Short Communication

Shu Hui Tang, Lin Zhi Lee, Vanissa Sandra Andrew, Aiman Rashidi Mohd Akhmar and Muhammad Abbas Ahmad Zaini*

Effects of zinc chloride impregnation states on specific surface and dielectric properties of activated carbons

https://doi.org/10.1515/ijcre-2021-0241
Received September 15, 2021; accepted March 27, 2022; published online April 12, 2022

Abstract: The present work was aimed at evaluating the roles of zinc chloride impregnation states on specific surface and dielectric properties in microwave-assisted activated carbon preparation. Activated carbons were synthesized using castor shell at dry impregnation ratios of 1 and 2 (material-to-activator), and in suspensions of distilled water and zinc chloride, at power intensity of 800 W and irradiation time of 5 min. The activated carbons exhibit an improvement in dielectric properties and specific surface with increasing impregnation ratio. Palm kernel shell was employed for comparison to verify the effect of power intensity. At 800 W, the magnitudes of surface area are 1684 m^2/g and 1150 m^2/g for castor shell- and palm kernel shell-based activated carbons, respectively. A high specific surface brings about a greater methylene blue adsorption for possible applications in wastewater treatment.

Keywords: activated carbon; dielectric properties; microwave-assisted activation; power intensity; specific surface.

***Corresponding author: Muhammad Abbas Ahmad Zaini**, School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81300 UTM Johor Bahru, Johor, Malaysia; and Centre of Lipids Engineering & Applied Research, Ibnu-Sina Institute for Scientific & Industrial Research, Universiti Teknologi Malaysia, 81300 UTM Johor Bahru, Johor, Malaysia,
E-mail: abbas@cheme.utm.my. https://orcid.org/0000-0003-2674-2670
Shu Hui Tang, Lin Zhi Lee, Vanissa Sandra Andrew and Aiman Rashidi Mohd Akhmar, School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81300 UTM Johor Bahru, Johor, Malaysia

1 Introduction

Over the last decades, adsorption has been widely applied in purification, separation, and recovery processes. Activated carbon is the most commonly used adsorbent for adsorption in wastewater remediation because of its high specific surface and rich in functional groups to remove water pollutants (Ming-Twang et al. 2015). Quest for low-cost feedstock from agricultural residues, which are known for their high carbon content and low ash content, has gained considerable attention as to find alternative to high-cost conventional activated carbons (Alias and Zaini 2015).

Microwave heating has emerged as an attractive way to produce activated carbon owing to its good energy efficiency (lower carbonization temperature and time), high heating rate, and volumetric and selective heating (radiating from inside to outside) (Namazi, Allen, and Jia 2016). In microwave, heating starts from the internal to the external part of material matrix through molecular interactions with electromagnetic field (Alias, Zaini, and Kamaruddin 2017). The dielectric heating converts electromagnetic energy into thermal energy, which allows the heat to be generated throughout the material. Dielectric properties are important to determine the interaction between the materials and the electromagnetic field that signifies their suitability to be heated under microwave (Yaw 2012). Commonly, material composition, frequency, temperature, and moisture content have been established as pertinent factors affecting the dielectric properties (Alias and Zaini 2015; Alias, Zaini, and Kamaruddin 2017).

Nevertheless, the roles of impregnation ratio and power intensity on specific surface and dielectric properties in microwave-assisted activation are not well documented. Neglecting the underlying principles in microwave operation often contributes to poor reproducibility of resultant activated carbon that may as well compromise its intended functionalities and performance for target applications

(Alias and Zaini 2015). Furthermore, the changing behaviours of agricultural residues in the electromagnetic field under specific conditions could provide a basis for economical and efficient microwave applicator design to accommodate mass production of activated carbon (Zaini et al. 2015). Therefore, the present work was aimed to evaluate the specific surface and dielectric properties of agricultural residue, namely castor shell at different zinc chloride impregnation states. Additionally, palm kernel shell was employed for comparison. The materials were activated using zinc chloride, and the resultant activated carbons were challenged with methylene blue at lower concentrations for potential dye wastewater treatment.

