The ability of silver-biochar green-synthesized from Citrus maxima peel to adsorb pollutant organic compounds and antibacterial activity

Ngoc Dai Nghia Tran, Thu Ha Bui, Anh Phung Nguyen, Tien-Thanh Nguyen, Van Minh Nguyen, Nhat Linh Duong and Tri Nguyen

ABSTRACT

Citrus maxima peel (CMP) was utilized for the green synthesis of multifunctional silver-biochar material (Ag-CMPB). An alternative, cost-effective and eco-friendly technique was performed using the CMP extract as a reducing agent for the biosynthesis of Ag-CMPB material, in which biochar is prepared from CMP residue. Ag-CMPB nanomaterials were characterized by various physico-chemical methods such as XRD, HRTEM, BET, FT-IR, EDX, and PZC. The results revealed the formation of the face-centered cubic structure of Ag with the particle size in a range of 3–10 nm and the stacking structure of layers of biochar. Flavonoids and phenolic acids in CMP extract as a reducing agent of Ag-CMPB material. The specific surface area of Ag-CMPB was determined to be 79.2 m²/g with a pore diameter of 22.4 Å. Ag-CMPB showed high efficiency in the short time in removing organic compounds. The adsorption efficiency was recognized in the following sequence for POPs adsorption: Methyl blue > Rhodamine B > Methyl orange, with the adsorption capacities of 95.5, 69.3, and 51.5 mg/g, respectively. The antibacterial activity of Ag-CMPB was evaluated on five bacteria against B. cereus, E. coli, P. aeruginosa, S. aureus, and Salmonella by the zone of inhibition and MIC value.

Introduction

Multifunctional materials have exposed great scientific-technological significance in engineering materials, environment treatment, and biomedicine (1–3). The promises offered by functional nanomaterials showed tremendous potential for developing multifunctional nanomaterials with great technological applications. With the rapid development of nanotechnology, the massive needs by a technological-centric society for materials pose environmental challenges to the safe and eco-friendly sustainable use of these materials (3, 4). Plant-based multifunctional materials seem to offer significant advantages in this respect. In which multifunctional materials incorporating silver nanoparticles (AgNP) and biochar (silver-biochar) can be explored to produce antibacterial materials for biomedical and environmental treatment (5–7). Typical parts of different plants such as stems, leaves, roots, bark, seeds, fruits, etc., can be considered as potential...
sources of raw materials for the synthesis of the multifunctional silver-biochar nanomaterials (5, 8). Citrus maxima, as a popular fruit, is widely grown in Southeast Asia, especially in Vietnam. In many countries, Citrus maxima peel (CMP) has always been considered a biomass waste in huge quantities. Bioconversion of CMP to added-value products, such as biomaterials such as biochar through physical or chemical activation and AgNP using CMP extract as a reducing agent, is a potential approach to enhancing their value (9, 10).

The development and use of plant-based activated carbon materials (biochar) for treating organic contaminants is a promising alternative to reducing the environment’s waste. Adsorption is considered one of the most effective methods to remove contaminated organic compounds in aqueous (11). This process offers outstanding advantages such as simplicity and low cost, no byproducts, eco-friendly, and inexpensive adsorbents. CMP contains several water-insoluble and soluble polymers and monomers (12). These compounds are rich in hydroxyl and carboxyl functional groups, thus making them a potential adsorbent material for removing organic compounds from wastewater (13, 14). The pollution of supplies by organic compounds has attracted significant global attention from the general public and government regulatory agencies (12). Many organic compounds are persistent in conventional water treatment processes or can be biodegraded and transformed into toxic byproducts (15). The toxicity of some organic compounds, as well as their potential adverse for human health associated with the long-term food chain, has been regarded (16). However, with growing potable reuse initiatives, the implementation of increasingly stringent environmental regulations compounded has provided strong incentives to develop alternative, eco-friendly, and cost-effective technologies for treating organic contaminants. Biochar is a porous, carbon-residue derived from the thermal conversion under limited oxygen or anaerobic conditions of waste biomass that has been a growing body of literature on their application in wastewater treatment (17, 18). In particular, the biochar application for the removal of persistent organic compounds from wastewater has been investigated (13, 14, 19). The greater adsorption of organic compounds to biochar than commercial activated carbons was described in some instances. Therefore, biochar is highly effective in treating organic compounds present in wastewater. However, an idea is raised to enhance the function of biochar, combining biochar with antibacterial nanoparticles, typically silver nanoparticles (AgNPs), could offer potential applications both in wastewater treatment and in disinfection and sterilization.

