DOI: 10.47743/achi-2024-2-0010 *ACTA CHEMICA IASI,* **32_2**, 161-182 (2024)

BANANA PEEL AS CARBON FEEDSTOCK – A COMMENTARY

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Abstract: The disposal of large amount banana peel in garbage dumps or landfills releases greenhouse and toxic gases as it decomposes. The cellulose-rich waste can be converted into adsorbent to remove water pollutants because it is abundantly available at no cost, environmentally friendly and sustainable. This paper aims to highlight banana peel as feedstock of activated carbon and hydrochar for removing various water pollutants. The preparation strategies through chemical treatment/activation and hydrothermal carbonization, physical characteristics and adsorption performance of carbon adsorbents derived from banana peel were compared and discussed.

Keywords**:** Adsorption; Activated carbon; Banana peel; Hydrothermal carbonization; Hydrochar

Introduction

The release of various pollutants into streams has long become an ecological problem because of the conceivable toxicity to aquatic creatures and humans. The water pollutants consist of various frequently used man-made chemicals such as pesticides, pharmaceuticals, dyes and heavy metals.

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The synthetic dyes in textile industry are generally water-soluble, toxic and less biodegradable.[1] The presence of dye in water, even at low concentration, interrupts the sunlight penetration for photosynthesis, so decreasing the dissolved oxygen for respiration.[2] Similarly, heavy metals, e.g., copper, nickel and lead in drinking water may result in birth defects, neurological disorders, respiratory failure and death.[3] Therefore, the removal of water pollutants is essential to safeguard human health and the environment.

The pollutants in water can be removed by several methods, namely electrochemical degradation,[4] reverse osmosis,[5] chemical precipitation,[6] ion-exchange,[7] nanofiltration,[8] irradiation,[9] adsorption[10] and biological treatment.[11] Of these, adsorption is more preferred as it endows ease of operation, simplicity of design and high removal efficiency.[12] This process also inhibits the production of secondary pollutions via oxidation or degradation.[13]

Activated carbon has been recognized as universal adsorbent in adsorption process owing to its well-developed porous texture and rich surface chemistry. Accordingly, the demand for activated carbon for water pollutants removal is increasing day by day. The high cost of commercial activated carbon has intensified the quest to produce activated carbon from natural resources and low-cost feedstocks, such as agricultural biomass and industrial residues.[2] The manufacture of activated carbon is economically attractive if the raw material is abundantly available and sustainable/renewable. The carbonaceous feedstock can be converted into activated carbon through physical activation using oxidizing agents (e.g., steam and CO_2) and/or chemical activation using dehydrating agents (e.g., $ZnCl_2$, KOH, NaOH, etc.). The activation is sometimes preceded by hydrothermal carbonization to improve the porosity of activated carbon produced.[14,15]

Banana peel is a promising precursor of carbon-based adsorbents. The peel makes up about 40% of the weight of banana fruit, thus creating a large volume of waste, especially in banana chips factory.[10] Typically, the waste is disposed in landfills, which eventually releases greenhouse and toxic gases as it degrades.[16] Thus, the reuse of banana peel as adsorbent contributes to sustainable development and environmental protection. The aim of this paper is to summarize the capitalization of banana peel as feedstock for activated carbon and hydrochar for adsorption applications, particularly in the removal of various water pollutants. The preparation strategies, physical characteristics and performance of banana peel adsorbents are discussed to provide new perspective on feasibility and industrial applications.

The characteristics of banana peel

The rejected fruits, peels, leaves, pseudo-stems and fibers are commonly collected as banana waste. The current management practice of banana waste includes mulch plantation, fertilizer and animal feed.[17] However, its accomplishment is hampered by rapid spread of plant deseases.[18] Generally, the banana waste, including the peel is a carbon-rich lignocellulosic material to render it suitable for activated carbon production.

Table 1 shows the composition of banana peel. The peel contains nutrients and minerals, mostly potassium at 64.5 mg/g.[19] It also has manganese content of 63.5 mg/g, that is higher than 0.702 mg/g as reported elsewhere.[20] The concentrations of calcium, nitrogen and sodium are 20.5 mg/g, 16.8 mg/g and 19.5 mg/g, respectively. However, zinc, iron, phosphorus and magnesium exist as trace elements at concentrations of 0.16 mg/g, 0.29 mg/g, 6.61 mg/g and 6.56 mg/g, respectively.