2 Materials and methods

Castor shell (CS) was supplied by local oil processing facility. It was ground to a particle size of 1.25 mm. Zinc chloride was purchased from QReC, and methylene blue was purchased from HmbG Chemicals. All chemicals used are of analytical grade.

CS was carbonized under anoxic environment in a muffle furnace at 350 °C for 2 h to produce char (CAS). A 10 g of CS was added into 100 mL of distilled water or 100 mL of $ZnCl_2$ solution (10 mg $ZnCl_2$ in 100 mL of water). Microwave activation of CS in distilled water and $ZnCl_2$ solution was carried out in a Teflon reactor inside a multimode microwave applicator at 800 W for 5 min. The resultant products were labelled as SR1 and SR2, respectively. CS activated carbons designated as IR1 and IR2 were prepared from dried $ZnCl_2$-impregnated CS at ratios of 1:1 and 2:1 (CS-to-$ZnCl_2$) at 800 W for 5 min. The impregnation was done by dissolving desired amount of $ZnCl_2$ in water, thereafter CS was homogenously mixed and dried in an oven at 110 °C overnight. For comparison, palm kernel shell (PS) was carbonized in a muffle furnace at 500 °C for 2 h to produce char (PAS). PS activated carbons, i.e., PI1 and PI2 were prepared at mass ratio of 1.5 at power intensities of 300 W and 800 W. SP1, analogous to SR2, was obtained by microwave activation of PS in $ZnCl_2$ suspension at 800 W for 5 min. All irradiated samples were thoroughly washed with distilled water to a constant pH and oven-dried prior to use.

The yield upon carbonization or activation was calculated by dividing the resultant mass with the original amount of dried precursor (CS or PS). The single point specific surface of activated carbons was determined using a BET analyzer (Pulse ChemiSorb 2705, Micrometrics) using N_2 at −196 °C. The pH of solid samples was measured using a pH meter. The sample was added in a 100 mL distilled water, heated at 70 °C for 10 min, and the solution is allowed to cool prior to pH measurement. The dielectric properties were determined at varying operating frequencies of 1 GHz–6 GHz using a Keysight 85,070 dielectric probe attached to the Keysight E5071C network analyzer. The dielectric probe aperture was immersed into the liquid samples or pressed to the solid samples prior to measuring the dielectric properties.

Methylene blue adsorption was carried out using a bottle-point technique to evaluate the performance of activated carbons. A 0.03 g of adsorbent was added into a 30 ml of methylene blue solution of varying concentrations (1–15 mg/L). The mixture was agitated for 72 h to attain equilibrium. The residual dye concentration was measured using a visible spectrophotometer (Halo Vis-10, Dynamica) at 600 nm. The adsorption capacity was calculated by simple mass balance.

3 Results and discussion

3.1 Physical properties of activated carbons

Castor shell and palm kernel shell are abundantly available and could be capitalized as activated carbon feedstock. Table 1 shows the yield and surface area of adsorbents derived from CS and PS.

The chars, PAS and CAS, endow the yields of 54.3% and 87.6%, respectively. The yield of CAS is greater because it was prepared at lower temperature of 350 °C. Nonetheless, IR1 displays a greater yield compared to PI2 upon activation at 800 W for 5 min. The yield of IR2 only

Table 1: Yield and specific surface of adsorbents.

Sample	Description	Yield (%)	Specific surface (m^2/g)
CAS	Char of castor shell; 350 °C for 2 h	87.6	n.d.
SR1	Microwave activation of castor shell in distilled water; 800 W for 5 min	89.4	n.d.
SR2	Microwave activation of castor shell in $ZnCl_2$ suspension; 800 W for 5 min	90.2	n.d.
IR1	Microwave activation of $ZnCl_2$-impregnated castor shell; ratio of 1, 800 W for 5 min	87.1	1684
IR2	Microwave activation of $ZnCl_2$-impregnated castor shell; ratio of 2, 800 W for 5 min	80.6	626
PAS	Char of palm kernel shell; 500 °C for 2 h	54.3	41
SP1	Microwave activation of palm kernel shell in $ZnCl_2$ suspension; 800 W for 5 min	98.4	n.d.
PI1	Microwave activation of $ZnCl_2$-impregnated palm kernel shell; ratio of 1.5, 300 W for 5 min	70.4	555
PI2	Microwave activation of $ZnCl_2$-impregnated palm kernel shell; ratio of 1.5, 800 W for 5 min	51.8	1150

