CHARACTERIZATION AND CIPROFLOXACIN ADSORPTION PROPERTIES OF ACTIVATED CARBONS PREPARED FROM VARIOUS AGRICULTURAL WASTES BY KOH ACTIVATION

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Agricultural waste is a renewable and readily available resource that is used as a precursor to synthesize coal to reduce production costs. Significantly, valorizing it would greatly improve the quality of living in rural and remote areas. In this study, agricultural waste from straw, *Limonia acidissima* shell, avocado shell, tea waste and banana peel were used as precursors to prepare activated carbon. The desired surface area and pore size of carbonized materials was achieved by the chemical activation method, using KOH as an activating agent at a temperature of 500 °C. Scanning electron microscopy (SEM) and X-ray diffraction were used to determine surface morphology and amorphous carbon formation. The surface functional groups of carbonized materials were characterized by Fourier transform infrared spectroscopy (FT-IR) and N_2 adsorption-desorption isotherms, which revealed the specific surface area (BET) of the five activated carbon materials. The analytical results show that the activated carbon produced from straw exhibits superior characteristics and the highest ciprofloxacin removal efficiency among the five types of activated carbon. The surface area reached 494.92 cm^2/g and total pore volume reached 0.494 cm^3/g. Moreover, the ciprofloxacin adsorption efficiency reached 93.34% at a concentration of 20 mg/L. The results of this study indicate that activated carbon made from industrial waste has the potential to be used for removing antibiotics from aqueous environment.

Keywords: agricultural waste, ciprofloxacin, activated carbon, adsorption

INTRODUCTION

For decades, new adsorbent generations have received much attention from many researchers due to the important benefits that they brought.[1-3] Regarding environmental issues, the major role of these adsorbents relies in the fact that they become capable of completely adsorbing a large amount of toxic pollutants, such as heavy metals,[4] organic dyes,[5] toxic solvents[6] and antibiotics[5] from aqueous media. When it comes to these adsorbents, the most prominent one is activated carbon due to its advantages, such as high porosity, high specific surface area, suitable pore

size and the presence of functional groups on the surface of the material, which can contribute significantly to the adsorption process.[9-11] The precursors, which are utilized as input materials for carbonization to create activated carbons, should be inexpensive in order to minimize the production cost of the final products and to widen their applications towards other potential fields, such as catalysis, drug delivery and electrocatalysis. Agricultural waste is a renewable and readily available resource that has been already used as a precursor to synthesize some products, such as biochar, biofuel and fertilizer. Therefore, expanded utilization of this resource in adsorbent manufacturing could reduce manufacture costs and significantly improve the quality of living in rural and remote areas.[12]

A wide range of studies are known to report on the use of activated carbons (AC) from agricultural waste in the adsorption field. For example, Inyang *et al.* published a short review on biochar-derived low-cost adsorbents and their applications in heavy metal removal from wastewater.[13] Norouzi *et al.* reported on the synthesis of activated carbon produced from date press cake (DPC) by using NaOH solution under various activation conditions. Thanks to the high specific surface area (2025.9 m^2/g) and microporous texture (86.01%), the as-synthesized activated carbon achieved very high adsorption capacities of Cr(VI) from aqueous solution, with maximum adsorption capacities reaching 282.8 mg g^{-1} (pH = 2) and 198.0 mg g^{-1} (pH = 5).[14] In the same trend, M. Brito *et al.* successfully synthesized AC from yellow mombin fruit stones to remove Dianix® royal blue CC dye, showing a maximum monolayer adsorption capacity of 147.47 mg.g^{-1} and 82.28 mg.g^{-1} for the acidic and basic treatments of activated carbons, respectively.[15] George Z. Kyzas *et al.* fabricated zero cost activated carbon through a pyrolysis pathway using potato peels (ACP) as a carbonaceous source in the model of lead (II) elimination (171 mg/g). Norsafiah Fazli *et al.* reported kinetics and equilibrium in-depth studies on textile dyes using coconut shell derived activated carbon *via* adsorption models and investigated a series of physiochemical factors (*e.g.* contact time, concentration, adsorbent dosage, particle size, pH) on the removal and adsorption efficiency.[16] More intensively, a series of other biomass-based materials, which can be derived from many biomass resources, *e.g.* sugarcane bagasse, rice straw, tea waste and

graphene oxide, have been used to remove heavy metals in these studies.[17-19] Therefore, activated carbon has been considered as an efficient adsorbent to remove pollutants from aqueous media.[20-26]