The use of plant resources in the AgNPs synthesis provides an effective platform because it provides natural capping agents and does not use toxic chemicals (20, 21). In particular, extracts from parts of different plant species such as stems, leaves, fruits, pods, and bark were used with high efficiency and environmental friendliness in synthesizing AgNPs. The phytochemicals such as phenolics, alkaloids, amino acids, proteins, enzymes, tannins, polysaccharides, terpenoids, saponins, etc., contained in the plant extract with environmentally benign performed the reduction of silver ions to AgNPs (22). The mechanism of silver nanoparticle formation can be summarized in two primary stages: (i) activation of reduced silver ions and formation of silver atoms; (ii) minor silver metals combine and grow to form silver nanoparticles (23). The mechanism of the formation of silver nanoparticles depends on the chemical composition of the plant extract. These components play a major role as a reducing and stabilizing agent for silver nanoparticles. Besides, the process of forming silver nanoparticles by the green chemistry method depends on many factors such as solution pH, temperature, time, AgNO3 concentration, etc. The authors (24) examined the synthesis of silver nanoparticles from the lemon juice extract at room temperature; The results show that citric and ascorbic acid is the essential reducing agents for synthesizing silver nanoparticles. Ramesh et al. (25) investigated the biosynthesis of AgNPs using the Bridelia retusa fruit extract as a reducing agent. The components contained in the fruit extract of Bridelia retusa, such as gallic acid, ellagic acid, b-sitosterol, and tannins, are responsible for the formation and stabilization of AgNPs. Thivaharan et al. (26) studied the green synthesis of AgNPs using extracts of Arachis hypogaea nuts. Various compounds of Arachis hypogaea, including salicylic acid, p-coumaric acid, carotenoids, proanthocyanidins, flavonoids, phenolic acids, stilbene, etc., act as reducing agent Ag ions to Ag0. Hence, the synthesis of silver nanoparticles using plant extracts provides advancements over other methods with more effectiveness in various applications, especially in bacterial activities (27–29). The bacteria have a low resistance to AgNPs, supporting their use as a suitable biocide. An earlier study showed that AgNPs penetrated bacterial cells and interacted directly with cellular macromolecules (30). Thus, AgNPs can break down the membrane/cell wall, inhibit aerobic respiration, damage deoxyribonucleic acid (DNA), and disturb biosynthesis and protein folding. Therefore, AgNPs can inhibit the activities of bacteria and kill them effectively. CMP contains many compounds such as phenolic acids, coumarin flavonoids, rutin, terpenoids, etc. (31, 32), rolling as reducing agents for the synthesis
of highly efficient AgNPs (33, 34). However, since AgNPs are easily oxidized by environmental conditions, which can cause aggregation and loss of antimicrobial activity over time, so their practical applications are limited (35). Therefore, AgNPs require a supporting substrate to enhance their morphological features’ stability as well as maintain antimicrobial efficacy. AgNP supported on biochar can overcome this shortcoming because biochar can improve the dispersion of AgNPs, leading to preventing aggregation and enhancing the stability of AgNPs. Consequently, the combination of biochar and AgNPs can create multifunctional composites with highly porous, excellent adsorption capacity and against bacteria. CMP can be utilized as a raw material to synthesize biochar as well as AgNPs. So, the use of CMP to synthesize biochar-silver multifunctional materials brings benefits both in environmental treatment, bactericidal, and medicine. However, there have been no studies using CMP as a dual agent for silver-biochar synthesis.

