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Sequentially citric acid-KMnO₄-modified surface of activated carbon microparticles to enhance the capability of loading silver nanoparticles as a bacterial sensor material

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ABSTRACT

The surface of activated carbon microparticles (ACMPs) has been successfully modified with potassium permanganate (KMnO₄) 0.5 M, and subsequently with citric acid 0.1 M by means of reflux for various times of 2, 4, and 6 h. These produced materials were then noted as citric acid-KMnO₄-modified ACMPs. This works aimed to significantly enhance the loading capacity of the ACMPs for silver nanoparticles (AgNPs) deposition. The Fouriertransformed infrared (FTIR) spectra showed that the -C=C- bonds linkage of the ACMPs molecular framework changed became carbonyl (-C=O)-based functional groups, and hydroxyl (-OH) groups. It could also be identified that the AgNPs have been deposited around both functional groups of C=O and OH rather than the other ones. It was well known that the loading capacity of the citric acid-KMnO₄-modified ACMPs materials for loading the given AgNPs increased by extraordinary significance became 600 % compared to that of the original ACMPs material. The bacterial sensor potency of the citric acid-KMnO₄-modified ACMPs materials loaded with AgNPs was demonstrated towards both *E. coli* and *S. aureus*. In this case, the material mentioned could detect 125.00 % (*E. coli*) and 53.85 % (*S. aureus*) compared with just citric acid-KMnO₄-modified ACMPs materials.

1. Introduction

The molecular framework of activated carbon materials and their derivatives is commonly constructed by carbon-carbon single (-C-C-) and carbon-carbon double (-C=C-) bonds forming graphitic-like molecular framework structures mixed with non-graphitic like one [1,2]. Exactly, the molecular framework structures of the activated carbon can vary, it is depending on the heating temperature and the heating duration when the carbonization and pyrolysis process was performed. The lower temperature (<700 °C) and the shorter duration of the pyrolysis heating in an inert atmosphere produce activated carbon with more varied functional groups such as hydroxyl (-OH), carbonyl (-C=O-), aldehyde (-HC=O), carboxyl (-HOC=O), etc., and vice versa the higher

temperature produce activated carbon with a limited functional group. Specifically, a lower temperature of heating pyrolysis will have commonly decomposed the strongly acidic functionalities such as carboxylic, anhydrides, and lactones, while a higher temperature (>800 °C) will have commonly decomposed the weakly acidic functionalities such as carbonyl, phenol and quinone [3,4]. In other words, higher pyrolysis temperature produces activated carbon with rich-electron π donors (Lewis's base) functional groups, whereas lower pyrolysis temperature produces activated carbon with rich-electron π acceptors (Lewis's acid) functional groups [1,5]. Accordingly, one may easily design any useful or even smart activated carbon-based materials and fabricate them by setting the temperature of the carbonization, pyrolysis, or thermal activation process to facilitate any desired surface modificatory agents

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easier to embedding to the surface to fulfill the desired requirements of applications.

In this relation, reference [6] has successfully produced no functional groups containing activated biobased carbon black by using lignin through nitrogen atmospheric-thermal activation at various temperatures of 600, 750, and 900 °C for >6 h. In this context, reference [7] has reviewed many kinds of research that used some kinds of hightemperature pyrolysis commercial activated carbon powder to fabricate superior adsorbent for the removal of organic as well as inorganic pollutants from an aqueous phase. One of the potential methods applied for that was using coordinated ligand anchorage on the activated carbon surface. Here, the ligand functional groups anchoring to the activated carbon surface can gain so much better the desired pollutants (dyes, pesticides, heavy metals, etc.) and then be removed them away from their associated media. While that, reference [8] used high-temperature pyrolysis commercial activated carbon powder (Norit SX plus, Norit Americas Inc., TX) as a catalyst when he and his team attempted to fabricate a microbial fuel cell cathode.

It is very clear that additional functional groups of the small organic molecules on the activated carbon molecular framework surface might also be able to enhance the loading capacity of the associated materials, see Supporting Information, Fig. S5 (Ag: 0.35 %), and Fig. S6 (Ag: 0.05 %). It is particularly for the removal of adsorptive materials in nanoscale sizes. However, enhancing the silver nanoparticle (AgNPs)loading capacity of activated carbon by means of modification of the activated carbon surface using citric acid molecule has not been conducted yet in previous research mentioned above. A citric acid molecule has three carboxyl groups (-HOC=O) so the AgNPs could be deposited close to either carbonyl (-C=O) or a hydrogen atom (H) through dipoledipole interaction. Therefore, this paper reports the addition of citric acid molecules onto the surface of the activated carbon molecular framework to enhance its loading capacity for AgNPs deposition. The strategy was performed through the oxidation process using potassium permanganate (KMnO4) oxidizing agent to crack the carbon-carbon double bonds (-C=C-) of the activated carbon molecular framework to become oxygen atom-bonded molecular framework moiety. This part leads to citric acid molecules being easier to attach to the surface of the material. Besides, this paper also reports the justification of the success in enhancing the loading capacity for the silver nanoparticles (AgNPs) uptake, and its antibacterial properties affect both local bacterial cultures of Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus).

2. Experimental section

2.1. Materials

Local commercial available activated carbon powder; Distilled water; Bacterial local culture of *E. coli* and *S. aureus*; Citric acid anhydrous ($C_6H_8O_7$ or HOC(CO₂H)(CH₂CO₂H)₂) (analytical grade, molecular weight of 192.12 g mol⁻¹, Sigma-Aldrich, Germany); Potassium permanganate (KMnO₄) (analytical grade, molecular weight of 158.03 g mol⁻¹, Merck, Germany); Silver nitrate (AgNO₃)(analytical grade, molecular weight of 169.87 g mol⁻¹, Merck, Germany).

2.2. Equipment

Common laboratories glassware such as Erlenmeyer, Beaker glass, Volumetric flask, etc.; Manual sieves of 100 mesh, Magnetic stirrer, Reflux set, and its accessories, Fourier-transformed infrared spectroscopy (FTIR Perkin Elmer, USA), Scanning electron microscope-Energy dispersive X-ray spectroscopy (SEM-EDX, JEOL JSM-6510LA, Japan); Autoclave sterilizer (All American electric sterilizer $50\times$, 50/60 Hz, 1650 watts/8.75 amps, USA); Furnace (Vulcan 3-130, USA).