Table 1. Elemental and chemical composition of banana peel.[21]

Elemental composition (mg/g)	
Nitrogen	16.8
Phosphorus	6.61
Potassium	64.5
Fe	0.29
Mg	6.56
Mn	63.5
Na	19.5
Zn	0.16
Surface composition by EDX (%)	
Carbon	69.1
Sulphur	0.30
Nitrogen	5.36
Potassium	0.24
Oxygen	23.4
Phosphorus	0.28
Na	0.27
Si	0.16
Cd	0
Mg	0.08
Pb	0
Ca	0

The surface composition of banana peel shows the presence of elements with high carbon (69.1%) and oxygen (23.4%) content, signifying its propensity as carbon feedstock. The EDX only detects a 0.24% of potassium on the material surface.[22] The composition of other elements is in the range of 0 - 5.36%.

Synthesis strategies of banana peel adsorbents

Shen and co-workers[23] reported the preparation of banana peel activated carbons by wet and dry impregnation methods using potassium hydroxide as dehydrating agent at 800 ºC for 3 h. The activated carbons exhibit surface areas of 3747 m^2/g and 3770 m^2/g, respectively. The synthesis strategies are illustrated in Figure 1. Prior to impregnation, the peel is carbonized at 500 ºC for 3 h to maximize the development of rudimentary pores. The superior surface area of activated carbon generally offers plentiful adsorption sites, making it easier to entrap adsorbate molecules. The dry impregnation (grinding approach) endows activated carbon with more micropores to allow extensive filling and condensation of benzene and toluene molecules at low pressure.[23]

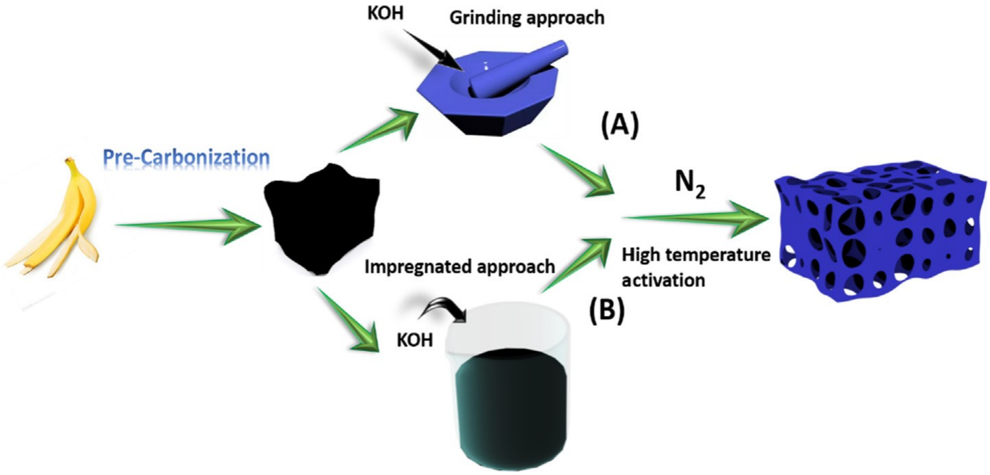

Figure 1. Preparation of banana peel-derived activated carbons for (A) dry and (B) wet impregnation methods.[23]

In a related work, hierarchically porous banana peel activated carbon with surface area of 1397 m^2/g demonstrates an outstanding methylene blue capacity at 1585 mg/g.[10] The KOH-impregnated peel is activated via step-wise heating at 400 °C for 1 h, followed by 800 °C for 1 h. The resultant material is refluxed in HNO_3 solution at 80 °C for 3 h to oxidize the surface of porous carbon. For methylene blue, the adsorption is governed by electrostatic interaction, π-π stacking and hydrogen-bonding. For Co(II) adsorption, the capacity is smaller because of its ionic state, in which the interactions with carbon surface include complexation and/or ion-exchange.

A number of papers in literature also recorded the performance of banana waste adsorbents towards methylene blue removal.[24-27] Among others, the disintegration of banana tree pseudo-stem fiber through hydrothermal carbonization provides thorough immersion of phosphoric acid within the carbon matrix, leading to activated carbon with surface area of 1975 m^2/g and dye capacity of 729 mg/g.[25] The hybrid of hydrothermal carbonization and activation also results in uniform surface morphology with a greater presence of acidic functional groups.

