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Reinforce the surface properties of domestic garbage activated carbon by low temperature plasma accustomed in energy storage applications

ABSTRACT

Since activated carbon is a highly porous material with a sizable internal surface area, it is simple to adsorb a wide range of substances when used in energy storage devices, sewage treatment, water purification, catalyst, food processing and other applications. This work focuses on the viability of using mixed fruit peels as a precursor for the carbonization process with physical activation to produce activated carbon. The Phase confirmation was examined using X-ray diffraction (XRD). Fourier transform infrared spectrometer (FTIR) concludes the functional groups present in mixed fruit peels activated carbon. Field emission scanning electron microscopy (FESEM) was used to analyze the morphological makeup and textural traits of the activated carbon that was produced. Energy Dispersive X-Ray Analysis (EDX) shows the elemental composition of nano powdered carbon. Raman spectroscopy confirms the presence of graphene that appears at 1580cm^{-1}. Electrochemical Impedance Spectroscopy (EIS) and Nyquist plot in order to evaluate the conductivity performance over the frequency range of 1μHz to 10 kHz, measurements were used.

Carbon yield analysis were conducted and analyzed. Wettability of the mixed fruit peels were examined using contact angle. The Mixed Fruit peels activated carbon were subjected to low temperature plasma to increase its surface properties, The outcomes were evaluated, and the charge transfer resistance and the polarization resistance for air plasma treatment is 1.43 and 0.2 ohms. Hydrophilic nature is occurred when treated with air plasma. According to these findings, air plasma treatment of mixed fruit peel activated carbon improves its surface characteristics, making it suitable for electrode in energy storage applications.

Keywords: *Mixed fruit peels, physical activation, low temperature plasma, surface modification, Nano powder*

1. INTRODUCTION

The ever-growing demand for sustainable solutions has led to an increasing focus on the utilization of natural resources and waste materials. In this pursuit, researchers and innovators have turned their attention to the vast potential hidden within fruit peels, recognizing them as a rich source of valuable compounds and fibers. Among these advancements, the emergence of mixed fruit peels activated carbon stands out as a promising development that not only addresses the issue of waste management but also offers numerous applications in diverse fields [1,2]. This revolutionary material, derived from a combination of discarded fruit peels and advanced activation techniques, has garnered attention as an eco-friendly alternative to conventional activated carbon [3]. With its exceptional adsorption properties, mixed fruit peels activated carbon has the potential to revolutionize industries such as water purification, energy storage, and environmental remediation, contributing to a greener and more sustainable future [4]. Fruit peels, until recently, were largely considered as waste products resulting from the consumption of fruits. Fruit peels, consisting of a complex matrix of cellulose, hemicellulose, lignin, and various bioactive compounds, possess unique chemical and physical properties that make them an attractive raw material for activated carbon

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production[5]. By diverting these peels from landfills and transforming them into activated carbon, not only reduce waste accumulation but also contribute to a circular economy by reusing a valuable resource that would otherwise go to waste. Due to its extraordinarily high surface area and purity, which activated carbons were directly related to the performance in the preferred electrode material in capacitors, batteries, and a variety of advanced batteries [6,7].

Plasma surface modification: The objective of Plasma surface treatment is to enhance the surface characteristics without compromising the bulk qualities, which is typically challenging to achieve through conventional methods[8]. Plasma treatment, as depicted in (Fig. 1), generates a greater number of free radicals, ions, and electrons, making it a promising approach for improving energy storage systems. The interactions between plasma species and the surface facilitate various energy and matter exchange processes, offering a wide range of options for modifying the surface.

Consequently, this technique enhances the properties of different materials and expands their applications in electrochemical systems[9]. Plasma modification serves multiple purposes, including the creation of functional groups that interact with other groups, alteration of surface free energy, and prevention of corrosion [10]. These modifications result in improved resistance, changes in interface nature and morphology, impurity removal, and the formation of cross-linking between molecules. The adhesion, bonding, and chemical inertness are also enhanced through these processes [11].