In this paper, multifunctional silver-biochar (Ag-CMPB) material was synthesized using CMP extract as a reducing agent, in which, biochar is prepared from CMP residue treated by KOH and activated conditions of 700 °C for 1 h in the CO2 flow. The physico-chemical properties of the Ag-CMPB material were investigated. Its antibacterial was evaluated against bacteria such as gram (+): B. cereus and S. aureus, and gram (−): E. coli, P. aeruginosa, and Salmonella. The adsorption capacity of the Ag-CMPB material is tested in the adsorption of various organic compounds, including Rhodamine B (RB), Methyl blue (MB), and Methyl orange (MO).

**Experimental**

**Synthesis of silver-biochar green-synthesized from Citrus maxima peel**

**Materials**

Citrus maxima peel (CMP) was collected from Ben Tre province, Vietnam. After washing, draining, and cutting into small pieces, CMP was dried completely at 60 °C for 24 h. The extraction process was carried out to obtain the CMP extract with deionized water: CMP mass ratio of 20:1 at 80 °C for two hours under stirring. Finally, the CMP extract was filtered and stored at 4 °C. The CMP residue was collected after the CMP extraction and utilized as a raw material for biochar synthesis.

After that, CMP residue was dried completely at 80 °C overnight and finely ground. The carbonization method of the CMP powder was performed at a temperature of 700 °C for 1 hr under N2 atmosphere. KOH was used as activation chemical for CMP powder experienced carbonization in a mass rate of 1/4 in 24 h at room temperatures. Then, the mixture was dried at 110 °C overnight. Next, the sample was activated to biochar form under CO2 atmosphere at 700 °C for 1 h and cooled down to room temperature. After activation, the biochar was washed with HCl 0.1M until the near-neutral pH of the sample (pH ∼ 7). Finally, the sample was entirely dried at 110 °C, ground, and sieved to obtain a fine biochar powder.

The synthesis of silver-biochar using CMP extract as a reducing agent was determined involving the presence of the light illumination. 40 mL of 1.25 mM AgNO3 solution was mixed with 10 mL CMP extract, then stirred at 300 rpm for 30 min in the dark. Subsequently, 0.53 grams of CMP biochar were added under stirring, and the synthesis duration was 5 h under sunlight to obtain silver-biochar (Ag-CMPB).

**Characterization**

Crystalline phases of prepared Ag-CMPB powder dried at 60 °C were investigated by X-ray diffraction (XRD) using Bruker D2 Phaser powder diffractometer. The presence of functional group on the silver-biochar surface was confirmed by Fourier transform infrared spectroscopy (FT-IR), carried out on a Tensor 27 Bruker spectrophotometer operating in the range of 400–4,000 cm−1 at a resolution of 2 cm−1. The morphology of silver-biochar was characterized by scanning electron microscopy (SEM) on the Hitachi S4800 instrument. The morphology of Ag-CMPB was characterized by high-resolution transmission electron microscopy (HRTEM) on JEOL JEM2100 instrument. BET surface, pore structure and nitrogen adsorption/desorption isotherms were measured on the Nova 2200e Instrument at −196 °C.

The point of zero charges (pHpzc) was determined from acid–base titration. Aliquots with 25 mL of 0.1 M KCl solution were prepared in various flasks. Their pH was adjusted from 2 up to 12 (pHf = 2, 4, 6, 8, 10 and 12) by addition of 0.1 M solution of NaOH or HCl. When the pH value was constant, 0.1 grams of the activated carbon sample was added to each flask and it was sealed and placed in a shaker at 180 rpm for 48 h. After completion of process, the resulting suspension was filtrated and determined the final pH value (pHf). The pHpzc value is the point where the curve pHf vs pHi (ΔpH = pHf – pHi) crosses the line pHi.

**Adsorption of organic compounds on Ag-CMPB**

Batch adsorption experiments were conducted by mixing Ag-CMPB with 200 mL of POPs solutions
(Rhodamine B, Methyl blue, and Methyl orange) under stirring of 300 rpm with same concentration (50 mg/L). The adsorption solutions by the time were separated by filtration and analyzed using a UV-visible spectrophotometer on UV-1800 (Shimadzu).