SP1 exhibits a high yield of 98.4%. This is also true for SR1 and SR2. Obviously, $ZnCl_2$ suspension and water did not react with the solid matrix to create porous texture in microwave-assisted activation. During the irradiation process, microwave energy is absorbed more by water and electrolyte, compared to the carbonaceous shells. Consequently, the heating in liquid mediums produces less temperature than it should be when the solids are directly exposed to microwaves. Because of the insufficient temperature to activate the matrix, the surface areas of SP1, SR1 and SR2 are not detected (n.d.). Accordingly, the notion that water and electrolyte (activator) can behave as high temperature steam to activate the solids under microwave heating is unjustified.

slightly decreased when the impregnation ratio increases from 1:1 to 2:1. It implies that suitability of CS as 'hard wood' feedstock of activated carbon. Moreover, the specific surface of IR1 (1684 m^2/g) is greater than that of P12 (1150 m^2/g), although the former utilizes a smaller impregnation ratio. Notwithstanding that, the specific surface of IR2 subsides to 626 m^2/g because of the high $ZnCl_2$ ratio encourages thermal degradation with intense volatilization and dehydration to expand the existing pores, thus decreasing the yield and pore volume.

The yield of PI2 is smaller than that of PI1 because a higher power intensity at 800 W renders a greater heating rate and temperature to expedite the burning-off of PS. Consequently, the PI2 shows a greater specific surface of 1150 m^2/g, which is nearly twice that of PI1. The decrease in yield is associated with the release of volatiles to enrich the carbon content which also signifies the pore drilling effectiveness by activating agent at higher temperature. The evolution of volatiles is accelerated because of the presence of $ZnCl_2$ (Alias, Zaini, and Kamaruddin 2017). Impregnation with $ZnCl_2$ first results in the degradation of the material and, on carbonization, produces dehydration that results in charring and aromatization of the carbon skeleton and creation of the pore structure (Zaini, Okayama, and Machida 2009). The pH of activated carbon is an important guide to its interfacial properties; so, the pH must be electrically natural, and the values are in the range of 4.5–6.0.

3.2 Dielectric properties

Figure 1 shows the effects of frequency on dielectric properties of CS samples. IR1 and IR2 possess a greater ε' that is possibly ascribed to the effective activation process, leading to pore development and high surface area. In addition, a high specific surface of activated carbons also attracts water vapour from the surrounding to lodge on the available pores, thus increasing the moisture content and ε'.

IR1 and IR2 show a bigger ε'' to convert the electromagnetic energy and dissipate it as heat. It implies the suitability of CS as activated carbon feedstock via microwave-assisted activation. The increasing pattern of tan δ with frequency is more prevalent for IR1 ($ZnCl_2$ ratio 1:1). The ε'' and tan δ increase with frequency because power absorption and heating rate in microwave are better at higher frequency. However, cautions should be exercised as the ability of a material to be heated under microwave becomes ineffective when it deviates from the optimum frequency, thus compromising the quality and reproducibility of activated