The as is banana leaf adsorbs a 110 mg/g methylene blue,[26] which is comparable to the capacity of banana stem activated carbon by H_3PO_4 activation.[24] Likewise, some activated carbons and chemically-treated adsorbents derived from banana peel possess low removal capacities.[28-30] The HCl-treated banana peel with a 21.5 m^2/g surface area adsorbs only 0.323 mg/g reactive red dye.[29] Meanwhile, the KOH-activated banana peel yields a 63.5 m^2/g specific area with small adsorption of Cu(II) and Ni(II) at 13.8 mg/g and 20.9 mg/g, respectively.[28] Although the adsorption often relies on porous texture and specific area of activated carbon/adsorbent, the roles of surface chemistry and functionalities should not be simply overlooked.

Table 2 summarizes the preparation and properties of banana waste-based adsorbents. Banana peel is foreseen a potential feedstock for adsorbent and carbon material. The correct activation and modification strategies are the bottom line in producing effective adsorbents that could draw the target pollutants. Nonetheless, there are actually plenty research gaps which are not well explored to unlock the true performance of this material, calling for further dedicated works in this field.

Table 2. Preparation and properties of banana waste adsorbents.

Banana residue	Pre-treatment	Activation strategy	Specific surface (m^2/g)	Pollutant model	Maximum capacity (mg/g)
Peel[23]	500 °C, 3 h, N_2 gas	Grinding: KOH, ratio 1:3.5 (char-to KOH), 800 °C, 3 h, N_2 gas	3747	Benzene Toluene	1484 1610
		Impregnation: KOH, ratio 1:4 (char-to KOH), 800 °C, 3 h, N_2 gas	3770		1441 1408
Peel[28]	500 °C, 1 h, N_2 gas	KOH, ratio 1:1 (char-to-KOH), 500 °C, 0.5 h, N_2 gas	63.5	Cu(II) Ni(II)	13.8 20.9
Peel[29]	400 ºC, 4 h	HCl, peel mixed with 2 M HCl, 24 h	21.5	Reactive red	0.323
Peel[10]	1) Suspension, 100 g in 100 mL 8 M KOH solution, 2) Ultrasound, 40 kHz ,1 h	1) 400 °C, 1 h; 800 °C, 1h, N_2 gas 2) Dispersion, 3 g in 100 mL 3 M HNO_3, 80 °C, 3 h	1397	Methylene blue Co(II)	1585 136
Peel[30]	-	H_3PO_4, ratio 1:1 (peel-to-H_3PO_4), 450 °C, 1 h	-	Phenol	80.6
Peel[64]	500 °C, 1 h	$ZnCl_2$, ratio 1:3 (char-to-$ZnCl_2$), 300 W, 5 min, microwave	-	CO Hydrocarbon (Exhaust gas)	97.6 % 84 %
		$ZnCl_2$, ratio 1:3 (char-to-$ZnCl_2$), 700 °C, 1 h	-		96.4 % 82 %
Peel[65]	600 °C, 1 h	1) H_2SO_4, 5 g char mixed with 250 mL, 1 M H_2SO_4, 12 h 2) Composite adsorbent by dropwise of gel (0.25 g chitosan in 0.2 M oxalic acid, 0.75 g acid-treated peel and 0.5 g Al_2O_3) to 0.7 M NaOH solution	362 (by H_2SO_4 treatment)	Cd(II) Pb(II)	46.9 57.1
		KOH, 5 g char mixed with 250 mL, 1 M KOH, 12 h	284	-	-