**Antibacterial activity of Ag-CMPB**

The obtained Ag-CMPB sample has been tested for antibacterial activity against gram (+) B. cereus and S. aureus and gram (−) E. coli, P. aeruginosa, and Salmonella by the zone of inhibition test and the minimum inhibitory concentration (MIC). The methods have been presented in our previous studies (36).

**Results and discussion**

**Characteristics of Ag-CMPB**

Powder XRD pattern for the silver-biochar is shown in Figure 1a. The prominent peaks at 2θ = 38.2°, 43.6°, 64.4°, and 77.2° confirmed the formation of AgNPs with corresponding lattice plane value at (111), (200), (220) and (311) of face-centered cubic phase (JCPDS card No. 89-3722). Meanwhile, the broad peak at 2θ in a range of 10°–30° indicated the formation of biochar related to the stacking structure of layers (graphite 002), which is attributed to the amorphous structure of carbon with the small dimensions of crystallites (37). The XRD peak established that the biochar maintains a heterogeneous surface. Besides, other unassigned peaks at 2θ = 28.05°, 32.34°, 46.3°, 54.7° and 56.8° were also observed in the nearness of AgNPs and biochar peaks. These peaks are because of the organic compounds contained in the extract of CMP and responding for reduction of silver ions and dispersion of nanoparticles.

FTIR measurements were carried out in order to identify the presence of function group on the silver-biochar surface (Figure 1b). The peak at 3420 cm⁻¹ was attributed to the O-H elongation oscillation of phenol groups on flavonoid rings. Adsorption bands at 1832 cm⁻¹ and 1620 cm⁻¹ are estimated to be due to prolonged fluctuation of C – H and C = C, respectively (38). The peak at 1374 cm⁻¹ is assumed to be because of bending vibrations in the plane of δ (O – H). Moreover, the peaks at 1056 cm⁻¹ can be associated with the oscillation of ν(C – O). The peak at 515 cm⁻¹ was generated by plane external bending of C–H. The FTIR results indicated that the produced carbons are rich in surface functional groups. Besides, the results demonstrated the presence of flavonoids and phenolic acids in phytochemical compositions of CMP extract as a reducing agent and stabilizer of Ag-CMPB material.

Based on the classification by the International Union of Pure and Applied Chemistry (39), Figure 2a showed that the N₂ adsorption/desorption isotherms of Ag-CMPB nanomaterials exhibited type IV isotherm with hysteresis loops at virtual P/P₀ in a range of 0.45-0.95 related to capillary condensation. As observed in Figure 2b, the pore size distribution for the sample was monomodal, with a peak pore diameter of 22.4 Å. The specific surface area of the Ag-CMPB nanomaterials was determined to be 79.2 m²/g. Thuan et al. (40) synthesized biochar from banana peel using KOH activation with the surface area was 63.5 m²/g. Swine manure biochar prepared by Zhang et al. had a surface area in a range of 23 – 32 m²/g (41). The silver-biochar in this study has a much larger specific surface area than the previous publications, leading to easy adsorption of organic compounds as well as uniform dispersion of silver nanoparticles on the biochar surface.

The SEM images in Figure 3a showed the porosity of the biochar. The pore diffusion of biochar displayed a well-developed mesoporous structure. The inset SEM image of the Ag-CMPB sample exhibited uniform distribution of silver particles on the biochar surface and a neatly arranged stacking structure of layers. Organic
compounds can be adsorbed efficiently because the mesoporous structure allows containing organic compounds, which are a smaller kinematic diameter than the pore, to enter insight biochar and contact the pores to allow the adsorption of pollutants. The particle size and morphology of the Ag-CMPB were detailly evaluated by the HRTEM image (Figure 3b). The HRTEM analysis showed the AgNPs were spherical (in dark-field) in shapes with a diameter range of 3–10 nm attached to the surface of biochar (in light-field) with the stacking layer structure. The SEM and TEM results were consistent with the XRD analysis as mentioned above.