Antibiotics are one of the most important groups of pharmaceutical compounds used to prevent and treat diseases.[27] Most antibiotics are not totally metabolized in the body of humans and animals, and could be released in the form of feces and urine wastes, leading to their appearance within aqueous media in hospital municipal wastes. On the other hand, excessive use of antibiotics for shrimp and fish farming can aggravate the issue, as wastewater discharged from farming activities into the environment usually remains untreated. Therefore, the removal of antibiotics is a topic that has attracted considerable attention in recent studies. For example, Mithun Sarker *et al.* reported on the huge potential for using carbon nanomaterials obtained from metal-organic framework melamine-loaded MAF-6 (CDM@M-6) to remove nitroimidazole antibiotics (NIABs) – including dimetridazole (621 mg/g) and metronidazole (702 mg/g) – from wastewater.[28] With very high adsorption capacities, CDM@M-6 is regarded as a nanomaterial capable of dealing with NIABs pollutants. Pharmaceuticals and personal care products are found as emergent polluting sources when their demand has been increasing. Biswa Nath Bhadra *et al.* indicated the vital role of bio-MOF-1 derived porous carbon in selectively treating compounds, such as atenolol (552 mg/g) and acidic clofibric acid (540 mg/g).[29] In particular, the materials synthesized could be easily recycled and were chemically stable, providing a promising case study to convert a lab-scale product to practical application.

Among typical antibiotics, ciprofloxacin (CIP) is a widely prescribed antibiotic for the treatment of bacterial and respiratory infections.[30] The occurrence of CIP antibiotic in the environment has been found in higher concentrations than other antibiotics.[7,31] More seriously, their existence, even in low concentrations, can lead to the development of antibiotic resistance in bacteria.[32] This impairs the potency of antibiotics that are normally effective in disease treatment or renders them useless. Therefore, the removal of antibiotics from the water environment by effective methods and the development of adsorbent materials from available and cheap raw materials are essential. In previous studies, the use

of nanomaterials has been widely reported for this purpose. El-Shafey *et al.* used date palm leaflets as an outstanding carbonaceous source to achieve a highly porous structure *via* anhydrous H_2SO_4 carbonization at 160 °C.[33] Since the proposed adsorption mechanisms *via* ion exchange and H bonding significantly contribute to fast CIP removal, it is concluded that this kind of carbon can be a prospective alternative adsorbent. *Via* an important chemical modification, amino groups (NH_2-) attachment on MIL−53(Fe) based nanomaterials has been proved to enhance their porosity, to achieve higher surface area and pore volume (215.1 m^2/g and 0.2 cm^3/g, respectively), as well as better maximum adsorption capacity, of 102.5 mg/g.[34] However, the use of high cost materials may be unfavorable to CIP adsorption, therefore, lower cost biomass derived materials are sought to be developed.

In this study, agricultural wastes, such as straw, *Limonia acidissima* shell, banana peels, tea waste and avocado shells, were used as precursors to remove CIP from the aquatic environment. All the carbon materials were activated with KOH and calcined at a temperature of 500 °C. The properties of the materials were characterized using XRD (X-ray diffraction method), SEM (scanning electron microscopy), FTIR (Fourier transform infrared spectroscopy) and BET surface area analysis. Adsorption experiments were also carried out to assess the adsorption capacity of the prepared activated carbon. The adsorbents made from biological materials can enhance cost effectiveness and are environmentally friendly.

EXPERIMENTAL
Preparation of activated carbon from agricultural waste

Five types of agricultural waste, such as straw, banana peel, avocado peel, tea waste and *Limonia acidissima* shell, were used to synthesize five kinds activated carbon. The precursors were dried in the sun for 2-3 days and crushed into powder. Then, 20 g of dry powder was activated with KOH in a ratio of 1:1 (g/g) for 24 hours. The impregnated samples were dried for 24 hours at 105 °C to prepare the physical carbonization stage, with 99.9% N_2 gas flow, at 500 °C, when layers peel off, leading to a volume expansion of the material. This is the formation process of activated carbon. After that, the activated carbon was washed with distilled water and 2% HCl solution several times until pH = 7, and then dried in an oven for 24 hours. The resulting activated carbon was stored in a desiccator for further analysis and characterization.