Peel[66]	400 °C, 1.5 h	KOH, 100 g char mixed with 300 mL, 3 N KOH, 3 h	-	Iodine CO SO_2	863 65.8 % 56.4 %
		H_2SO_4, 100 g char mixed with 300 mL, 3 N H_2SO_4, 3 h	-	Iodine CO SO_2	914 77.7 % 78.8 %
		$ZnCl_2$, 100 g char mixed with 300 mL, 3 N $ZnCl_2$, 3 h	-	Iodine CO SO_2	786 52 % 91.4 %
Peel[67]	600 °C, 1 h	HCl, char mixed with 200 mL, 0.1 M HCl, 24 h	-	Cyanide Lead Cadmium	80 % 78 % 100 %
Trunk[27]	-	H_3PO_4, 10 g dried trunk powder in 5.09 mol/L H_3PO_4, 774 °C, 51 min	-	Methylene blue	64.7
Trunk[33]	-	Washed, 50 °Cm 24 h, ground, sieved	-	Cu As Pb Zn	31.5 1.75 3.51 1.36
Leaf[26]	-	Ground, sieved, washed with hot distilled water, 70˚C, 12 h	-	Methylene blue	110
Stem[24]	-	H_3PO_4, 400 °C, 15 min, N_2 gas	837	Methylene blue	101
Pseudo-stem fibre[25]	Hydrothermal carbonization, 1 g in 50 mL deionized water, 200 °C, 4 h	1) H_3PO_4, ratio 1:1 (char-to-H_3PO_4), 60 °C, 2 h 2) Slow pyrolysis, 300 °C, 2 h; 500 °C, 1 h, N_2 gas	1975 (yield = 11.7 %)	Methylene blue	729
Bract[31]	-	1) H_2SO_4, 600 °C, 12 h 2) Magnetization, 5 g in 50 mL magnetic solution, stirring for 2 h; suspension of 10 mL NaOH, 80 °C, 6 h 3) Crosslinking, N_2 gas, addition of 5 mL N, N dimethylformamide, 60 °C	135	Phosphate Nitrate ions	91.8 75.8

Hydrothermal Carbonization

The process known as hydrothermal degradation was developed at the end of 19th century to harvest fuel in the forms of gaseous and liquid from organic feedstock.[34] Recently, more emphasis has been put on the production of hydrochar via hydrothermal carbonization for various engineering and environmental applications. It is now recognized as a promising technology to convert biomass into bioproducts such as solid fuel,[35] biodiesel,[36] low-cost adsorbent,[37] soil amendment[38] and nanostructured carbon material.[39]

The factors that affect the production of hydrochar is shown in Figure 2. In hydrothermal carbonization, the carbon feedstock is submerged in water in a confined reactor at temperature range of 180 – 350°C and autogenous pressure of 2 – 6 MPa for 5 – 240 min.[40] It is a green technique because water is used as a catalytic medium for carbonization that occurs at lower temperature compared to conventional pyrolysis. About 75 – 80 % of the feedstock remains as solid (hydrochar), 15 – 20 % is dissolved in liquid phase and the remaining 5 % is converted into flue gas, mainly CO_2.[41] The solid hydrochar is readily separated/filtered from water, while the leftover liquid is highly loaded with organic components that could be used as fertilizer and soil enhancer. The process conditions, i.e., feed water, temperature and retention time play a vital role on the physiochemical properties of the final products.

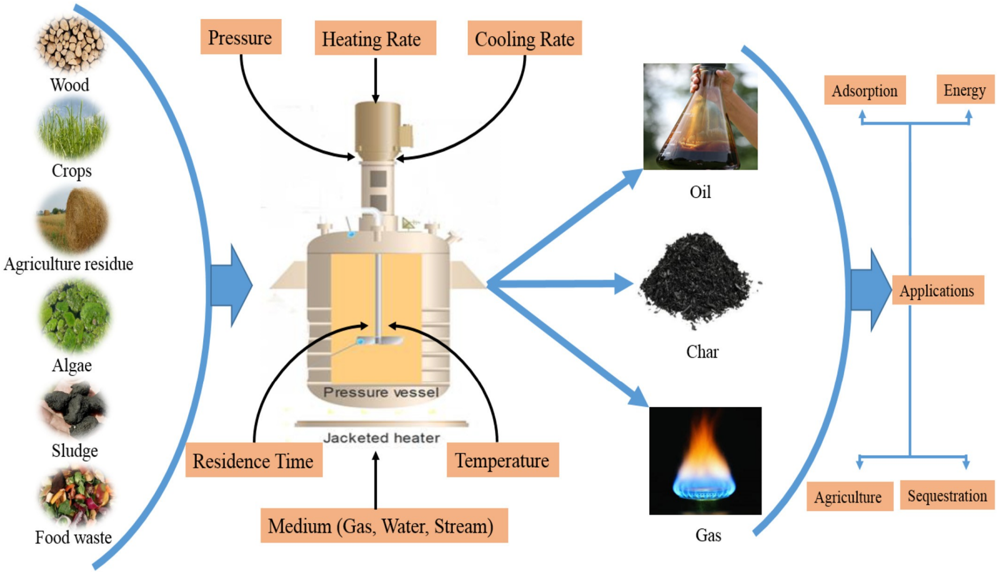

Figure 2. Factors effecting the production of hydrochar.[42]

