



Banana Peels as Heavy Metals Bioadsorbent in Wastewater Treatment: A Review

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KEYWORDS	ABSTRACT
Banana peels Bioadsorbent Heavy metals Thermal carbonization	Discharge of industrial wastewater containing heavy metals has resulted in serious problems thus effective solution to prevent such pollution is vitally needed. Adsorption technique is a popular method in wastewater treatment and studies are focusing on the development of alternative adsorbent derived from biomass as alternative material with low cost, abundantly available and environment friendly. This paper goes through the treatment of banana peels as bioadsorbent in reducing heavy metals in wastewater, followed by the removal of aqueous heavy metals and the functional groups involved in the adsorption process. Such technology will reduce the cost of adsorbent production and the cost of banana peels biomass disposal as well.

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1.0 INTRODUCTION

In recent years, developing green, efficient and cheap strategies for heavy metal ion treatment has become an important research issue all over the world. Several techniques, including microbial degradation, bioaccumulation, chemical precipitation, reverse osmosis, ion-exchange, membrane separation and coagulation–flocculation have been used to remove heavy metal ions from aqueous environment [1-2]. However, these methods have several disadvantages, such as incomplete removal of trace-level heavy metals, consumption of massive chemical reagents and energy, and generation of toxic byproducts that require further treatment. In comparison, adsorption is generally preferred due to the properties of wide suitability, high efficiency, environmental compatibility, and easy handling and regeneration [3-5].

Reported adsorption agents mainly include synthetic polymers, natural minerals (zeolite, kaolin, diatomite, etc.) and their derivatives. Synthetic polymers are generally associated with the characteristics of high cost and short life, while low adsorption capacity of natural minerals with limited storage is the bottleneck for large-scale metal removal. Green materials obtained from bio-wastes and agricultural by-products as adsorbents owing to low cost, abundant sources and easy preparation have been attracting much interest in present studies. Materials like wood, bark, rice

husk, straw, leaf and fruit peel have been reported to play a role in the removal of heavy metals and exhibit desirable metal-binding performance.

Bioabsorbents, also called biosorbents, have attained considerable attention for their application in cleaning the environment pollutants. Bioadsorbents are the materials derived from different biological sources like agricultural by-products [6-7]. Agricultural wastes, vegetable and fruits peels are the discarded waste materials and may have wide significant application. The main aim to use these agricultural by-products is to minimize their accumulation and reuse them for productive purpose. This has led to their application as biosorbents for removal of environmental pollutants. Biosorbents derived from agricultural solid waste are cheap and readily available.

Banana peel, a common biological waste, is an attractive and inexpensive option and has been employed to get rid of dissolved heavy metals from wastewater but poor removal performance impeded its widespread application. Some researcher reported the use of banana peel as a precursor agent for preparing adsorbent via chemical modification with alkaline and acid. However, adsorption capacity only gained limited enhancement after these treatments. Accordingly, new physical and/or chemical modification of banana peel is highly required in order to improve the performance of the obtained adsorbents [8].

Biochar is a porous carbonaceous material produced during the thermochemical decomposition of biomass feedstock in the presence of little or no oxygen. Biomass feedstock can be any organic waste materials which include crop and forest residues, wood chip, algae, sewage sludge, manures, and organic municipal solid wastes [9]. Methods for thermochemical decomposition include pyrolysis, hydrothermal carbonization, gasification, torrefaction, and microwave heating, varying in thermochemical temperature and duration. Interest in biochar is largely based on its two distinct benefits: First, biochar production can offset greenhouse gas emission because it stores carbon in a stable form, preventing the release of greenhouse gases into the atmosphere from biomass degradation. Second, biochar is an effective, low-cost, and environment-friendly adsorbent, which is related to its relatively large surface area and abundant surface functional groups. Biochar is thought to be a promising adsorbent for the removal of various pollutants in wastewater and soil, due to their abundant specific surface area. The adsorption capacity of biochar was considered to be correlated to specific surface area and aromaticity.