$$(\%) \text{ yield } = \frac{\text{weight of activated carbon}}{\text{weight of raw material}} * 100 \tag{1}$$

Characterization of activated carbon

The crystal structure of the material was confirmed by X-ray diffraction (XRD) on a D8 Advance Bruker system, using Cu Kα stimulation with a scanning rate of 0.030°/s in the 2θ region of 5-80°. The crystal morphology of the material was observed by scanning electron microscopy (Scanning Electron Microscope, SEM, JSM 7401F, Jeol). The surface area and pore volume of the activated carbons were determined by the Brunauer-Emmett-Teller (BET) method, using a surface area analyzer (Gemini VII 2390, Micromeritics). The FT-IR spectra of the prepared activated carbons were recorded using a Fourier transform infrared spectrometer (Perkin-Elmer Spectrum One). The light absorption properties of the materials were analyzed *via* visible ultraviolet diffuse reflectance (UV-Visible Diffuse Reflectance Spectroscopy, UV-Vis-DRS, Shimadzu UV-2450) in the 300-900 nm wavelength range.

Batch adsorption studies

The adsorption efficiency of the materials was assessed based on the efficiency removal of CIP antibiotic.[35] The CIP adsorption capacity of AC was evaluated by the following procedure: 1 g/L of adsorbent (AC) and 100 mL of CIP solution (20 mg/L) were added into a 250 mL glass beaker. The solution was stirred by a shaker, at a speed of 200 rpm for a specified time period, and then centrifuged (7000 rpm) to separate the material from the antibiotic solution. Finally, the concentration of the remaining antibiotic was determined by spectrophotometry at the wavelength of 497 nm. The removal efficiency was calculated based on the concentration before and after the adsorption process, according to the following equation:

$$\text{Removal efficiency}(\%) = \left(1 - \frac{C}{C_o}\right) * 100 \tag{2}$$

where C_o and C_e are the initial and equilibrium antibiotic concentrations (mg/L), respectively.

RESULTS AND DISCUSSION
Abbreviations of activated carbons

The chemically activated carbon samples obtained from agricultural wastes, including straw (ST), *Limonia acidissima* shell (LAS), avocado shell (AS), tea waste (TW) and banana peel (BP), were named AC-ST, AC-LAS, AC-AS, AC-TW and AC-BP, respectively.

The straw was collected from Long An Province, Vietnam, which is located in the Mekong Delta. The humidity and ash contents of the straw were 11.2% and 2.25%, respectively.

The straw was cut to pieces with the length of 2-3 cm before being used.

Characterization of activated carbons

The crystal structure of the samples was determined by the X-ray diffraction method, as shown in Figure 1. A strong diffraction peak at 2θ = (23.8°-24.8°), and a weak diffraction peak at 2θ = (42.6°-43.7°) were observed in all the samples. These peaks confirm the presence of amorphous carbon in the currently studied samples.[36-38]

To identify functional groups on the surface of activated carbon, infrared spectra (FT-IR) of the as-synthesized AC materials were taken. Figure 1 (B) presents the infrared spectrum of activated carbon obtained by KOH activation, at a calcination temperature of 500 °C. A broad spectrum band is found in the areas of surface functional groups, such as phenols, carboxylic acids and carboxylic acid derivatives, as well as the presence of physical adsorbed water on the material surface within 3554-2947 cm^{-1}.[39] These bands are formed due to the stretching vibrations of the O–H functional group and become wider in the case of oxidized coal.[40] The valence oscillations of C-H bonds of -CH_2, -CH_3 groups were related to the peaks at 2898 cm^{-1} and 2810 cm^{-1}. In addition, the characteristic position for C-O and C=O oscillations of ester, ketone, aldehyde, lactone or carboxylic acid groups appears in the area of 1486-1728 cm^{-1}.[41,42] The average adsorption of the carbonyl ester group C=O of the lactone and phenol groups was observed in the range of 919-1438 cm^{-1}.[43] These functional groups greatly contribute to improved adsorption efficiency.

Besides, to assess the morphological structure of the materials obtained, SEM images of the activated carbon samples were taken (Fig. 2). The results show that five samples of the obtained materials have rough external surfaces and are relatively porous, with different pore shapes and sizes, varying from a few tens to several hundred nanometers. In addition, the cell walls of parenchyma can be observed as common structures in plant parts, such as peel and petioles.[43] Porosity can be observed on activated carbon surfaces, showing the effectiveness of activation and carbonization. However, a physical morphological characterization, such as "N_2 adsorption–desorption", is necessary to determine these properties.