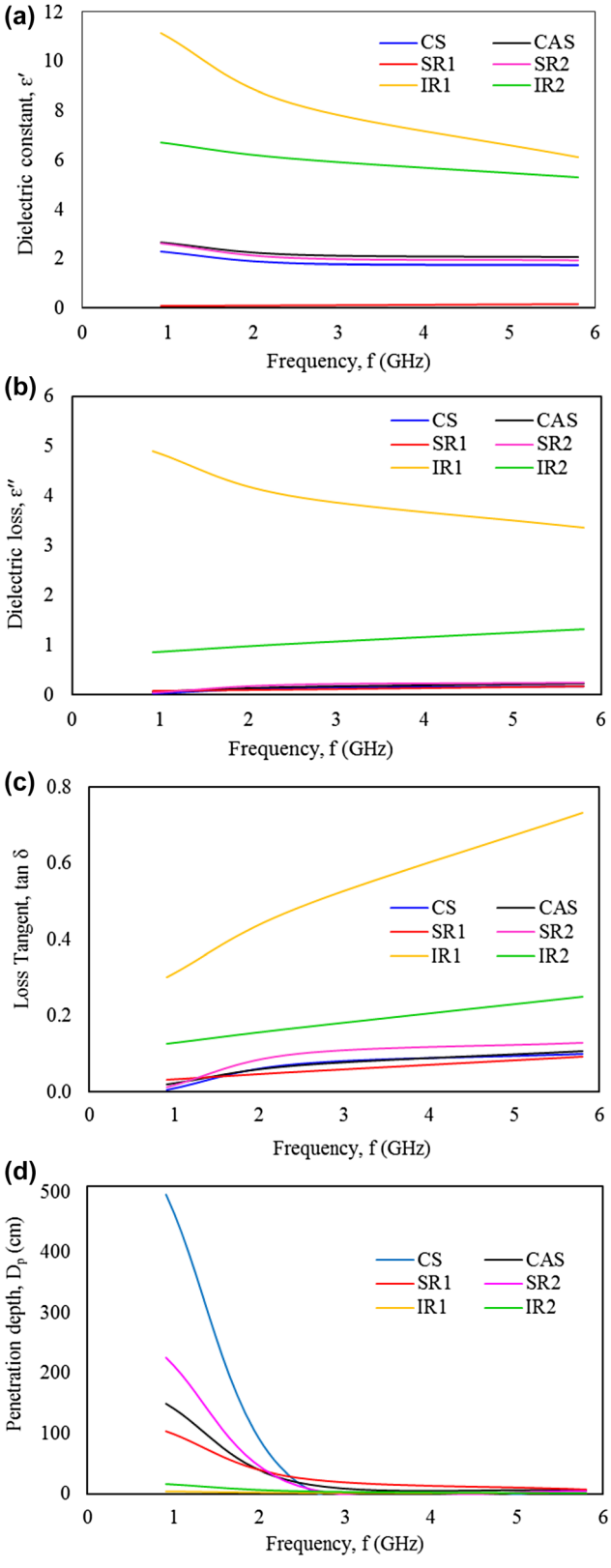

Figure 1: Effects of frequency on (a) dielectric constant, (b) loss factor, (c) loss tangent and (d) penetration depth of CS samples.

Table 2: Dielectric properties of PS samples at microwave frequencies.

Sample	ε'	ε''	tan δ	D_p (cm)
***f* = 0.92 GHz**				
PS	1.96	0.001	0.003	1260
PAS	3.11	0.14	0.05	63.9
SP1	2.22	0.05	0.02	159
PI1	2.83	0.17	0.06	50.8
PI2	7.58	2.50	0.33	5.75
***f* = 2.45 GHz**				
PS	1.57	0.06	0.04	37.9
PAS	2.55	0.24	0.09	13.2
SP1	1.70	0.11	0.07	22.7
PI1	2.30	0.22	0.09	13.6
PI2	5.55	2.25	0.41	2.03
***f* = 5.8 GHz**				
PS	1.61	0.07	0.04	15.9
PAS	2.46	0.27	0.11	4.75
SP1	1.71	0.11	0.07	9.45
PI1	2.24	0.23	0.10	5.41
PI2	4.36	1.83	0.42	0.94

carbon produced. Therefore, it is crucial to determine the best microwave frequency to achieve efficient heating, especially in mass production of activated carbon. From the perspective of D_p, the simple rule is, the higher the frequency, the shorter the D_p as the electromagnetic energy might be absorbed only on the material surface. Activated carbon often bears high moisture content because of its high surface area, at which the water accumulates at the surface and causes the electromagnetic wave to attack the hotspot on the material surface, so resulting in a short D_p (Alias, Zaini, and Kamaruddin 2017).