2.3. Preparation of 0.5 M potassium permanganate (KMnO₄) 250 ml solution stock

About 19.75 mg of solid potassium permanganate was perfectly solved in 100 ml distilled water in a 250 ml beaker glass. This solution was then gently poured into a 250 ml volumetric flask and made up the volume to 250 ml total with distilled water until the scratch mark. Shake vigorously this solution, and kept it in a dark bottle until used.

2.4. Preparation of 0.1 M citric acid ($C_6H_8O_7$) 250 ml solution stock, and preparation of 0.1 M silver nitrate (AgNO₃) 250 ml solution stock

About 4.80 mg of solid citric acid was perfectly solved in 100 ml distilled water in a 250 ml beaker glass. This solution was then gently poured into a 250 ml volumetric flask and made up the volume to 250 ml total with distilled water until the scratch mark. Shake vigorously this solution, and kept it in a dark bottle until used.

On the other hand, about 4.25 mg $AgNO_3$ was perfectly solved in 100 ml distilled water in a 250 ml beaker glass. This solution was then gently poured into a 250 ml volumetric flask and made up the volume to 250 ml total with distilled water until the scratch mark. Shake vigorously this solution, and kept it in a dark bottle until used.

2.5. Surface modification of activated carbon microparticles (ACMPs)

About 8.00 g of the local commercially available activated carbon powder was gently sieved with a 100-mesh manual sieving. After that, the obtained fine powder of the activated carbon namely activated carbon microparticles (ACMPs) was oxidized using 0.5 M, 80 ml KMnO₄ in a piece of reflux equipment for various times of 2, 4, and 6 h. The solid produced was carefully separated from its liquid using a Whatman filter paper, and subsequently rinsed with distilled water until neutral in pH. Finally, the KMnO₄ modified-ACMPs were then dried up in an electrical oven setup at 120 °C temperature for 1 h and kept in a desired desiccator until used.

2.6. Citric acid incorporation on the KMnO₄-modified ACMPs molecular framework

About 4 g of the KMnO₄-modified ACMPs was properly reacted with 0.1 M, 40 ml citric acid in a piece of reflux equipment for various times of 2, 4, and 6 h. The solid produced was carefully separated from its liquid using a Whatman filter paper, and subsequently used with distilled water until pH was around 6. Finally, the KMnO₄-citric acid-modified ACMPs were then dried up in an electrical oven setup at 50 °C temperature for 3 h, and kept in a desiccator until used.

2.7. Silver nanoparticles loading

About 4 g of the KMnO₄-citric acid-modified ACMPs were properly reacted with 0.1 M, 40 ml silver nitrate (AgNO₃) in a piece of reflux equipment for 4 h. The solid produced was carefully separated from its liquid using a Whatman filter paper, and subsequently rinsed with distilled water until pH was around 6. The KMnO₄-citric acid-modified ACMPs loaded with AgNO₃ were then dried up in an electrical oven setup at 50 °C for 3 h. Finally, the latest material produced was calcined at 400 °C for 2 h to convert the loaded AgNO₃ to silver nanoparticles (AgNPs) so that the desired KMnO₄-citric acid-modified ACMPs loaded with AgNPs could be produced, and kept in a desiccator until used.

2.8. Test of the bacterial sensor potent

The potency of the bacterial sensor capability of the produced citric acid-KMnO₄-modified ACMPs loaded with AgNPs was performed by using an agarose disk method towards both local bacterial cultures of *E. coli* and *S. aureus.* Exactly method was performed according to the

reference [9]. In this method, the clear zone generated around the paper disk given represents the capability of the bacterial sensor of the associated materials tested; the wider the clear zone the higher the bacterial sensor potency, and vice versa. As a comparator (negative control), it used both materials of citric acid-modified ACMPs (without AgNPs) and AgNPs-loaded original ACMPs (without citric acid).

2.9. Characterization and analysis

2.9.1. Functional groups analysis

The typical functional groups that existed in the several samples of the produced ACMPs mentioned above, before and after modification with potassium permanganate (KMnO₄), citric acid (C₆H₈O₇), and silver nanoparticles (AgNPs) loaded were analyzed using an FTIR spectrophotometer. This FTIR instrument was operated at default mode commonly used to scan samples equipped with convenient software by referring to reference [10,11]. A small amount of ACMPs materials were made into KBr pellets for FTIR analysis, and the KBr pellet was used as a blank. The infrared transmittance data was collected over a 4000 cm⁻¹ to 500 cm⁻¹ wave number range. The spectral data were compared with a reference to identify the functional groups and the covalent bonds vibration type that existed in the associated sample.

2.9.2. Surface morphology analysis and the atomic elements mapping

Surface morphology images of the desired produced ACMPs materials and related to it were characterized by SEM. The SEM instrument was operated on the default parameters that are commonly employed for the best surface morphology images with various magnifications of 5000; 10,000 and 20,000 times. The SEM parameters employed in this research were adapted from reference [11,12] for the best images. That is as follows, the samples were carefully loaded on a specific SEM sample holder and then introduced into the SEM chamber setup on a vacuum of about 10×10^{-5} Pa. The surface morphology images were then scanned with an electron beam of about 20 kV, LEI SEM detector mode, and scanning wide distance (WD) of about 10 mm.

3. Result and discussion

3.1. FTIR analysis

FTIR spectra of the produced KMnO₄-modified ACMPs materials at 70 $^{\circ}$ C for 2, 4, and 6 h refluxes and that were implanted with citric acid molecules were depicted in Fig. 1.