A range of heavy metals can be absorbed by biochar products. The possible adsorption mechanism involves several kinds of interactions, including electrostatic attraction, ion-exchange, physical adsorption, surface complexation and/or precipitation. The special mechanisms of different heavy metals are varied. Abundant surface groups (mainly oxygen-containing groups, such as COOH, and OH) have strong interactions with heavy metals, which can be evidenced by changes in functional groups of biochar before and after metal adsorption.

It has been well researched that feedstock, thermochemical decomposition methods and their temperature and duration can significantly affect biochar's physical and chemical properties. Several previous researchers have discussed decomposition methods, characterization, and applications of biochar in the removal of different contaminants from aqueous solutions [10-11]. The current article highlighted the processes involve in banana peels bioadsorbent synthesis and adsorption of heavy metals by banana peels bioadsorbent.

2.0 SYNTHESIS OF BANANA PEEL BIOADSORBENT

Bioadsorbent production mainly consists of the following three technologies: pre-treatment of raw material, thermal carbonization method and post-treatment of adsorbent.

For biochar development of various raw materials, pre-treatment is the earliest step. Generally, the pre-treatment can be physically or chemically. The technology of physical pre-treatment typically involves drying, crushing and screening banana feed. The rich lignocellulosic feedstock is usually dried at 105 °C or other temperatures to a constant weight, then ground into smaller, hammer-milled particles, and cut into various pieces.

Chemical pre-treatment technologies often depend on chemical reactions in order to change feedstock material properties or compositions. The chemical pre-treatment method is more widely used to treat feedstock biomass materials with chemical compounds to incorporate the precursors or functional groups into the raw material. During the process, the biomass material is submerged in a chemical solution or a colloidal suspension and dried before the production of biochar. Corrosive chemicals including acid, alkaline, and oxidants have been used for the pre-treatment of biomass in manufacture of the engineered biochar with exceptional pore structure, large surface area and rich in functional surface group.

2.1 Thermal Carbonization

The methods of thermal carbonisation for biochar transformation mainly involve pyrolysis, pyrolysis aided by the microwave, hydrothermal carbonisation, gasification and torrefaction.

Pyrolysis is a thermochemical method to decompose biomass into high-value materials such as biochar, bio-oil and syngas with limited oxygen supply at 300 – 900 °C [12]. The pyrolysis may in general be divided into slow pyrolysis (low heating rate and long residence time) and rapid pyrolysis (high heating rate and short time of residence), based on temperature, heating rate, pressure and time of residence. Slow pyrolysis requires a thermal cycle of processing at 400-600 °C to increase the production of biochar, along with a small volume of concentrated bio-oil, syngases of H₂, CH₄, CO₂, CO and C1-C2 hydrocarbons. The process is conducted at atmospheric pressure, defined by a fairly long time of residency (> 1 h) and a slow heating intensity (5-7 °C / min). But quick pyrolysis provides promising advantages to optimize biomass yields (up to 75%), in which the heating intensity is normally over 200 °C / min and the residence period is below 10 seconds.

The operating temperature, heating rate and residence time are factors affecting the physicochemical composition and properties of the materials in pyrolysis processes. Biochar yields decline with elevated temperature of the pyrolysis, whereas ash and carbon content rise. It is primarily associated to cellulose, hemicellulose and lignin breakdown, saline-alkali separation, carbonization and other biomass factors. The heating intensity influences the pyrolysis speed and affects biochar characteristics and bio-oil and bio-gas yield. Long-time provides more total decomposition of biomass and reduces the output of biochar. Prolonged residence time provides more total decomposition of biomass and reduces the output of biochar.

The sustainable method of producing bio-energy materials, including biochar, bio-oil and biogas, is recognized as microwave-assisted pyrolysis (MAP). MAP provides shorter cycle time, lower electricity usage, more effective transmission of heat and improved targeted heating compared with conventional methods. The microwave strength and irradiation duration mainly influence the MAP operation. Biochar production also reduces as the strength of the microwave rises, owing to the high heating rates at elevated microwave power levels. Through a microwave device, biochar with a large particular surface area may be collected. Further microwave treatment, however, led to loss of a specific surface area that can be attributed to the degradation after microwave overheating of the micropore structure of the biochar. Although perceived to be a potential alternate energy source, microwave-assisted pyrolysis technology faces many challenges such as electricity that is costly and often made of fossil fuels, furthermore microwave heating systems are more expensive than traditional heating systems.