Table 2 summarizes the dielectric properties of PS samples at microwave frequencies. The dielectric constant, ε' gives the information on the ability of material to store the external electric field of microwave energy through polarization mechanism. Generally, ε' decreases with increasing operating frequency, f. It signifies that the ability of the material to store the microwave energy decreases as frequency increases. Besides, a high ε' at low frequency reflects the effect of space charge polarization and/or conducting ionic motion, whereas it decreases at higher frequency due to the decrease in space charge carriers or interfacial polarization (Murali et al. 2017). Among the PS samples, PI2 exhibits a greater ε' at all microwave frequencies. PI2 also bears a high moisture content of 8.24% when compared to the other counterparts. A high moisture content usually results in a high ε' because of high permittivity during microwave heating. Other than that, the values of ε' for PI2 which was prepared at higher power intensity are always greater than that of PI1. This could be related to the increase of carbon content and aromatic structure within the material matrix as a result of chemical activation at the higher temperature and power intensity.

The loss factor, ε'' for PI2 also exhibits a decreasing pattern from low to high frequency. PI2 demonstrates a higher loss factor ε'' compared to other PS samples, indicating that it is more likely to successfully dissipate microwave energy at high power intensity. The loss tangent, tan δ describes the efficiency of a material to convert microwave energy to heat energy. It is largely dependent on ε'' and implies a decreasing ability of a material to be heated under microwave if it goes beyond a certain frequency (Zhang et al. 2016). From Table 2, PI2 exhibits a higher tan δ with increasing frequency, while ε' decreases. The $ZnCl_2$-impregnated samples are more susceptible to microwave absorption at lower frequency because they also contain electrolyte. The presence of conductive charge carrier enhances the loss system due to charge migration. Conversely, PS (untreated) has a better and faster microwave absorption at higher frequency because it contains more moisture that acts as microwave absorber (Zaini et al. 2015).

Penetration depth, D_p refers to the thickness of a material that microwave has to pass through in order for it to be heated. A high D_p is essential for effective microwave heating. The ability of microwave to penetrate into a material is linked to its moisture content. Accordingly, PS displays a higher D_p, while for activated carbons, PI1 endows a greater D_p than PI2 because the carbon-rich matrix would not be heated thoroughly as hotspots are mainly centred in heating the moisture that is often entrapped on the surface top of a material, thus decreasing D_p. Also, the decrease of D_p as frequency increases can be explained that the microwave will only penetrate at short distance and get absorbed just on the surface at higher frequency (Alias and Zaini 2015).

3.3 Methylene blue adsorption

Figure 2 shows the performance of adsorbents/activated carbons for methylene blue removal. Generally, all adsorbents exhibit an increasing pattern of dye adsorption with increasing concentration. From Figure 2, a high capacity of 15 mg/g was recorded at concentration, C_o = 15 mg/L by IR2, which brings about a 100% removal efficiency. The increase in $ZnCl_2$ ratio produces more mesopores in IR2 than that in IR1 to accommodate dye molecules despite the

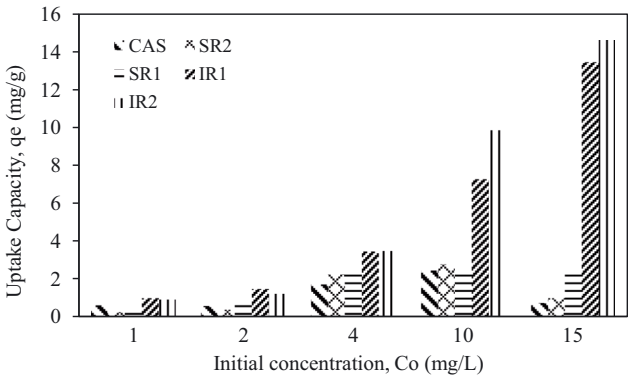

Figure 2: Methylene blue removal by CS at low concentrations (1–15 mg/L).

decrease in specific surface (Zaini, Okayama, and Machida 2009). It should be noted that the presence of mesopores enhances the affinity towards methylene blue for favourable adsorption process, while the micropore-rich texture could, to some extent, restrict the diffusion of dye molecules into the pores (Tang and Zaini 2017).

PI2 that was produced at higher power intensity also exhibits a greater capacity at 12 mg/g that is equivalent to 95% removal efficiency. IR1 which was prepared at the same operating conditions displays a better performance owing to the high specific surface. Moreover, IR1 gives a higher yield than PI2 (Table 1), indicating its potential use as activated carbon precursor. The dye capacities of PS samples begin to deviate at C_o = 5 mg/L, wherein the concentration gradient offers the driving force to overcome the solid mass transfer resistance, which tied-up with the available adsorption sites.