Investigating the FTIR patterns one by one and then comparing it each other we found that wavenumber peaks of around 3400 cm⁻¹, 1700 cm⁻¹, and 1500 cm⁻¹ of original ACMPs, Fig. 1(a) drastically changed due to KMnO₄ oxidation for 2, 4, and 6 h as shown in Fig. 1(b), (c), and (d) respectively. Referring reference [13–15] we assigned the wavenumber peaks of around 3400 cm⁻¹ (broad), 1700 cm⁻¹, and 1500 cm⁻¹ represented stretching vibrations of non-free hydrogen bond (H... OH), carbonyl groups bond (-C=O), and carboxylic acids groups bond (-CO₂) respectively. It is proof convincingly that the molecular structures that architecturally build the original activated carbon material basically have hydroxyl groups (-OH), carbonyl groups, and carboxylic acid groups tightly attached to its hydrocarbon framework. This fact matches some of the molecular structures of the activated carbon materials reviewed in detail by reference [4].

The most interesting is the appearing multiple peaks located at 750–400 cm⁻¹ range after the ACMPs materials were modified with potassium permanganate (KMnO₄) as shown in Fig. 1(b), (c), and (d). Surprisingly, even wavenumber peaks of 1387 cm⁻¹ and 1120 cm⁻¹ were also generated clearly when the ACMPs materials were modified with KMnO₄, especially for 2 and 6 h. Referring reference [16], carbon-carbon double (C=C) bonds of organic compounds susceptible to oxidation using several strong oxidizing agents such as KMnO₄, peroxide acids, ozone, and so on. This oxidation commonly produces glycol,

ketone, or aldehyde depending on the typical C—C and pH of the solvent employed. It is similar to the previous publications that stated C=C-bonds could be oxidized to become glycol, -C(OH)-C(OH)- [14], ketone, aldehyde, lactone, and carboxylic acids [17,18].

Focusing our attention on a wavenumber peak of 750–400 cm⁻¹. It represents the stretching vibration of carbon-oxygen-manganese (C-O-Mn) [19,20] of the intermediate structure of the change of C=C constructing the ACMPs molecular framework became glycol-like structure due to KMnO₄ oxidation process. This phenomenon very matches the fact of the FTIR spectra shown in not only Fig. 1(b), (c), and (d) but also in Fig. 1(e), (g), (h), and (i). We can see that only when ACMPs material was modified with KMnO₄ the FTIR wavenumber of 750–400 cm⁻¹ was generated, others nothing. The change of the C=C bond aforementioned could then be expressed in Fig. 2.

Furthermore, the glycol, ketone, and aldehyde formed during the oxidation process as shown in Fig. 2 could facilitate citric acid molecules to attach on the surface of ACMPs through one covalent bond C—O and two hydrogen bonding formations. In this case, the glycol would like to form a gem-ether structure, while ketone and aldehyde would like to form hemiketal and hemiacetal structures respectively [21], as shown in Fig. 3. Later on, the existence of citric acid on the surface of the modified ACMPs could significantly enhance the loading capacity of the associated material for receiving AgNPs.

On the other hand, the possibility of the formation of glycol was justified by the wavenumber peaks band at around 3400 cm^{-1} which was significantly higher and wider in intensity compared to that of the original activated carbon as shown in Fig. 1(b) and (d). Moreover, the wavenumber peaks intensity of around 1700 cm⁻¹ shown in Fig. 1(b) and (d) also confirm that the C=C bonds had been successfully converted to become C=O bonds since the wavenumber intensity aforementioned was higher than that of the original ACMPs material, Fig. 1 (a).

While that, 1387 cm⁻¹ wavenumber peak represents stretching vibration of C=C bonds closed to the carbon-carbon single bonds (C-C=C) [13–15]. Another one, i.e., 1120 cm⁻¹ wavenumber peak represents the C-O bond stretching vibration of secondary alcohol structure (R₂-C-OH), and that of cyclic ether large ring (C-O-C) [13,22]. This situation demonstrated that the molecular structure that throughout constructed the ACMPs materials consists of unsaturated hydrocarbon polycyclic sheets with high stability conformational framework and on its border was accessorized by several functional groups of -OH, O=C-O, C=O, and C-O-C.

In addition, wavenumber peaks located at 750–400 cm⁻¹ also possibly represent an out-of-plane bending vibration of O—H bonds of secondary alcohol [13–15]. Accordingly, in this context, it signals that the molecular framework constructing the ACMPs material was sheets that form several layers with the distance between the layers approximately equal to the O—H bond length, i.e., about 0.9710 Å at least [23].

We have an interesting phenomenon if we see the FTIR spectra of Fig. 1(e) that is similar to Fig. 1(a). Comparing the two FTIR spectra patterns aforementioned we know that citric acid molecules could not be properly attached to the surface of the molecular framework of the original ACMPs materials (not be oxidized) since the two FTIR spectra are precisely similar to each other. Normally, the OH groups, as well as C=O ones of ACMPs molecular framework, enable binding either the -CO₂H groups or the OH ones of the citric acid molecule. Unfortunately, in this case, such desired bonding could not happen at all. It might be because both OH and C=O groups of the associated ACMPs molecular framework be positioned bent perpendicular towards its molecular plane and getting pressure force from the closer upper molecular plane layer, as already explained above. This situation leads them to fail to free-rotate to catch either CO₂H or OH groups of the citric acid counterpart. Another possibility is the citric acid molecules have been decomposed during reflux as their decomposition point is about 160 °C [24].

The similar phenomena were also shown in Fig. 1(b), (c), and (d)



Fig. 1. FTIR spectra of (a) Original ACMPs, (b) 2 h KMnO₄-modified ACMPs, (c) 4 h KMnO₄-modified ACMPs, (d) 6 h KMnO₄-modified ACMPs. (e) 6 h citric acid-modified original ACMPs, (f) 2 h citric acid-KMnO₄-modified ACMPs, FTIR spectra of (g) 4 h citric acid-KMnO₄-modified ACMPs, (h) 6 h citric acid-KMnO₄-modified ACMPs, (i) 2 h citric acid-KMnO₄-modified ACMPs, (j) Original ACMPs, (j) 2 h citric acid-KMnO₄-modified ACMPs, (j) Original ACMPs, (j) Characteristic acid-KMnO₄-modified ACMPs,



Fig. 2. The C-O-Mn intermediate structure of the change of carbon-carbon double bond constructing the ACMPs molecular framework become glycol-like structure, ketone, and aldehyde due to the KMnO₄ oxidation process.