Gasification is the method of transforming biomass to gas fuel using gasification agents. Gasification temperature typically approaches 800 °C [13]. Gasification's average biochar yield is around 10 wt% of biomass, while the main substances are syngas, and char is seen as a side product of much lower yield. In general, biochar formed during the gasification method is less than pyrolysis due to carbon monoxide (CO) conversion in the presence of oxidizing agent (O₂ or steam). The biochar formed during gasification typically contains strong alkaline salts and extremely poisonous alkaline earth minerals (Ca, K, Si, Mg, etc.). These can precipitate several heavy metal compounds and can be used specifically in problematic soils as a remediator. Gasification agent type, reaction temperature,

particle size, residence period, pressure, and gasification agent/biomass ratio can influence the component compositions (gas, liquid and solid).

Hydrothermal carbonization (HTC) is the successful thermochemical method that transforms wet feedstock from 120-260 °C to biochar without the need of pre-drying [14-15]. This is more suited for handling high moisture content biomass and is regarded a cost-effective solution to biochar processing because it is typically performed at low temperatures. Within a confined environment, wet biomass is heated and pressurized (2-10 MPa) 5-240 min. Reaction pressure is autogenic of subcritical-water saturation vapor pressure corresponding to reaction temperature.

The key parameters influencing product characteristics are reaction temperature, pressure, residence time, and water-to-biomass ratio. HTC's biochar is called hydrochar, with a yield of around 40-70 wt%. During HTC, reaction temperature is defined as the governing parameter. When temperature rises, hydrochar produces acidic functional groups on its surface, which may support the capacity to absorb pollutants. Higher holding temperature and time will increase the hydrochar's porous nature, increasing the likelihood of hydrochar as an adsorbent. The hydrochar surface often shows a greater degree of aromatization of more oxygen-containing groups. Hydrothermal conversion typically develops by dehydration, polymerization and carbonization reactions. Chemical hydrochar structures contain aromatic polymer crosslinks, surface porosity, organic functional groups and ultimate elements. These characteristics thus can be altered and influenced the hydrochars reactivity and properties.

2.2 Post-Treatment

Post-treatment techniques typically require either physical or chemical alteration approaches to post-treat biochar to improve its particular surface area, pore volume, surface composition, and functional groups. These modified biochars can be cost-effective and environmentally sustainable carbon products with tremendous promise in many fields. Post-treatment methods include electrical, ball-milling, and corrosive treatment (i.e., acid, alkali, or oxidation).

Magnetization is the process of transforming biochar into a magnetic substance where magnetic iron oxides are loaded into biochar. In the technique, ball milling is an effective and simple process that uses kinetic energy by shifting balls to break chemical bonding, alter particle form, and create nanoscale particles. After ball milling, biochar's characteristics were improved including surface area, pore volume, oxygen-containing functional groups, and adsorption ability.

Corrosive treatments including acid, alkali, and oxidation methods are widely employed chemical modification methods that change biochar surface chemistry. Corrosive chemicals like HCl, HNO₃, KOH, NaOH, KMnO₄, and H₂O₂ are used to modify biochar for various purposes. The chemical modified biochar has greater surface area, more microporous, more functional groups, and improved sorption ability. Combination of alkali (NaOH)-acid (HNO₃) modification reveals improved surface area, porosity and oxygen-containing functional groups of biochar. H₂O₂ is another powerful biochar-modifying oxidant that can effectively remove heavy metals due to improved oxygen and carboxyl content. Figure 1 shows the processes involve in banana peels bioadsorbent synthesis.