The elemental compositions of Ag-CMPB sample were determined by EDS analysis. The EDX results revealed the presence of C, Ag, and O in the silver-biochar nanomaterials (Figure 4). EDX mapping showed the appearance of C element at energy levels 0.28, 1.25, and 2.11 keV; Ag at 2.68, 2.97, and 3.45 keV; and O at the highest energy level of 0.53 keV. The distributions of the elements in the Ag-CMPB sample are really synchronous. The presence of O’s signal may be due to the presence of phytochemicals in CMP extract covering the surface of Ag-CMPB. The mass percentage of elements C, Ag, and O of Ag-CMPB identified from the EDS spectrum as 88.79%, 0.96%, and 10.25%, respectively. The EDX analysis entirely agreed with the XRD, SEM, and TEM results that Ag-CMPB sample was successfully synthesized.

In Figure 5, the pHpzc value of the Ag-CMPB sample was approximately 6.6. At initial pH solution < pHpzc, the silver-biochar surface has a net positive charge, while at initial pH solution > pHpzc, the surface has a net negative charge. At the pH = pHpzc, the interaction between the organic pollutants and biochar surface is minimal due to the absence of electrostatic force. Therefore, the initial pH solution values equal to or above the pHpzc will ensure a negatively charged surface of bio-char and favor adsorption by electrostatic attraction between bio-char and the cationic ions of organic pollutants.

**Adsorption of pollutant organic compounds on Ag-CMPB sample**

UV-Vis spectral study of the adsorption process of various organic pollutants by the time on the Ag-CMPB sample was shown in Figure 6. The appearance of Methyl blue, Methyl orange, and Rhodamine B was recognized at 666 nm (42), 464 nm (43), and 553 nm (43, 44), respectively. With the increase in contact time, the removal percentage improved all organic pollutants.

Figure 2. N₂ adsorption/desorption isotherms (a) and BJH pore diameter distribution (b) of Ag-CMPB sample.

Figure 3. SEM (a) and HRTEM (b) images of Ag-CMPB sample.
with a strong reduction in absorbance intensity. The strong decoloration of the solution for MB, MO, and RB confirmed the great adsorption efficiency. The efficiency is exhibited more obviously than by the adsorption isotherms by time shown in Figure 7. MB adsorption efficiency increased from 0 to 95.3% and was nearly unchanged after 60 min (Figure 7a). Meanwhile, the adsorption efficiency of Ag-CMPB for MO and RB reached up corresponding to 62.1 and 50.1% with the same time taken to reach the equilibrium of 105 mins. The sequence for the adsorption of Ag-CMPB for organic pollutants is observed as follows: Methyl blue > Rhodamine B > Methyl orange. This result is more clearly shown through the adsorption capacity after 120 min of Ag-CMPB for MB, MO, and RB achieved 95.5, 51.5, and 69.3 mg/g, respectively (Figure 7b). As analyzed above, the initial pH solution is the most factor that affects the adsorption capacity of Ag-CMPB for organic compounds. Apparently, the pH of MB solution (7.4) and RhB (7.1) is higher than pHpzc (6.6). Meanwhile, the initial pH solution of MO (5.5) solutions is lower; therefore, the adsorption efficiency of this compound is lower than that of the others.