Fig. 3. Schematic illustration of the formation of (a) gel-ether structure, (b) Hemiketal structure, and (c) Hemiacetal structure between acetic acid and glycol, ketone, and aldehyde respectively.

compared with Fig. 1(f), (g), and (h). We can see in all the Figures aforementioned, specific double peaks of the FTIR spectra represent the existence of citric acid molecule, i.e., at 4000–3000 cm⁻¹ was not appeared. It means, the KMnO₄-oxidized ACMPs materials failed to bind citric acid molecules, or the citric acid has been decomposed during the reflux process. The fact can be additional evidence for both OH and C=O groups of the associated ACMPs molecular framework be positioned prohibited sterically to bind citric molecules. Besides, the situation also became evident that the intermediate structure of the C-O-Mn ring linkage (see Fig. 2) was very stable as it did not collapse due to citric acid exposure. Recapitulation of the FTIR spectra peaks of Fig. 1 completely and their assignment is displayed in Table 1 in detail.

Furthermore, we now focus attention on Fig. 1(i) and (j) where silver nanoparticles (AgNPs) have been already embedded into the associated ACMPs materials targeted. Here, either free-dissolved electrons, or lone pair electrons of oxygen-containing groups attached on the surface of the ACMPs, such as OH, and COOH, would have reduced the Ag⁺ ions of AgNO3 crystalline salt to become Ag atoms obeying the common equation of reduction reaction of $Ag^+ + e^- \rightarrow Ag$. Subsequently, a lot of Ag atoms would be doing self-assembly facilitated by inter-atomic forces to be Ag nanoparticles (AgNPs), and then citric acid molecules stabilized the formed AgNPs through Van der Waals forces as well as dipole-dipolelike ones. To analyze where the AgNPs were properly embedded, we can compare the FTIR spectra pattern between Fig. 1(i) and (f) as well as that of Fig. 1(j) and (a). We can see here, that the FTIR spectra peak of the 4000–3000 cm^{-1} range of Fig. 1(i) is significantly so much lower in intensity (after AgNPs incorporation) compare to that of Fig. 1(f) (before AgNPs incorporation. Even the FTIR spectra peak of the 1600-1400 cm^{-1} range of Fig. 1(i) disappeared while that of Fig. 1(f) clearly appeared. Accordingly, we can guess that the AgNPs have been embedded rather around both OH groups and ionic CO₂⁻ ones than at C-O-Mn ring linkage of the molecular framework of the 2 h-citric acidtreated KMnO₄-oxidized ACMPs material when they were incorporated on it.

However, a little bit of difference in the location of the AgNPs

deposition happen when the AgNPs mentioned were embedded in the original ACMPs material. In this context, we can see FTIR spectra of Fig. 1(j) and (a), spectra peak of 1206 cm^{-1} that represented aromatic ether (R-O-Ar, where R: non-aromatic chain, Ar: aromatic chain) stretching vibration as well as spectra peak of around 1700 $\rm cm^{-1}$ that represented C=O stretching vibration [22] in Fig. 1(j) (after AgNPs incorporation) is significantly stronger in intensity compared to that of in Fig. 1(a) (before AgNPs incorporation). It demonstrated the AgNPs have been embedded at both around the R-O-Ar groups and the carbonyl (C=O) ones instead of at around both OH groups and ionic CO_2^- ones. Such a situation leads to the conformational structure of the R-O-Ar groups and C=O ones mentioned change so that free to do stretching vibration. In this case, the 2 h KMnO₄-citric acid modified ACMPs material has got AgNPs particles in more quantity compared to the original ACMPs so that they press both OH groups and ionic CO₂ ones so that they are unable to free doing stretching vibration.

The above data proves that the incorporation of AgNPs on the surface of KMnO₄-modified ACMPs material could be properly performed by using reflux methods as described in Section 2.5. In this method, during reflux, AgNO₃ crystalline salt would have been ionized to Ag⁺ ion and NO_3^- ion. After that, the active functional groups located on the surface of the ACMPs material, such as hydroxyl (OH) and carbonyl (C=O) attracted both ions Ag⁺ ion and NO₃⁻ through dipole-dipole or electrostatic-like forces to enter the pore of the ACMPs material. At this moment, covalently coordination bonding between Ag⁺ ion and OH, or between Ag^+ ion as well as NO_3^- ion and C=O to form a complex structure of $(NO_3^- \rightarrow C - O \rightarrow Ag^+)$ might be established. Furthermore, during calcination, the coordination electron of the oxygen atom might really have converted the Ag^+ ion to a silver atom (Ag), while the $NO_3^$ ion was changed to NO_x family gases such as nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), etc., and oxygen (O₂) with various moles ratio. All the formed gases would have been released out into atmospheric air. Accordingly, the reproducibility of the method described in Section 2.5 might be good enough.

Table 1

Recapitulation of the FTIR spectra wavenumber peaks of the various fabricated ACMPs material and its derivatives ones.