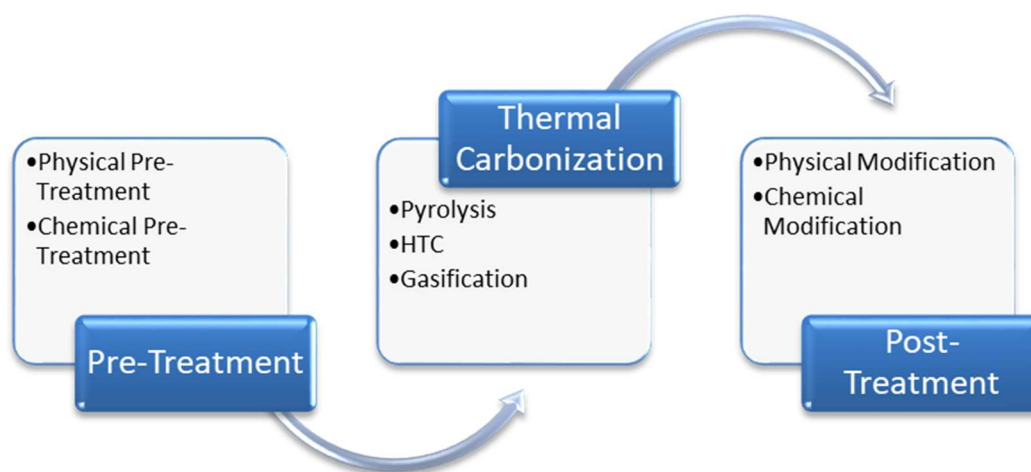


Figure 1: Synthesis of banana peels bioadsorbent

3.0 REMOVAL OF AQUEOUS HEAVY METALS

Heavy metals in wastewater can damage humans, animals and plants. Long-term aqueous exposure to heavy metals may pose significant health risks even at low concentration. Recent research shows that banana peel bioadsorbent can successfully adsorb heavy metals in water and wastewater.

High metal ions are poisonous to marine animals and humans at small concentration. Pollution from heavy metal ions primarily caused by electricity and fuel development, fertilizer and pesticide industry and metallurgy applications to name a few. Since the metal ions are non-biodegradable, it accumulates and passes through food chain to another living entity. Their harmful results are therefore reflected in animals at higher levels and trigger human severe and permanent health issues. Researchers thoroughly investigated banana waste as bioadsorbent against a large variety of metal ions. Previous work has reviewed various elimination of heavy metal. Table 1 describes the adsorption of banana waste bioadsorbent to eliminate various heavy metals.

Table 1: Adsorption of heavy metals by banana peels bioadsorbent

Heavy metals	Thermal Process	Pre-Treatment/Modification	Post-Treatment	Removal efficiency (mg/g) or %	References
Cu	-	Dried	Soaked in HNO ₃ , NaOH	4.75	[16]
	Pyrolysis	Dried	-	75.99	[17]
	-	Minced in ball mill	-	20.97	[18]
	HTC	Dried	Calcined in Ar to obtained BP carbon foam	49.5	[19]
	Carbonized under nitrogen	Dried, ground	Char soaked in KOH, heated under nitrogen at 500 °C	14.3	[20]
	-	Washed, grinded, dried	-	12.85	[21]
Co	-	Dried	Soaked in HNO ₃ NaOH	2.55	[16]
Ni	-	Dried	Soaked in HNO ₃	6.88	[16]