The Advantages

Hydrothermal carbonization is a thermochemical process that mimics natural coalification of biomass by converting complex organic material in plant biomass into simpler chemical compounds, similar to that of coal.[41] While the process of natural coalification needs millions of years to transform the biomass, the hydrothermal carbonization needs only less than 12 h.[43] This process offers several advantages over conventional heating such as torrefaction and pyrolysis. It is suitable for wet feedstocks as pre-drying is not necessary, requires relatively low energy, and produces high carbon yield (solid phase) and water-soluble organic compounds (liquid phase).[40,42]

The resultant hydrochar exhibits high aromaticity due to dehydration and decarboxylation reactions during carbonization.[44] It has been reported to possess good self-binding properties for pelletization.[45] The hydrochar is often characterized as material with high carbon content,[46] low oxygen content and high energy density as solid fuel.[47] Furthermore, some may contain considerable fractions of inorganic components such as nitrogen, calcium, sodium and magnesium.

Unlike the conventional pyrolysis, the hydrothermal carbonization is relatively clean as no toxic gas and tar are generated.[48] The process is viable in stabilizing waste streams, minimizing the release of greenhouse gases and producing materials with intrinsic value.[49] Under sub-critical water condition, the alkali and alkaline earth metals are reduced to intensify the combustion reactivity of char, better than that of torrefaction or pyrolysis.[50] To date, the valorization of fruit wastes via hydrothermal carbonization is still limited in much of research studies.[51] Among others, banana peel is readily available to be used as carbon feedstock for the production of hydrochar. The high moisture content in banana peel makes it an ideal candidate for hydrothermal carbonization as opposed to ‘dry’ torrefaction or pyrolysis. Accordingly, moisture is not an obstacle; it is even used as the reaction medium for hydrothermal reactions.

Mechanisms

The reaction mechanisms of hydrothermal carbonization in the presence of water, acid/base or metallic ion as catalyst include hydrolysis, dehydration, decarboxylation, polymerization and aromatization.[52,53] The main reaction is hydrolysis, an endothermic reaction that dominates the overall process. However, at high temperature ca. 260 °C, the exothermic reaction of simple carbohydrate sugars (e.g., monosaccharides, etc.) gradually dominates the process.

Throughout hydrothermal carbonization, the bridges between cellulose, hemicellulose and lignin are disrupted. The carbonization of lignocellulosic biomass leads to hydrolysis and dissolution of hemicellulose and cellulose, and demethoxylation and condensation of lignin.[36] The hydrolysis of hemicellulose and cellulose is governed temperature; it begins at temperature above 180 °C and 230 °C, respectively.[42] During which, water reacts with cellulose and hemicellulose, and breaks ester and ether bonds.

The hydrothermal process reduces the content of oxygen and hydrogen in the carbon feedstock by dehydration and decarboxylation.[54] It is a hybrid of physical and chemical processes; the physical dewatering removes water from biomass due to increased hydrophobicity, while the chemical process eliminates the hydroxyl groups, thereby decreasing the H/C and O/C ratios. The molecular structure of saccharides (sucrose, fructose, glucose and starch) determines the chemical mechanisms of hydrochar formation.[55] The decarboxylation often takes place after dehydration reaction.[56] The elimination of carboxyl groups happens largely due to degradation at temperature above 150 °C, although no detail mechanism of decarboxylation reaction has been reported in literature.[42]

Figure 3 illustrates the formation of hydrochar by hydrothermal carbonization. During polymerization, the reactive compounds like 5-HMF and aldehyde are easily polymerized by aldol-condensation and intermolecular dehydration.[46] The disintegrated linear structure of cellulose gets agglomerated to form cross-linked polymer. After which, the aromatization of linear carbohydrate chains of hemicellulose and cellulose occurs to form aromatic-graphitic structures or building blocks of hydrochar. Besides, the carbon microspheres are also formed as a result of precipitation of aromatic clusters at supercritical point.