No.	Material	FTIR spectra wavenumber peaks/cm ⁻¹ and their assignment [13–15]								
		4000–3000		1800–1600	1600–1400	1400–1200	1200–1000	850–750	750–400	
		Double peaks, sharp: OH-free stretching vibration	Broad band: OH- bounded stretching vibration	Double peaks, sharp strong: C=O stretching vibration	Multiple peaks; sharp weak: CO_2^- or C=C-C stretching vibration	Multiple peaks; sharp medium: O—H bending vibration	Multiple peaks; sharp strong- medium: C—O stretching vibration	Broad band, strong: C—H bending vibration	Multiple peaks, sharp and strong: C-O-Mn stretching vibration	
0	1	2	3	4	5	6	7	8	9	
1	Citric acid	\checkmark	n. o		n. o	\checkmark	\checkmark	\checkmark	n. o	
2	ACMPs_ pristine	n. o	weak			n. o	n. o	n. o	n. o	
3	KMnO ₄ -modified ACMPs_2h	n. o	$\sqrt{\text{strong}}$	\checkmark	\checkmark	n. o	\checkmark	n. o	\checkmark	
4	KMnO ₄ -modified ACMPs 4h	n. o	\sqrt{medium}	\checkmark	\checkmark	n. o	n. o	n. o	\checkmark	
5	KMnO ₄ -modified	n. o	$\sqrt{\rm strong}$	\checkmark	\checkmark	\checkmark	\checkmark	n. o	\checkmark	
6	Citric acid- ACMPs original 6h	n. o	$\sqrt{\rm medium}$	n. o	\checkmark	\checkmark	\checkmark	n. o	n. o	
7	KMnO ₄ -Citric acid modified ACMPs 2h	n. o	$\sqrt{\rm strong}$	\checkmark	\checkmark	n. o	n. o	n. o	\checkmark	
8	Citric acid-treated oxidized ACMPs 4h	n. o	$\sqrt{\rm strong}$	\checkmark	\checkmark	n. o	n. o	n. o	\checkmark	
9	KMnO ₄ -Citric acid modified ACMPs 6h	n. o	$\sqrt{\rm strong}$	\checkmark	\checkmark	n. o	n. o	n. o	\checkmark	
10	KMnO ₄ -Citric acid modified ACMPs_2h loaded with AgNPs	n. o	$\sqrt{\mathrm{weak}}$	\checkmark	n. o	n. o	n. o	n. o	\checkmark	
11	AgNPs-loaded ACMPs_original_2h	n. o	$\sqrt{\rm medium}$	\checkmark	\checkmark	n. o	\checkmark	n. o	n. o	

n. o: not observable; $\sqrt{}$: observable.

3.2. SEM-EDX analysis

SEM images of the surface morphology of the KMnO4-modified ACMPs were then subsequently gently treated with citric acid and loaded with AgNPs, and their relation to the others is depicted in Fig. 4. Fig. 4(a) & (b) shows the surface morphology of the KMnO₄-modified ACMPs materials subsequently treated with citric acid and loaded with AgNPs is extremely different from that of the KMnO₄-modified ACMPs materials and just treated with citric acid, without loaded AgNPs, Fig. 4 (c) & (d). The difference is clearer if we see an inset of Fig. 4(a) compared to an inset of Fig. 4(c) as well as comparing the redrawing duplication of the isolated most particles unit representatives of the two kinds of the material aforementioned, Fig. 4(b) and (d). We can see here that the shapes and sizes of their particle are quite different from each other. In this case, the shape of the KMnO4-modified ACMPs material unit containing AgNPs is more varied than that if it does not contain one. While the particle sizes of the KMnO4-modified ACMPs material unit containing AgNPs is much smaller than that if it does not contain one.

It is about 0.13–0.65 μ m and 0.625–1.250 μ m for the first and the second mentioned, respectively. It is also very interesting that several layers of the agglomerated particles of the KMnO₄-modified ACMPs materials that were just modified with citric acid were clearly formed as shown in Fig. 4(c) layers a, b, c, and d. This fact demonstrated that the existence of AgNPs could reduce significantly the size of the ACMPs unit of particles, avoid the formation of agglomerated layers, but lead the shape of the particles unit more vary. This situation might be attributed ed. to the electrostatic interaction between valence electrons of silver nanoparticles, [Kr] 4d¹⁰5s¹, and positive partial charge that is generated due to being electronegativity gap of O and H atom of OH groups as well as that of O and C atom of ionic CO₂ ones, already confirmed with FTIR spectra of Fig. 1(i).

In this relation, the effect of the existence of AgNPs in reducing the particle sizes as well as varying the shape of ACMPs materials is also justified when we compare Figs. 3(e) & (f) and 4(g) & (h). Fig. 4(e) & (f) shows the surface morphology of AgNPs-loaded original ACMPs which is generating several various particles units of the cubes in shape (*i* and *v*, 0.125 μ m and 0.100 μ m in size respectively), cylindrical in shape (*iv*, 0.175 μ m in size), and rectangular in shape (*ii* and *iii*, 0.800 μ m and 0.125 μ m respectively). In contrast, Fig. 4(g) & (h) shows agglomerated spherical shape of particles units of original ACMPs material forming some agglomerated clusters with various sizes of approximately *i* (0.750

 μ m), *ii* (0.500 μ m), *iii* (0.625 μ m), and *iv* (0.750 μ m). However, the isolated particle size of the original ACMPs could be approximately determined by using its associated barcode which was about 0.050–0.100 μ m or 50–100 nm.

Accordingly, the oxidation process using KMnO₄ has relatively increased the particle size of the ACMPs material. It was because some carbon-carbon double bonds, C=C, of the molecular framework throughout constructed the ACMPs especially of those located on the surface of its particle body, changed became diol, OHC-COH and carbonyl groups, C=O as well as ionic CO₂ ones as presented by its FTIR spectra shown in Fig. 1. Such active functional groups could then facilitate the formation of new chemical bonds with the other similar groups that came from either the other molecular framework of the same particles or that came from the other particles. This process leads the size of the particles to change and became bigger than the original ones. Besides, the shape of the particles also became more varied than the original ones as shown in Fig. 4.

Furthermore, EDX analysis of the KMnO4-modified ACMPs materials that were subsequently treated with citric acid and AgNPs loaded is depicted in Fig. 5. Figs. 5(b)-4(c) show four peaks of the EDX diffractogram of the mentioned ACMPs material due to electrons moving from L-shell to K-shell of carbon (C), oxygen (O), silicon (Si) atoms with emission energy of 0.277 keV, 0.525 keV, and 1.739 keV respectively. It is very interesting that four isotopes of Ag atom was detected where one of them had released emission energy of >0.277 keV but <0.525 keV due to electrons moving from N-shell to M-shell. While the other three isotopes of the Ag atom released an emission energy of around 2.983 keV on average due to electrons moving from M-shell to L-shell. The facts above demonstrated that AgNPs have been successfully loaded on the desired ACMPs material. In correlation to that, the atomic composition of the ACMPs material aforementioned has been summarized in Fig. 5 (c), where the Ag atom is just about 0.35 % (2.35 % in mass), whereas C, O, and Si atom was 57.37 %, 25.95 %, and 16.36 % respectively.

