaminants from wastewater than using single adsorbents. Since bamboo biochar and modified EFB show effective removal rate, combining them may be more practical as an adsorbent in wastewater treatment. Apart from that, bamboo and EFB are abundant, grow abundantly and are relatively cheap. Moreover, both shows high carbon, lignin and cellulose content which makes them good choice of adsorbent. Furthermore, both adsorbent show effective adsorption for different types of adsorbates and modifications of both show increases in adsorption capacity [60-62].

Table 2. Adsorption capacities of combined, mixed and hybrid adsorbents

Combined/Hybrid Adsorbents	Pollutants	Adsorption Capacity (mg/g)	Reference
Tea waste and dolomite	Copper and methylene blue	150.4	[56]
Coconut mesocarp, sawdust and termite nest	Cadmium and lead ions	138.9	[63]
Waste tea and coffee	Copper, zinc, cadmium and lead ions	0.528	[64]
Apricot stone and iron oxides	Arsenic	2.023 – 3.009	[57]
Dried pinecone and sodium alginate	Copper and nickel ions	112 – 156	[65]
Bamboo waste and iron	Arsenic	0.019 – 0.027	[66]
Mixed recyclable waste and ionic liquid	Mercury	124	[67]

While hybrid and combined adsorbent systems offer significant potential for improving wastewater treatment efficiency, the practical application of such systems can be further explored through specific materials. In this context, the potential of bamboo biochar and empty fruit bunches as effective adsorbents is presented in the following section, highlighting their unique properties and advantages in the combined adsorbent approach for ammonia nitrogen removal.

2. Potential of Bamboo Biochar and Empty Fruit Bunch as Materials for Combined Adsorbent

Both bamboo biochar and modified empty fruit bunch (EFB) are chosen as they have potential to be combined as an embedded multi adsorbent system. This is mainly due to their characteristics and ability to adsorb ammonia nitrogen especially as both are commonly used as adsorbents for ammonia nitrogen removal as shown in Table 3. On top of that, both of these materials are categorised as good sources of material to be chosen as adsorbents due to their unlimited supply, abundant growth and relatively low cost.

Biochar is a carbon-enriched substance that can be obtained from a combination of renewable and waste sources, such as trees and agricultural residue, industrial by-products and municipal solid waste under restricted oxygen conditions via pyrolysis [68-69]. Chemical activation is a key method used to improve its adsorption properties. For example, bamboo biochar is often treated with potassium hydroxide (KOH) or phosphoric acid (H₃PO₄) to increase its surface area and pore volume. These chemical treatments create additional porosity and introduce functional groups such as hydroxyl, carboxyl, and lactone groups on the biochar's surface. The increased surface area and additional functional groups enhance the material's capacity to interact with and adsorb ammonia nitrogen. The presence of these functional groups promotes better binding of ammonia through both physical adsorption and chemical interactions. Due to its outstanding features, including high surface area, high porosity, and enriched surface functional groups, biochar has shown enormous potential for a variety of applications [25].

Table 3. Adsorption studies of modified empty fruit bunch and bamboo biochar for ammonia nitrogen removal

Adsorbent	Adsorbate	Adsorption Capacity	Isotherm Model	Kinetic Model	Reference
Modified empty fruit bunch	Ammonia nitrogen	0.01 – 0.60 mg/g	n/a	n/a	[74]
Modified empty fruit bunch	Ammonia nitrogen	0.32 mg/g	n/a	n/a	[75]
Modified empty fruit bunch	Ammonia nitrogen	0.83 mg/g	n/a	n/a	[21]
Modified empty fruit bunch	Ammonia nitrogen	79.50 %	Langmuir	n/a	[27]
Modified empty fruit bunch	Ammonia nitrogen	0.56- 0.83 mg/g	Tempkin	Pseudo second order	[74]
Empty fruit bunch biochar	Ammonia nitrogen	0.46 – 2.49 mg/g	Freundlich	Pseudo second order	[76]
Unmodified empty fruit bunch	Ammonia nitrogen	n/a	Freundlich	Pseudo second order	[6]
Modified empty fruit bunch	Ammonia nitrogen	0.53 - 10.89 mg/g	n/a	N/a	[21]
Unmodified empty fruit bunch	Ammonia	n/a	Freundlich	Pseudo second order	[77]
Ball-milled bamboo biochar	Ammonia nitrogen	22.90 mg/g	Langmuir	Pseudo second order	[78]
Bamboo biochar	Ammonia nitrogen	7.00 mg/g	Langmuir	Pseudo second order	
Bamboo biochar	Ammonia nitrogen	6.38 mg/g	Freundlich	N/a	[79]
Hydrous bamboo biochar	Ammonia nitrogen	6.38 mg/g	Freundlich	Pseudo second order	[80]
Modified bamboo biochar	Ammonia nitrogen	12.60 mg/g	Langmuir	Pseudo second order	[81]
Unmodified bamboo biochar	Ammonia nitrogen	3.23 - 5.66 mg/g	Langmuir	Pseudo second order	
Unmodified bamboo charcoal	Ammonia	0.80 – 5.80 mg/g	n/a	n/a	[82]
Modified bamboo charcoal	Ammonia	0.90 - 9.50 mg/g	n/a	n/a	
Modified bamboo charcoal	Ammonia nitrogen	0.65 mg/g	Langmuir	n/a	[83]