Nitrogen adsorption is an effective method to determine the properties of activated carbon, including porosity, surface area, pore volume and pore size. Figure 3 illustrates the nitrogen adsorption/desorption curves of the five activated carbons. The presence of mesopore-size pores in the five structures is evidenced by the hysteresis loops occurring on the adsorption curve at a relative pressure above 0.3.

This indicates mesoporous adsorption of the activated carbon samples and signifies the formation and increase of mesoporosity as the temperature increases.[36] The activation by KOH at high temperatures leads to widening the distance between the carbon atomic layers and an increase in the pore volume due to the burning of micropores into mesopores. Table 1 summarizes the results of the isotherms in terms of surface area, total pore volume and micropore volume.
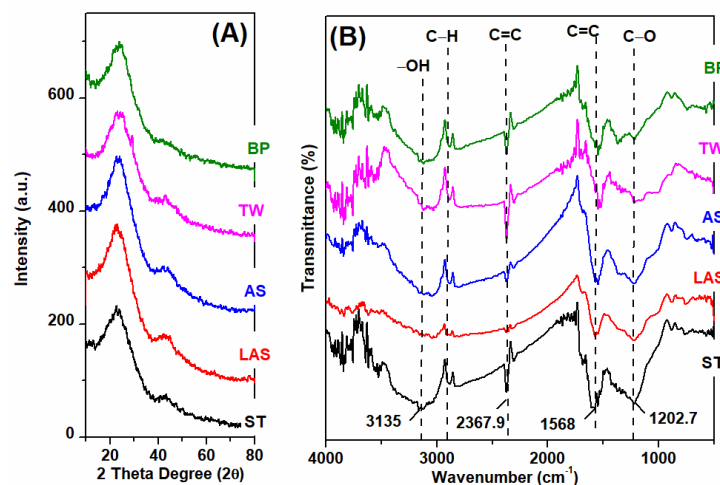

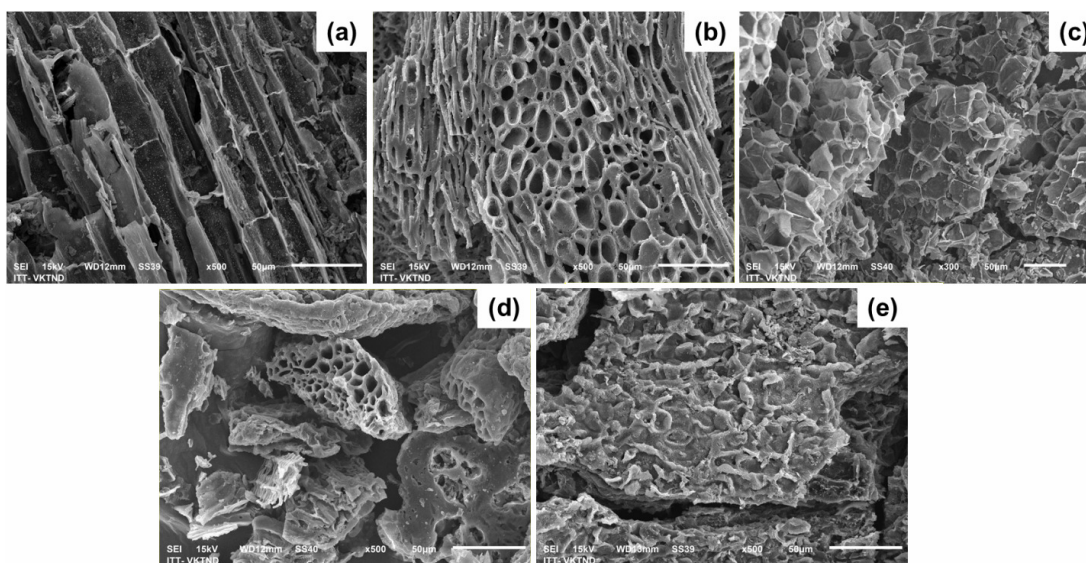Figure 1: (A) X-ray diffraction patterns and (B) FT-IR spectra of prepared AC samples