	Carbonized under nitrogen	Dried, ground	Char soaked in KOH, heated under nitrogen at 500 °C	27.4	[20]
Pb	-	Dried	Soaked in HNO ₃	7.97	[16]
	Pyrolysis	Dried	-	247.1	[17]
	-	Dried,ground and sieved	-	2.18	[22]
	-	Minced in ball mill	-	41.44	[18]
	HTC	Dried	Calcined in Ar to obtained BP carbon foam	45.6	[19]
	Carbonized under nitrogen	Dried, ground	Char soaked in KOH, heated under nitrogen at 500 °C	34.5	[20]
	-	Washed, grinded, dried	-	10.9	[21]
Zn	-	Dried	Soaked in HNO ₃	5.8	[16]
Cd	Pyrolysis	Dried	-	121.3	[17]
	-	Dried,ground and sieved	-	5.71	[22]
	HTC	Dried	Calcined in Ar to obtained BP carbon foam	30.7	[19]
	-	Dried, crushed and sieved	Modified using acidic methanol	35.52	[23]
Mn	-	bleached with sodium chlorate	acrylonitrile Grafted BP	94 %	[24]
Cr ⁴⁺	-	bleached with sodium chlorate	acrylonitrile Grafted BP	96%	[25]
	-	Dried, crushed and sieved	Modified using acidic methanol	131.56	[26]
	-	Dried, ground and sieved	Banana peel dust in KNO ₃ solution	26.46	[27]
Cr ⁶⁺	HTC	Dried	Calcined in Ar to obtained BP carbon foam	25.2	[19]
	Carbonized	Modified with ZnCl ₂	-	97.92	[28]
	Carbonized	Treated with H ₃ PO ₄	-	94	[29]
Hg	-	Grinded, Protonation with HCl	-	52.2	[30]

4.0 FUNCTIONAL GROUPS INVOLVED IN ADSORPTION PROCESS

Biochar's surface area and porous structure often affect heavy metal adsorption. It is well established that biomass composition has a great effect on biochar's surface properties, but biochar's surface characteristics can be greatly modified by using various carbonization methods and changing reaction conditions, particularly when coupled with in situ or after activation processes. Note that biochar activation greatly increased the removal performance of heavy metals [31]. This could be triggered by improved heavy metal adsorption site owing to enhanced pore structure. Nevertheless, as previously reported, biomass surface area and porous structure tend to impact heavy metal adsorption less than functional groups including oxygen. Zhou et al. [32] researched Pb ion

adsorption utilizing biochar banana peels, and their findings revealed that higher adsorption can be accomplished even with lower surface area, indicating less importance of surface area.

The particular functional groups involved in the adsorption process are carboxylic groups, amino groups, and hydroxyl groups. The oxygen-containing functional groups are able to bind effectively to the heavy metal, and the amount of oxygen often rises due to oxidation reaction on the biochar surface. Thermal carbonization temperature influences these groups which supposed to aid in metal adsorption. In certain situations, the rise for pH, porosity, surface area etc. does not influence the structure of functional groups while temperature and a high degree of carbonization have led in these groups' significant amount decline.

FTIR (Fourier Transform Infrared Spectroscopy) is employ to distinguish surface functional groups. FTIR works by generating a broad spectrum at various temperatures indicating cellulosic and ligneous dehydration compounds in plant material. This will display peaks of from 1600-3500 cm^{-1} . Together with FTIR, nuclear magnetic resonance (NMR) is also used to demonstrate various functional groups of biochar.

Biochar's adsorption activity involves a certain mechanism determined by biochar properties such as surface area, mineral component, porous structure, and surface functional groups. Heavy metal removal requires different mechanisms, including cation exchange, precipitation, electrostatic reaction, and chemical reduction, complexation. Surface functional groups such as hydroxyl (-OH) and carboxylate (-COOH) are found to bind strongly with heavy metal. Functional group changes are visible during and before metal adsorption.

5.0 CONCLUSIONS

Banana peel is an effective and low-cost bioadsorbent that can be generated from low-cost solid waste, readily accessible and environmentally safe to be used in wastewater treatment. The key findings of this paper are: (1) Banana peel bioadsorbent properties are linked to the method of feedstock processing that is pre-treatment, thermal operation, and post-treatment. Modifications of biochars bioadsorbent through increasing the surface area, reaction activity or developing functional groups are becoming increasingly relevant as a recent research field and its application to enhance environmental sustainability. (2) Engineered banana peels as a bioadsorbent to eliminate aqueous toxins, such as heavy metals, are generally controlled by ion exchange, adsorption, surface precipitation and surface complexation. In conclusion, while laboratory studies have shown that biochar from banana peels effectively absorbs pollutants from industrial wastewater, further research is needed for practical, onsite applications.

Author Contribution

N. A. Nadhirah Zainudin: Conceptualization, investigation, visualisation, writing and editing. R. M. Mohamed: Investigation, supervision, writing, and editing.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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