In addition, empty fruit bunch (EFB) is also known as a carbon-rich substance that is produced during palm oil production. Previous research has found that the carbon content of EFB ranges from 40.93% to 68.3% [70-72]. As a result of its characteristics and availability, it is attracting research interest in adsorption investigations. However, the utilisation of EFB is a challenge as its processing cost is high and direct utilisation of raw EFB is time consuming at large scales [62]. Besides its high carbon content, the lignin and cellulose content of EFB also make it a good choice as an adsorbent. Furthermore, EFB's alkali nature allows it to adsorb cationic contaminants owing to electrostatic interaction [73]. Similarly, with bamboo, these characteristics of EFB make it a suitable adsorbent, and the effectiveness

of EFB also affected by its BET surface area, as high surface area corresponds to high adsorption capacities [62]. The authors also mention various research studies that reveal raw EFB's ability to remove dyes and heavy metals from aqueous solutions, as well as a limited investigation of EFB as an adsorbent, indicating a data gap in its potential.

Apart from that, both bamboo biochar and EFB have been proven to have good adsorption efficiency not only in ammonia removal but also for several other contaminants. Hence, the combination of these materials can be used universally to remove different types of contaminants instead of focusing only on ammonia nitrogen. For instance, several studies have shown that bamboo biochar can be used as an adsorbent to remove undesirable pollutants. Viglasova et al. (2020), for example, investigated the performance of biochar as a viable wastewater treatment option and linked nitrate sorption ability to the substance's features [81]. On top of that, Mohan et al. (2014), Tan et al. (2016) and Cha et al. (2016) in their past review articles have addressed and discussed the methods of decomposition and characterization of the biochar as well as its use in the removal of dye from different contaminants [84-86]. Another research by Wang et al. (2017) and Yang et al (2019) also suggested the pre-treatment and post-treatment properties of both feedstock and biochar respectively may also influence biochar properties [87-88]. Yang et al. (2004) used bamboo-derived biochar to examine the high potential of adsorption for the removal of metal-complex pigments in wastewater [71]. In the study, the equilibrium, kinetics and modelling of the artificial neural network were investigated using a biochar where it was generated by pyrolysis. Bamboo biochar is an efficient low-cost adsorbent for metal-complex removal from aqueous solutions, according to the findings. The adsorption capacity of the metal-complex, acid black 172, was unaffected by ionic strength throughout the experiment, and the kinetics investigation revealed that intraparticle transport was not the only rate-limiting phase. With a pH of 1.0, the adsorption capacity was found to be 401.88 mg/g [71].

Sajab et al. (2013) on the other hand, studied the ability of oil palm EFB to remove dyes from aqueous solution [89]. This study was conducted by pre-treating the EFB by sodium hydroxide (NaOH) first, and the pre-treatment EFB was modified by using citric acid (CA) (CA-EFB) and polyethylenimine (PEI) (PEI-EFB) to make it cationic and anionic adsorbent. The removal efficiency of CA-EFB and PEI-EFB was tested by using cationic methylene blue (MB) and anionic phenol red (PR) as adsorbate, at various pHs, temperatures and initial dye concentrations. The negative charges of CA-EFB increased with an increase in pH range from 3 to 7, meanwhile, the PEI-EFB was positive charge for the pH range. Thus, the different ion charges will attract one another, which suggests that MB and PR will attract to CA-EFB and PEI-EFB respectively. The study recorded that the maximum removal capacity of MB by using CA-EFB as adsorbent is 103.1 mg/g and 158.7 mg/g of maximum removal capacity of PR when using PEI-EFB adsorbent. The data of the experiment showed that the adsorption of MB onto CA-EFB and PR onto PEI-EFB fitted the Langmuir isotherm and Freundlich isotherm, respectively. This suggests different adsorption behaviours of dyes onto both adsorbents [89].

Most importantly, these materials have potential to be reused, recovered and regenerated. As the adsorbent used in this study are not physically or chemically combined, the chance for them to be reused again in the same form or regenerated and reused should be considered. On

top of that, both materials are commonly used as soil amendment or for potting media and for composting. Hence, this ability should not be taken for granted as it will help to reduce waste, promote circular economy, and introduce sustainability concepts. In addition, the concept of reuse, recovery and regeneration of waste have been gaining attention by researchers as it is a way of maintaining and sustaining our environment on top of growing our economy.

4. Conclusion and Future Perspectives

This review demonstrates that bamboo biochar and empty fruit bunch (EFB) fibres are promising, low-cost adsorbents for ammonia nitrogen removal from wastewater. Both materials exhibit significant adsorption capacities, which are notably enhanced through specific modifications. Combining these adsorbents could offer an even more effective solution, utilising their complementary properties to address ammonia nitrogen contamination more efficiently. Future research should focus on optimising these modifications to further enhance adsorption performance. Additionally, exploring the practical applications of combining bamboo biochar and EFB in wastewater treatment could yield valuable insights. The potential for reuse, recovery, and regeneration of these materials should be investigated to promote sustainability and circular economy practices. Addressing any limitations and understanding the interactions between different adsorbent materials will be crucial for developing effective and sustainable wastewater treatment solutions. Overall, the continued exploration of these materials holds promise for advancing environmental management and improving wastewater treatment technologies.

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