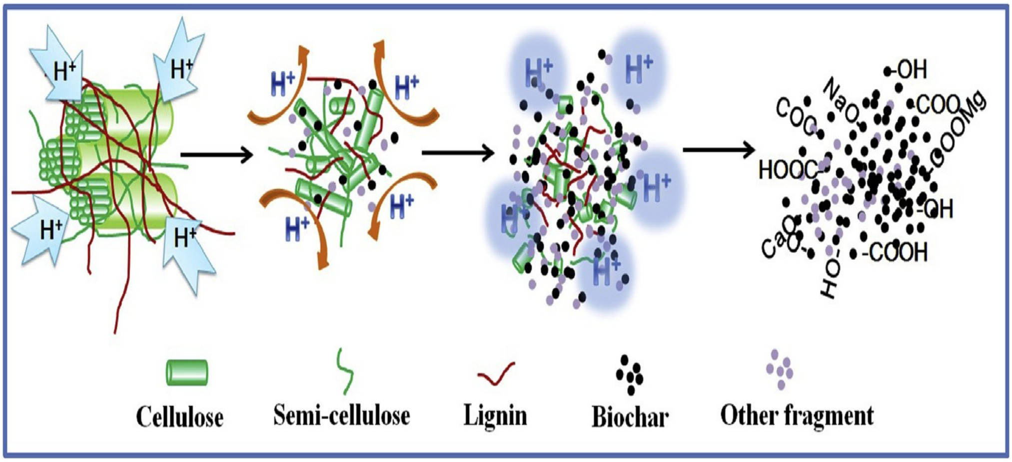

Figure 3. Mechanisms of hydrochar formation by hydrothermal carbonization.[57]

Banana Peel Hydrochar

Table 3 summarizes the preparation strategies and performance of hydrochar adsorbents. The hydrochar activated carbon from banana pseudo-stem fiber displays methylene blue capacity at 729 mg/g because of its high surface area of 1975 m^2/g.[25] The hydrochar activated carbon from bamboo comparably adsorbs 704 mg/g of methylene blue despite its low specific area of 26.2 m^2/g.[58] Obviously, the latter exhibits a texture-independent adsorption, wherein the plentiful surface acidic groups could lead to the high removal capacity. The non-activated banana peel hydrochar exhibits the lower dye capacity of 4.17 mg/g.[59] However, the hydrochar enhances the cadmium removal from 75 % (raw banana peel) to 99 %.

Table 3. Preparation strategies and performance hydrochar adsorbents.

Material	Hydrothermal carbonization	Activation strategy	Yield (%)	Specific surface (m^2/g)	Pore width (nm)	Model pollutant	Maximum capacity (mg/g)	Affinity (L/mg)
Banana peel[59]	5 g banana peel in 50 mL deionized water, 200 °C, 2 h	-	-	1.60	-	Cd(II)	4.17	0.12
Banana peel[57]	4 g banana peel in 50 mL 30 wt.% H_3PO_4 solution, 230 °C, 2 h	-	28.9	31.5	-	Pb(II)	356	0.004
Banana peel[60]	5 g of banana peel in 50 mL 20 vol.% H_3PO_4 solution, 230 °C, 2 h	-	35.8	15.8	-	Pb(II)	550	0.003
Banana tree pseudo-stem fibre[25]	1 g of pseudo-stem in 50 mL deionized water, 200 °C, 4 h	1) H_3PO_4, ratio 1:1 (char-to-H_3PO_4), 60 °C, 2 h 2) Slow pyrolysis, 300 °C, 2 h; 500 °C, 1 h, N_2 gas	11.7	1975	-	Methylene blue	729	-