Despite the Ag atom being the least in quantity, they could be properly spread out on the surface of ACMPs materials as confirmed in Fig. 5(d), where yellow lines that represented Ag atoms are correctly matching with the red line that represented C atoms. In this context, it was clear that Si atoms totally constructed the supporting material made of silicon wafer used in this analysis, then provided the highest spectrogram intensity. Whereas, O atoms come from the oxygen-containing surface functional groups such as OH, C=O, and ionic CO₂ of produced



Fig. 4. SEM images of the surface morphologies, $5000 \times \text{magnification of (a) \& (b) KMnO_4-citric acid modified ACMPs material loaded with AgNPs, (c) \& (d) KMnO_4-citric acid modified ACMPs material, (e) & (f) AgNPs-loaded original ACMPs material, and (g) & (h) Original ACMPs material.$



Fig. 5. EDX analysis of the KMnO₄-oxidized ACMPs materials that were subsequently treated with citric acid and AgNPs loaded, (a) surface morphology area of the material scanned, (b) EDX diffractogram, (c) elements list existed in the material, and (d) Parallel mapping of the associated elements.

ACMPs materials that have been already confirmed by FTIR spectra depicted in Fig. 1, while, C atoms, of course, came from the associated produced ACMPs molecular framework.

Similar to that, the EDX analysis of the AgNPs-loaded original ACMPs material and its related one, in terms of the AgNPs distribution mapping, are depicted in Fig. 6. Focusing our attention on the existence of Ag atom, Fig. 5(c) shows it was about just about 0.05 %.

This Ag atom was quite little in quantity compared to the Ag atom that was loaded on KMnO₄-oxidized ACMPs material as shown in Fig. 4 (c), i.e., 0.35 %. This fact is convincing proof that a series action of oxidation process using KMnO₄ followed by the citric acid treatment performed on the ACMPs material could very significantly enhance the loading capacity of the ACMPs for AgNPs loading. The enhancement percentage of the AgNPs loading is very surprising, it is about 600 % if we calculate using the equation as follows, % Enhancement of AgNPs = {(% Ag in ACMPs final - % Ag in original ACMPs) \div % Ag in original ACMPs} × 100 %. It means, the % enhancement of AgNPs = {(0.35–0.05) \div 0.05} × 100 % = 600 %.

The extraordinary phenomenon mentioned above is attributed to the

higher surface area of the unit particles of the $KMnO_4$ -oxidized ACMPs material and their various particles shape that have many nano-scale basins on their surface. In addition, the number of voids generated among the smaller unit particles, as shown in Fig. 4, also leads to enhancing the capacity loading of the associated ACMPs material for the AgNPs uptake.

3.3. The bacterial sensor capability

The bacterial sensor capability of the AgNPs-loaded citric acid-KMnO₄-modified ACMPs materials has been summarized and displayed in Table 2.

Table 2 shows the produced ACMPs_MnCA_AgNPs material provided a clear zone of about 0.45 mm and 1.00 mm in diameter for *E. coli* and *S. aureus* respectively. While ACMPs_AgNPs material provided a clear zone of about 0.25 mm and 1.45 mm in diameter for *E. coli* and *S. aureus* respectively. Another one is ACMPs_MnCA material provided a clear zone of about 0.20 mm and 0.65 mm in diameter *E. coli* and *S. aureus* respectively. Due to the wider the diameter of the clear zone the higher



Fig. 6. EDX analysis of the AgNPs-loaded original ACMPs material, (a) surface morphology area of the material scanned, (b) EDX diffractogram, (c) elements list existed in the material, and (d) parallel mapping of the associated elements.

Table 2

The summary of the AgNPs-loaded citric acid-KMnO₄-modified ACMPs materials towards *E. coli* and *S. aureus* bacteria.

Material*	The generated clear zone around the given paper disk, in mm unit				
	E. coli	S. aureus			
ACMPs_MnCA_AgNPs	0.45	1.00			
ACMPs_AgNPS ACMPs_MnCA	0.23	0.65			

*ACMPs_MnCA_AgNPs: KMnO₄-modified ACMPs were subsequently treated with citric acid and loaded with AgNPs.

ACMPs_AgNPs: AgNPs-loaded original ACMPs.

ACMPs_MnCA: KMnO₄-modified ACMPs and then treated with citric acid.

in antibacterial activity, so the best antibacterial activity is ACMPs_MnCA_AgNPs material just for *E. coli*, and ACMPs_AgNPs material for *S. aureus*. In relation to the EDX analysis (Figs. 5 and 6) where

the quantity of AgNPs existed in the ACMPs_MnCA_AgNPs material is higher than that in the ACMPs_AgNPs, it demonstrated antibacterial activity of the ACMPs_MnCA_AgNPs materials increases as the quantity of AgNPs existed in the associated materials are also increase, just happen to *E. coli* (negative-Gram bacteria), not to *S. aureus* (positive-Gram bacteria).

This fact convincingly indicated that almost all of the AgNPs existed in the ACMPs_MnCA_AgNPs materials could be released and then infiltrate through the bacterial cell membrane of *E. coli*. This situation leads to the *E. coli* bacteria dead. On contrary, just a few amounts of AgNPs existed in the ACMPs_MnCA_AgNPs could be released to infiltrate through into the bacterial cell membrane of *S. aureus*. However, in this case, despite the quantity being a few, but might almost all of the AgNPs of which existed in ACMPs_AgNPs could be released to infiltrate through into the *S. aureus* bacterial cell membrane. It is a very interesting phenomenon, where despite the existence of citric acid could significantly enhance the loading capacity of the ACMPs materials to load AgNPs in coincide, the citric acid could restrict the AgNPs to release from the associated material when in particular it was applied to kill *S. aureus* bacteria.