PI2 shows only a slight better removal within the concentration range studied than PI1, despite the former holds nearly twice specific surface than the latter. A higher power intensity (heating rate) improves the texture development of activated carbon, giving more pore channels and active sites, thus increasing the interaction probabilities between the carbon surface and target molecules. On the other hand, SR1, SR2 and SP1 depicts a lower adsorption percentage due to limited number of active sites (under-developed porous textures) for methylene blue removal.

4 Conclusions

Activated carbons were prepared from castor shell and palm kernel shell by microwave-$ZnCl_2$ activation. Activated carbons prepared at power intensity of 800 W exhibit well-developed surface area of 1150 m^2/g to 1684 m^2/g. The dielectric properties of activated carbon are linked to material composition and moisture content. A higher power intensity offers a greater heating rate to produce activated carbon with better dielectric constant and loss tangent, which are associated with high carbon content and rich aromatic structure within the material matrix. To conclude, the dry-state of $ZnCl_2$ impregnation and high-power intensity render a positive effect on the textural characteristics of activated carbon and its adsorption properties.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This work was partly funded by UTM-ICONIC Grant No. 09G54.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

Alias, N., and M. A. A. Zaini. 2015. "On the View of Dielectric Properties in Microwave-Assisted Activated Carbon Preparation." *Asia-Pacific Journal of Chemical Engineering* 10 (6): 953–60.

Alias, N., M. A. A. Zaini, and M. J. Kamaruddin. 2017. "Relationships between Dielectric Properties and Characteristics of Impregnated and Activated Samples of Potassium Carbonate- and Sodium Hydroxide-Modified Palm Kernel Shell for Microwave-Assisted Activation." *Carbon Letters* 24 (1): 62–72.

Ming-Twang, S., L. Lin-Zhi, M. A. A. Zaini, Q. Zhi-Yong, and A. Y. Pei-Yee. 2015. "Activated Carbon for Dyes Adsorption in Aqueous Solution." In *Advances in Environmental Research*, Vol. 36, edited by J. A. Daniels, 217–34. New York: Nova Science Publishers, Inc.

Murali, N., S. J. Margarette, V. K. Rao, and V. Veeraiah. 2017. "Structural, Impedance, Dielectric and Modulus Analysis of $LiNi_{1-xy-0.02}Mg_{0.02}Co_xZn_yO_2$ Cathode Materials for Lithium-Ion Batteries." *Journal of Science: Advanced Materials and Devices* 2 (2): 233–44.

Namazi, A. B., D. G. Allen, and C. Q. Jia. 2016. "Benefits of Microwave Heating Method in Production of Activated Carbon." *Canadian Journal of Chemical Engineering* 94 (7): 1262–8.

Tang, S. H., and M. A. A. Zaini. 2017. "Malachite Green Adsorption by Potassium Salts-activated Carbons Derived from Textile Sludge: Equilibrium, Kinetics and Thermodynamics Studies." *Asia-Pacific Journal of Chemical Engineering* 12 (1): 159–72.

Yaw, K. C. 2012. *Measurement of Dielectric Material Properties. Application Note*, 1–35. Munich, Germany: Rohde & Schwarz.

Zaini, M. A. A., R. Okayama, and M. Machida. 2009. "Adsorption of Aqueous Metal Ions on Cattle-Manure-Compost Based Activated Carbons." *Journal of Hazardous Materials* 170 (2–3): 1119–24.

Zaini, M. A. A., N. Zamani, M. Sabri, and M. Johari. 2015. "Composition- and Temperature-dependent of Dielectric Properties of Zinc Chloride-Palm Kernel Shell Mixture at Microwave Frequencies." *International Journal of Materials Science and Engineering* 3 (4): 301–9.

Zhang, S., L. Zhou, B. Ling, and S. Wang. 2016. "Dielectric Properties of Peanut Kernels Associated with Microwave and Radio Fequency Drying." *Biosystems Engineering* 145: 108–17.