Bamboo[58]	20 g in 80 mL 1 M HCl solution, 200 °C, 24 h	Hydrochar in 0.25 M 100 mL NaOH solution, stirred for 1 h	-	26.2	3.78	Methylene blue	704	0.557
Peanut shell[62]	25 g in 150 mL distilled water, 190 °C, 24 h	Pyrolysis, 800 °C, 4 h	-	596	2.30	Naproxen	324	0.00895
Glucose and urea[61]	10 g glucose, 0.25 g sodium dodecylsulfate and 3 g urea in 100 ml deionized water, 185 °C, 3 h; nitrogen-doped carbon sphere	KOH, ratio 3:1 (carbon sphere-to-KOH), 800 °C, 2 h	-	1601	2.19	Cr(VI)	394	12.6
Calcium alginate[63]	1) Annealing, 200 °C, 2 h; carbonization, 900 °C, 1 h, N_2 gas; porous graphitic carbon 2) 1.0 g carbon in 60 mL 0.1 M $KMnO_4$ solution and 20 mL ethanol, 180 °C, 12 h	-	-	-	-	Sulfide	500	-

The hydrothermal carbonization in phosphoric acid feed water renders a carbon yield of 35.8 %.[57,60] The use phosphoric acid promotes the crosslinking reactions, from which some low molecular species are retained in the solid matrix. The concentration of acid renders a substantial effect on surface chemistry and adsorption capacity because too high a concentration could prompt further loss of hydrogen and oxygen.[57] The hydrochar produced in a 20 vol.% phosphoric acid feedwater exhibits a superior capacity of 550 mg/g due to rich acidic functional groups rather than intermolecular structure of carbon.[60]

From Table 3, the capacities of banana peel hydrochars are comparable with other carbon-based adsorbents in literature.[57,60-63] Figure 4 visualizes the adsorption mechanisms of naproxen onto peanut shell hydrochar. The adsorption mechanisms include ion-exchange and surface complexation.[57,60] Dual mechanisms are reported for sulfide removal at 500 mg/g by porous graphitic carbon/manganese dioxide nanocomposite.[63] It has been postulated that the sulfide species are oxidized to elemental sulphur by MnO_2 active sites, and to metal sulphates on oxygen-rich active sites. Similarly, several mechanisms are reckoned for naproxen adsorption onto peanut shell hydrochar, i.e., pore filling, π-π interaction, hydrogen bonding, n-π interaction, van der Waals force and electrostatic attraction.[62]

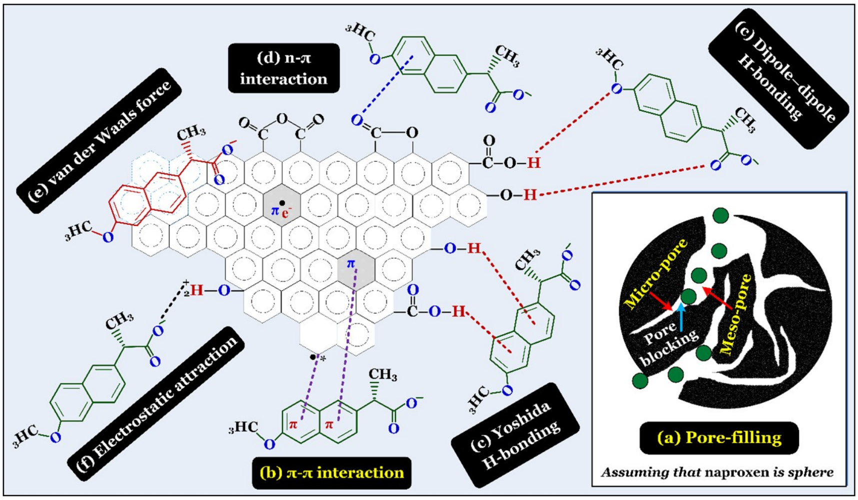

Figure 4. Adsorption mechanisms of naproxen onto the peanut shell hydrochar.[62]

Conclusion

Banana peel is a promising feedstock to manufacture carbon adsorbents for the removal of various water pollutants. The utilization of banana peel offers sustainable waste management solution and cost-effective method for the production of activated carbon and hydrochar with exceptional performance for water and wastewater treatment. The conventional pyrolysis to produce activated carbon and hydrothermal carbonization to produce hydrochar has been explored in literature. Nonetheless, the exploitation of banana peel is still limited, thus calling for more dedicated studies to unlock the true potential of this carbon feedstock for industrial applications.

Acknowledgements

This work is supported by Ministry of Higher Education Malaysia through Fundamental Research Grant Scheme, FRGS/1/2022/STG05/UTM/02/5.

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