Figure 2: SEM micrographs of (a) AC-ST, (b) AC-LAS, (c) AC-AS, (d) AC-TW, and (e) AC-BP
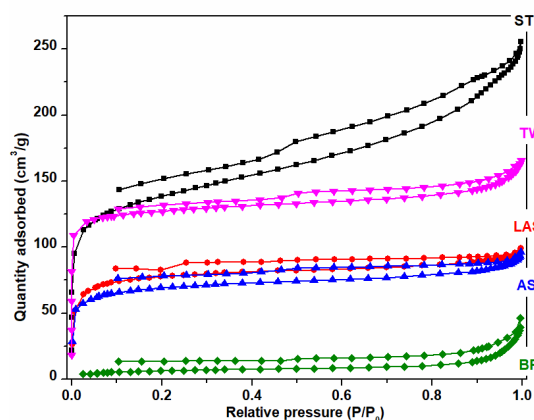

Figure 3: Nitrogen adsorption–desorption isotherms of activated carbon samples: (a) AC-ST, (b) AC-TW, (c) AC-LAS, (d) AC-AS, and (e) AC-BP

Table 1
Results of isotherms in terms of surface area, total pore volume, micropore volumeof AC materials from variousprecursors

No	Precursor	Activator	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	D_p (nm)	Ref.
1	Straw	KOH	494.92	0.494	0.110	3.991	This work
2	*Limonia acidissima* shell	KOH	250.73	0.149	0.052	2.388	This work
3	Avocado shell	KOH	218.12	0.144	0.046	2.652	This work
4	Tea waste	KOH	393.01	0.252	0.158	2.568	This work
5	Banana peel	KOH	22.11	0.062	0.002	11.391	This work
6	Date (*Phoenix dactylifera* L.) stone	H_3PO_4	1225	0.618	-	-	[44]
7	Peanut shell	$ZnCl_2$	1642	0.42	-	-	[45]
8	Coconut shell	$ZnCl_2$	11652 ± 132	1.29 ± 0.01	0.768 ± 0.094	-	[46]
9	Corncob	KOH	3530	1.94	0.322	0.65	[47]
10	Lignocellulosic biomass	$FeCl_3$	780.06	0.573	0.468	0.8	[48]

According to BET analysis, the surface area of the activated carbons is in the following order: straw (494.92 cm^2/g) > tea waste (393.01 cm^2/g) > *Limonia acidissima* shell (250.73 cm^2/g) > avocado shell (218.12 cm^2/g) > banana peel (22.11 cm^2/g). These results revealed that KOH activation helps increase the surface area and significantly enhances pore development, allowing to obtain activated charcoal from straw with the largest surface area of 494.92 cm^3/g. Therefore, the activated carbon from straw is expected to be a potential material to remove ciprofloxacin (CIP) from aqueous media.

Effect of contact time and initial concentration

The influence of initial concentration and contact time on the adsorption performance of the five activated carbons is shown in Figure 4 (a, b). To assess the removal efficiency of the five adsorbents, the antibiotic concentrations and the adsorbent dosage were fixed at 20 mg/L and 1 g/L, respectively. Figure 4 (a) shows that the AC-ST sample has the highest CIP removal efficiency, reaching 93.34%. While the remaining four materials have adsorption efficiencies below 50%. Specifically, CIP removal efficiency reaches 47.97%, 39.49%, 31.67% and 23.43% for AC-BP, AC-AS, AC-TW and AC-LAS samples, respectively.

Figure 4 (b) illustrates variations in CIP removal over 240 minutes of contact time. For all the AC samples, the CIP removal efficiency seemed to increase rapidly in the first 10 minutes. Specific to the AC-ST sample, the equilibrium was attained after 60 min, and after this point the efficiency ceased to improve and remained stable for the rest of the duration. As for the remaining four AC samples (AC-LAS, AC-AS, AC-TW and AC-BP), increasing contact time from 10 to 180 minutes improved the adsorption efficiency. However, the improvements were modest and varied with the type of the AC sample. Therefore, the experiment can last 60 minutes for AC-ST, and 180 minutes for samples AC-LAS, AC-AS, AC-TW and AC-BP. For the sake of comparison, Table 2 provides results on removal efficiencies attained by various adsorbents.
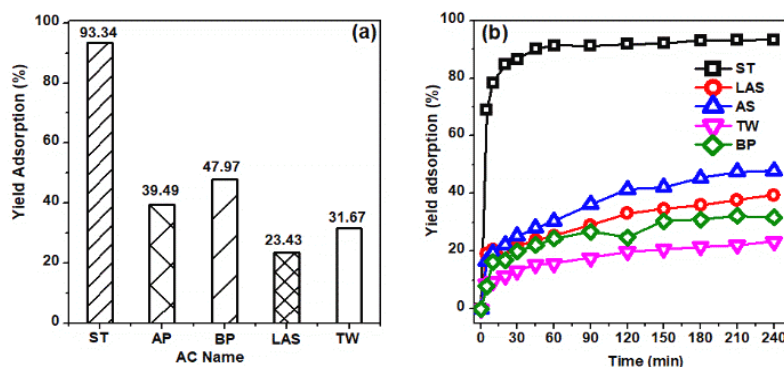