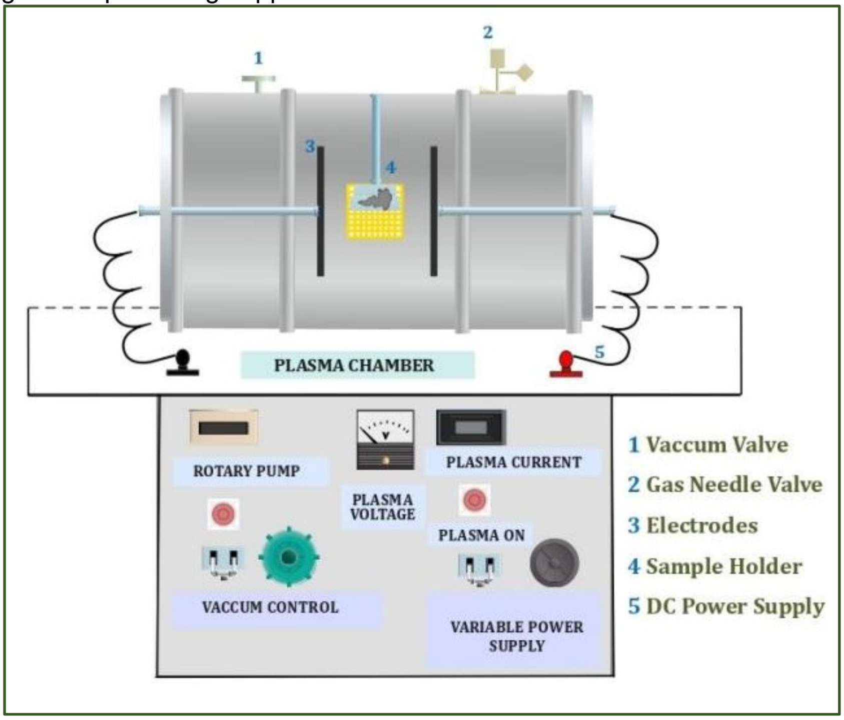

Figure 1. Schematic diagram of plasma chamber

Slika 1. Šematski dijagram plazma komore

Porous electrodes have a substantially higher surface area than conventional electrodes in capacitors, activated carbon has proven excellent properties and can be used in energy storage devices allows them to store much more energy. Activated carbon also enhances the adsorption properties [7,12,13]. To achieve high energy density for such devices, high capacitance materials must be used. In order to boost the energy density of these devices without reducing their power capacity, research efforts are currently concentrated upon the development of electrode materials and electrolytes. The use of electroactive materials in carbon-based electrodes is also gaining popularity as a means to boost the amount of energy that can be stored in such a device. Low temperature plasma treatment improves the properties and surface of the carbon material without altering its fundamental nature.

2. MATERIALS AND METHODS.

The garbage from mixed fruit peels (MFP) is created by physical processes. The fruit peels from apple, pomegranate, papaya, mango and muskmelon were obtained from a nearby local fruit market. The peels were cleaned with tap water first, then with distilled water. They were then set for drying in direct sunlight, and after seven days, the dried peels were stored for synthesis. Carbonization and activation are the two processes that was used in the processing of synthesis. The dried peels were carbonized in an air muffle furnace (KEMI-KMF-1S) for two hours at 300°C, then well ground and maintained for 30 minutes at 400°C for activation in an air muffle furnace. Obtained mixed fruit peel activated carbon was labeled as MFPAC and it was subject to characterization.

In this study, a DC glow discharge cold plasma, which is suitable for heat-sensitive materials, was used. A stainless-steel chamber measuring 30 cm in diameter and 50 cm in length serves as the DC glow discharge plasma reactor for the experiment. Two aluminum electrodes were placed within the chamber, six centimeters apart and symmetrically arranged perpendicular to the axis. A vacuum pump was used to initially suction the chamber down to a pressure of 0.03 mbar. By modulating the gas input using a controlled needle valve and monitoring it with a Pirani gauge, the necessary low pressure was maintained.

Figure 2. Synthesis of Mixed fruit peel activated carbon

Slika 2. Sinteza mešovitog aktivnog uglja od kore voća

X Ray diffraction – XRD (XPERT-PRO with CuK radiation) is used to analyze the nature of the sample and the particle size. Functional groups were identified by Fourier-transform infrared spectroscopy - FTIR (SHIMADZU FTIR-8400S). Field emission scanning electron microscopes - FE-SEM (VEGA3, TESCAN (Czech Republic)) analyze the morphological character of the activated carbon and the porosity of the material. Energy-dispersive X-ray spectroscopy - EDX (BURKER Nano, GmbH, D-12489(Germany)) confirms the presence of element in the activated carbon. Raman analysis (WiTec alpha 300, Germany) shows the existence of two bands (D and G band). Electrochemical Impedance Spectroscopy - EIS confirms, resistivity of the material. Hydrophobic and hydrophilic nature is identified by wetting angle.

3. RESULTS AND DISCUSSION

This section presents the experimental findings about the elements, functional groups, functional morphology, resistivity and nature of the activated mixed fruit peels.