Another interesting phenomenon could also be encountered when we compare the antibacterial effectivity of the several ACMPs materials listed in Table 2 each towards both *E. coli* and *S. aureus* bacteria. According to the generated clear zone diameter, the antibacterial activity of the mentioned ACMPs materials was so much more effective towards *S. aureus* than towards *E. coli*. The fact has a correlation with the chemical composition of the bacterial cell wall and its thickness. In this relation, the bacterial cell wall is commonly constructed by peptidoglycan with 3 nm thickness which contains teichoic acid covered by lipopolysaccharide, phospholipid, and lipoprotein form of *E. coli* whereas about 25 nm for *S. aureus* [25]. The thicker cell wall will provide more lipopolysaccharide, phospholipid, and lipoprotein so that AgNPs are easier to react with them, and finally, the bacterial cell is broken down, and subsequently the associated bacteria death.

In this relation, basically, there are two possible mechanisms of bacterial cell lysis due to the interaction with AgNPs proposed [26]. The first one is AgNPs infiltrate the outer bacterial cell membrane, accumulating in the inner one so which increases its surface tension and permeability over to a critical point and finally the membrane breakdown, and subsequently the associated bacteria death [26–28]. The second one is, after AgNPs successfully infiltrate through the bacterial cell membrane and enter into the cell plasma, they interact with some bacterial organelles, such as deoxynucleotide acid (DNA), and protein enzymes including metabolic enzymes and respiratory ones, and subsequently alter their structure and functions so that the associated bacteria death [26–30].

4. Conclusion

The unsaturated hydrocarbon framework especially its carboncarbon double bonds (C=C) of which constructed the ACMPs material and particularly positioned on the surface of the associated material can be oxidized by using KMnO₄ 0.5 M to become hydroxyl (OH) or carbonyl (C=O) functional groups. The additional OH and C=O groups due to the oxidation of C=C bonds can facilitate AgNPs to stay around the groups. It can happen due to obeying under dipole-dipole interaction or a partially electrostatic one as the consequence of the electronegative difference generated between all the associated atoms. Accordingly, the more C=C bonds could be oxidized to become OH and C=O groups the more AgNPs could be loaded onto the ACMPs material. However, citric acid molecules could not form chemical bonds including hydrogen bonds with OH and C=O groups of the ACMPs material framework due to the existence of the AgNPs around them. Owing to those, the citric acid molecules could just be incorporated physically on the surface of the ACMPs material. Unfortunately, the citric acid molecules aforementioned could restrict the AgNPs from releasing away from the ACMPs material particularly when it was applied to the S. aureus bacterial culture. The facts mentioned above signal the future prospect of the application of the ACMPs material as a bacterial sensor working based on the capability of bacterial cell lysis. The most limitation of the ACMPs material for bacterial sensor material is its brittleness. Nevertheless, the brittleness might be overcome by incorporating it with other materials belonging to high modulus elasticity.

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Ethical approval statement

This research did not contain any studies involving animal or human participants, nor did it take place on any private or protected areas. No specific permissions were required for conducting the research at the corresponding locations.

CRediT authorship contribution statement

Conceptualization, P.J.W.; methodology, P.J.W., S. and P.; validation, P.J.W., S. and P.; formal analysis: P.J.W., H.A.S.N., P.D., and Z.U.F. A., investigation, H.A.S.N., P.D., and Z.U.F.A.; resources, P.J.W., H.A.S. N., P.D., and Z.U.F.A.; data curation: P.J.W.; writing—original draft preparation: P.J.W., H.A.S.N., P.D., and Z.U.F.A; writing—review and editing: P.J.W.; supervision: P.J.W., S. and P.; funding acquisition: P.J. W. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pratama Jujur Wibawa reports financial support was provided by Diponegoro University Faculty of Science and Mathematics. Pratama Jujur Wibawa reports a relationship with Diponegoro University that includes: funding grants.

Data availability

The relevant data which is related to the FTIR spectra, Molecular structure of the common carbonaceous material framework, Molecular structure of citric acid, Surface morphology and EDX analysis of the fabricated materials, and Antibacterial test result of the fabricated materials that are not displayed in this paper, they have been presented as Supplementary Information file of S1- S7, and it can be accessed freely from the given link of "Diamond and Related Material".

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.diamond.2023.109900.

References

- O.D. Nartey, B. Zhao, Biochar preparation, characterization, and adsorptive capacity and its effect on bioavailability of contaminants: an overview, Advances in Materials Science and Engineering (2014), 715398, https://doi.org/10.1155/ 2014/715398, 12 pages.
- [2] J.A.M. Díaz, I.M. Gullón, Types of carbon adsorbents and their production, in: T. Bandosz (Ed.), ActivatedCarbon Surfaces in Environmental Remediation, Interface Science and TechnologySeries, 7, Elsevier, 2006, pp. 1–48. ISBN: 0-12-370536-3.
- [3] N. Hagemann, K. Spokas, H.P. Schmidt, R. Kägi, M.A. Böhler, T.D. Bucheli, Review on activated carbon, biochar and charcoal: linkages and synergies across pyrogenic carbon's ABCs, Water 10 (182) (2018) 1–19, https://doi.org/10.3390/ w10020182.
- [4] M.S. Shafeeyan, W.M.A.W. Daud, A. Houshmand, A. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, J. Anal. Appl. Pyrolysis 89 (2010) 143–151. https://doi.org/10.1016/i.jaap.2010.07.006.
- [5] L. Yang, M. Jin, C. Tong, S. Xie, Study of dynamic sorption and desorption of polycyclic aromatic hydrocarbons in siltyclay soil, J. Hazard. Mater. 244–245 (2013) 77–85, https://doi.org/10.1016/j.jhazmat.2012.11.029.
- [6] M.R. Snowdon, A.K. Mohanty, M. Misra, A study of carbonized lignin as an alternative to carbon black, ACS Sustain. Chem. Eng. 2 (2014) 1257–1263, https:// doi.org/10.1021/sc500086v.
- [7] J.R. Utrilla, M.S. Polo, V.G. Serrano, P.M. Alvarez, M.C.M.A. Ferraz, J.M. Dias, Review on activated carbon modifications to enhance its water treatment applications, J. Hazard. Mater. 187 (2011) 1–23, https://doi.org/10.1016/j. jhazmat.2011.01.033.