Figure 4: Effect of (a) contact time, (b) initial concentration on removal CIP using AC

Table 2
Surface area and pore volume of AC materials from various precursors

No	Adsorbent	% Removal	Ref.
1	Straw-based AC	93.34	This work
2	*Limonia acidissima* shell-based AC	23.43	This work
3	Avocado shell-based AC	39.49	This work
4	Tea waste-based AC	31.67	This work
5	Banana peel-based AC	47.97	This work
6	Horizontal-flow anaerobic immobilized biomass	97	[48]
7	Nano-sized magnetite	45-80	[49]
8	Lignocellulosic biomass by microwave pyrolysis	96.12	[50]
9	Low-cost biochar derived from herbal residue	36-100	[51]
10	Duckweed *Lemna minor*	> 80	[52]
11	Freshwater microalga *Chlamydomonas mexicana*	13 ± 1	[53]
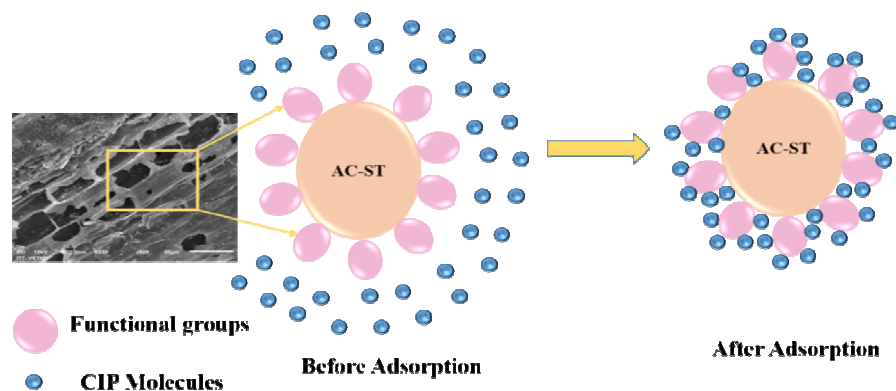
Scheme 1: Proposed adsorption mechanism of CIP antibiotics onto AC−ST

Mechanism for adsorption

To gain a further insight into the adsorption process onto AC, the corresponding mechanism was proposed in Scheme 1. On the AC surface, a large number of functional groups, such as carboxyl, hydroxyl and ketone groups, are present[54] and play an important role in improving the removal properties of the adsorbent. These functional groups bond with CIP molecules, thus causing the surface adsorption phenomenon. A possible explanation for the proposed interaction may be the p–p dispersion interaction, the hydrogen bonding formation and the electron donor–acceptor complex mechanism.[55] However, the exact mechanism that is responsible for the surface adsorption is still unclear and thus requires further investigation.

CONCLUSION

Five activated carbon samples were successfully synthesized by KOH activation and their properties were analyzed. All the samples exhibited amorphous carbon structure, were porous materials, with many surface pores. The results showed that the activated carbon produced from straw has the highest surface area (494.92 m^2/g) and the highest pore volume (0.494 cm^3/g) among all the samples produced from agricultural wastes in the present study. More interestingly, the surface consists of many functional groups, contributing to enhanced adsorption capacity. Thus, the results of the adsorption experiments showed that activated carbon from straw reached the highest CIP removal efficiency of 93.34%, compared to the remaining activated carbon samples. Besides, a mechanism was proposed to provide a further insight into the adsorption

process onto AC-ST. Therefore, activated carbon from straw has the potential to be used as an effective adsorbent to remove CIP from aqueous media.

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