**Antibacterial activity of activated carbon**

Figure 8 exhibited the inhibition zone of the as-prepared silver-biochar sample against five bacterial strains. The average inhibition zone diameters against *B. cereus*, *E. coli*, *P. aeruginosa*, *S. aureus*, and *Salmonella* of the Ag-CMPB sample reached 15.0, 17.7, 13.5, 9.2, and 14.5 mm. Obviously, the inhibition zone by Ag-CMPB prepared from CMP extract exposed maximum inhibition against gram (−) *E. coli* and minimum inhibition against gram (+) *S. aureus*. The Ag-CMPB of our study against *E. coli* was much higher than other previous publications using the pure silver nanoparticles synthesized by various plant sources, such as Neem leaves (6.0 mm) (45) lemon extract (3.0 mm) (46), Nicotiana tobacco leaf (4.0 mm) (47), and Pomegranate fruit seeds (2.2 mm) (48) as reducing agents. This may be explained that the silver nanoparticles are uniformly dispersed on the
surface of the biochar, thereby preventing the agglomeration and reducing the particle size of the silver nanoparticles, leading to improved antibacterial activity. The antibacterial properties of Ag-CMPB were further determined by their minimum inhibitory concentration (MIC). It was observed that the exponential phase of bacteria was delayed in the presence of Ag-CMPB and this phenomenon was more obvious with the rise of Ag-CMPB concentration. The Ag-CMPB could inhibit the exponential stage of both gram (-) and gram (+) bacteria. The MIC against *E. coli*, *S. aureus*, *P. aeruginosa*, *Salmonella*, and *B. cereus* of Ag-CMPB sample were described in Table 1. In which, the Ag-CMPB material could completely inhibit the growth of *E. coli*, *P. aeruginosa*, and *Salmonella* bacteria at a similar MIC of N/64 (78.13 µg.mL⁻¹); *S. aureus* and *B. cereus* at a similar MIC of N/16 (312.5 µg.mL⁻¹). From the antibacterial ring and MIC results, it can be seen that gram (-) bacteria are more sensitive to Ag than a gram (+). The results are described by the fact that the cell wall of a gram (+) bacteria is thicker than the cell wall of a gram (-) bacteria (49, 50), so Ag can easily penetrate the cell wall of gram (-) bacteria. The MIC of Ag-CMPB against *E. coli* is higher than that of other publications using Ag nanoparticles synthesized using different plant extracts, such as *Carob leaf* (500 µg/mL) (51), Sasa

Figure 6. UV-Vis spectra of the solution of POPs by the adsorption time on Ag-CMPB sample. a) MB; b) MO, and c) RB.

Figure 7. The POPs removal efficiency at 25 °C (a) and the POPs adsorption capacity (b) of Ag-CMPB sample.
**borealis leaf** (80 μg/mL) (52), as well as their high antibacterial activity against *P. aeruginosa*, such as *Ducrosia Anethifolia* (128 μg/mL) (53) and *Sasa borealis leaf* (80 μg/mL) (52). The enhanced antibacterial activity of AgNPs may be due to silver supported on biochar leading to an increase in the dispersibility of silver and preventing their ability to agglomerate, thereby reducing particle size and improving uniformity. Tahir et al. (54) obtained similar results using CdS-supported Ag₂S against *P. aeruginosa*, *E. coli*, and *S. aureus*; the antibacterial activity of Ag₂S has significantly improved with the support of CdS thanks to enhancing the dispersibility of Ag₂S, resulting in a decrease in particle size and improving the stability of Ag₂S.

**Conclusion**

Our research has emphasized the usefulness of CMP as the eco-friendly and cost-effective bio-resources in the green synthesis of multifunctional Ag-CMPB material. The successful Ag-CMPB synthesis was expressed through their characteristic results. Besides, Ag-CMPB material showed effective adsorption of various organic compounds, including Rhodamine B, Methyl blue, and Methyl orange. The antibacterial efficacy of A has also been demonstrated through effective inhibition against *B. cereus*, *E. coli*, *P. aeruginosa*, *S. aureus*, and *Salmonella* with high inhibition zone (>9.2 mm) and low minimum inhibitory concentration (<312.5 μg.mL⁻¹). Hence, the use of Ag-CMPB material may suggest potential applications in future antibacterial systems as well as removing organic compounds, disinfection, and sterilization in drinking water treatment.

**Consent for publication**

This study does not contain any individual person’s data.
Data availability
The data used to support the findings of this study are included within the article.

Ethics approval and consent to participate
This article does not contain any studies with human participants or animals performed by any of the authors.

Disclosure statement
No potential conflict of interest was reported by the author(s).

ORCID
Anh Phung Nguyen http://orcid.org/0000-0002-5816-9832
Tien-Thanh Nguyen http://orcid.org/0000-0003-3737-3065
Tri Nguyen http://orcid.org/0000-0001-9486-5096

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