- [8] W. Yang, W. He, F. Zhang, M.A. Hickner, Bruce E. Logan, Single-step fabrication using a phase inversion method of poly(vinylidene fluoride) (PVDF) activated carbon air cathodes for microbial fuel cells, Environ. Sci. Technol. Lett. 1 (2014) 416–420, https://doi.org/10.1021/ez5002769.
- [9] P.J. Wibawa, M. Nur, M. Asy'ari, Wijanarka, H. Susanto, H. Sutanto, H. Nur, Molecules 26 (3790) (2021) 1–14, https://doi.org/10.3390/molecules26133790.
- [10] S.M. Yakout, G.S. El-Deen, Characterization of activated carbon prepared by phosphoric acid activation of olive stones, Arab. J. Chem. 9 (2016) S1155–S1162, https://doi.org/10.1016/j.arabjc.2011.12.002.
- [11] P.J. Wibawa, M. Nur, M. Asy'ari, H. Nur, SEM, XRD and FTIR analyses of both ultrasonic and heat generated activated carbon black microstructures, Heliyon 6 (2020), e03546, https://doi.org/10.1016/j.heliyon.2020.e03546.
- [12] P.J. Wibawa, H. Saim, M.A. Agam, H. Nur, Design, preparation and characterization of polystyrene nanospheres based-porous structure towards UV-vis and infrared light absorption, Phys. Procedia 2011 (22) (2011) 524–531, https://doi.org/10.1016/j.phpro.2011.11.081.
- [13] J. Coates, in: R.A. Meyers (Ed.), Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd, 2019, p. 123. Online accessed on Wednesday, August 28, 2019 at 08.00 a.m. Indonesian western time, http://www3.uma.pt/jrodrigues/disciplinas/QINO-II/Teorica/IR. ndf
- [14] S. Wolfe, C.F. Ingold, R.U. Lemieux, Oxidation of olefins by potassium permanganate. Mechanism of alpha-ketol formation, J. Am. Chem. Soc. 103 (4) (1981) 938–939, https://doi.org/10.1021/ja00394a037.
- [15] R.M. Silverstein, G.C. Bassler, T.C. Morril, Spectrometric Identification of Organic Compounds, 4th. Edition, John Wiley & Sons, New York, 1981.
- [16] R.T. Morrison, R.N. Boyd, in: Organic Chemistry, 5th. Edition, Printice-Hall of India, New Delhi, 1990, pp. 334–338.
- [17] N. Feng, Y. Zhang, M. Zhu, Characterization of oxidized activated carbon obtained from astragalus residue and its adsorption application for Cu2+ from aqueous solution, IOP conf. SeriesMater. Sci. Eng. 392 (2018), 032031, https://doi.org/ 10.1088/1757-899X/392/3/032031.
- [18] D. Rathnayake, S.M.K. Gamage, G. Kastl, A. Sathasivan, Effect of KMnO4 treatment of granular activated carbon on the removal of natural organic matter, Desalination and Water Treatment 71 (2017) 201–206, https://doi.org/10.5004/ dwt.2017.20570.

- [19] M. Perachiselvi, M.S. Bagavathy, J.J. Samraj, E. Pushpalaksmi, G. Annadurai, Synthesis and characterization of Mn3O4 nanoparticles for biological studies, Appl. Ecol. Environ. Sci. 8 (5) (2020) 273–277, https://doi.org/10.12691/aees-8-5-13.
- [20] A. Dhanalakshmi, B. Natarajan, V. Ramadas, A. Palanimurugan, S. Thanikaikarasan, Structural, morphological, optical and antibacterial activity of rod-shaped zinc oxide and manganese-doped zinc oxide nanoparticles, Pramana J. Phys. 87 (2016) 57, https://doi.org/10.1007/s12043-016-1248-0.
- [21] R.J. Fessenden, J.S. Fessenden, in: Organic Chemistry, 4th Edition, Brooks/Cole Publishing Company, California, 1990, pp. 540–543.
- [22] B.D. Mistry n.d. A Handbook of Spectroscopy Data Chemistry, 2009 Edition, Oxford Book Company, Jaipur, India, page: 26-30.
- [23] D.R. Lide, in: CRC Handbook of Chemistry and Physics, 82nd Edition, Copyright CRS Press LLC, New York, 2002, pp. 9–30, 12 pages.
- [24] D. Wyrzykowski, E. Hebanowska, G.N. Wiczk, M. Makowski, L. Chmurzyn'ski, Thermal behaviour of citric acid and isomeric aconitic acids, Journal of Thermal Analysis and Calorimetry 104 (2011) 731–735, https://doi.org/10.1007/s10973-010-1015.
- [25] I.E. Alcamo, in: Fundamentals of Microbiology, 2nd Ed. 62-65, The Benjamin/ Cummings Publ. Ltd, California, 1987, pp. 106–112, 162-187, 738.
- [26] T. Bruna, F. Maldonado-Bravo, P. Jara, N. Caro, Silver nanoparticles and their antibacterial applications, Int. J. Mol. Sci. 22 (2021) 7202, https://doi.org/ 10.3390/ijms22137202.
- [27] M. Seong, D.G. Lee, Silver nanoparticles against salmonella enterica serotype typhimurium: role of inner membrane dysfunction, Curr. Microbiol. 74 (2017) 661–670, https://doi.org/10.1007/s00284-017-1235-9.
- [28] A. Ivask, A. Elbadawy, C. Kaweeteerawat, D. Boren, H. Fischer, Z. Ji, C.H. Chang, R. Liu, T. Tolaymat, D. Telesca, et al., Toxicity mechanisms in Escherichia coli vary for silver nanoparticles and differ from ionic silver, ACS Nano 8 (2014) 374–386, https://doi.org/10.1021/nn4044047.
- [29] J.T. Seil, T.J. Webster, Antimicrobial applications of nanotechnology: methods and literature, Int. J. Nanomedicine 7 (2012) 2767–2781, https://doi.org/10.2147/ IJN.S24805.
- [30] W.R. Li, X.B. Xie, Q.S. Shi, H.Y. Zeng, Y.S. Ou-Yang, Y. Chen, Ben antibacterial activity and mechanism of silver nanoparticle on Escherichia coli, Appl. Microbiol. Biotechnol. 85 (2010) 1115–1122, https://doi.org/10.1007/s00253-009-2159-5.