In order to calculate the carbon yield fifteen grams of dried peels were carbonized and activated. A yield of 82% was achieved. Using (Eq. 1), the carbon yield percentage is calculated.

$$Yield\ (in\ \%) = (\,Quantity\ of\ activated\ carbon / Quantity\ of\ raw\ material) * 100 \qquad (1)$$

3.1. XRD Analysis

In the Figure 3 XRD spectrum of untreated MFP, air plasma MFP and oxygen plasma MFP were presented. A few sharp peaks are visible in the XRD profile in the range of 10° - 80° at an angle 2θ. In this investigation, crystalline carbon makes up the majority of the product. The pyrolysis reaction was finished as a result[14] The peak at 2θ value was 28.3°, which is evidence that this could be the carbon structure of graphite[15]. Its crystalline nature is represented by the peak 2θ range at 40.41°[16]. MFPAC that has been plasma-treated gains intensity without altering its nature or structure. (Fig. 3) illustrates that MFPAC treated with air plasma has a higher intensity than MFPAC treated with oxygen plasma[17]. The grain size of the air plasma treated MFPAC is 26.75nm.

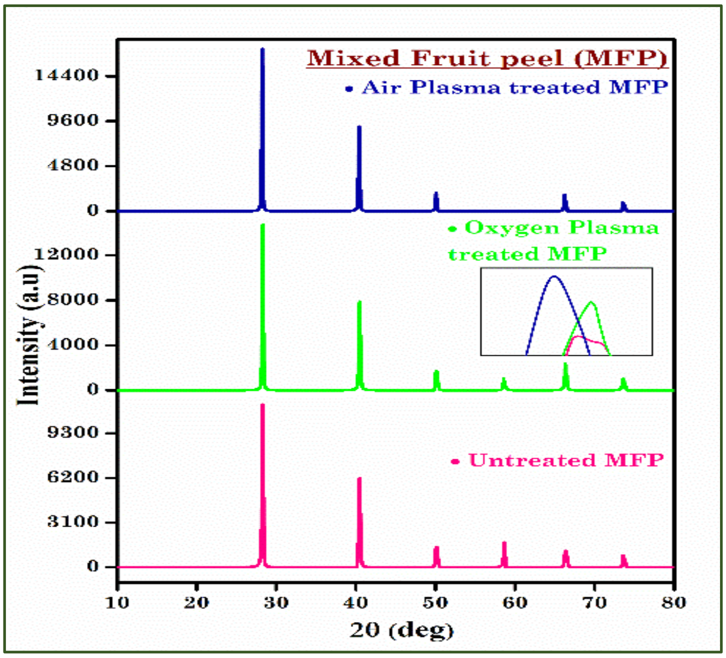

Figure 3. XRD of Untreated, Air plasma treated and oxygen plasma treated MFPAC

Slika 3. XRD netretiranog, vazdušnom plazmom tretiranog i MFPAC tretiranog plazmom kiseonikom

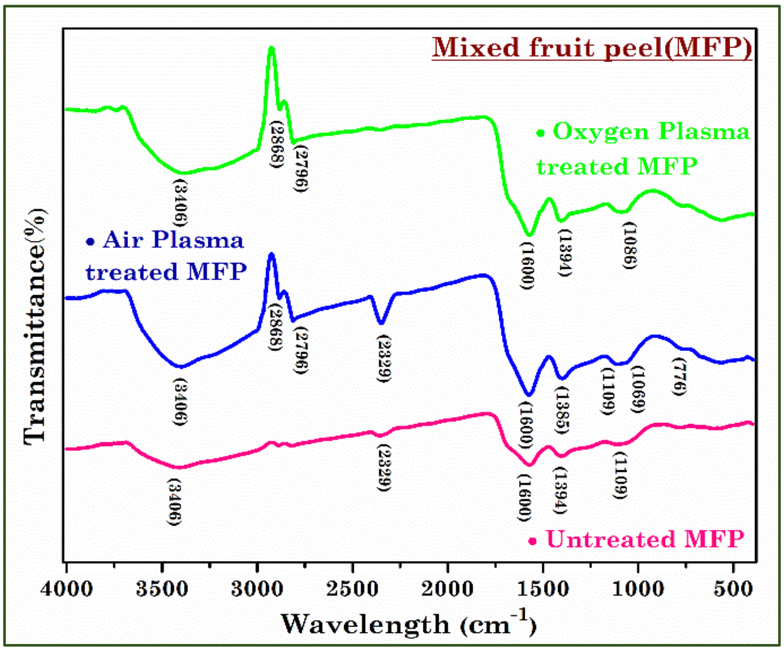

Figure 4. FTIR of Untreated, Air plasma treated and oxygen plasma treated MFPAC

Slika 4. FTIR netretiranog, MFPAC tretiranog vazdušnom plazmom i kiseoničkom plazmom

3.2. FTIR evaluation

By using FTIR analysis, functional groups of obtained materials can be observed. The results are presented in (Fig. 4) and cover the 400 cm^{-1} to 4000 cm^{-1} range. Band at 1109 cm^{-1} in the untreated MFPAC spectrum could be assigned to the C-O group, while band at 1394 cm^{-1} indicate C-H bending. Bands between 1600 cm^{-1} and 2344 cm^{-1}, could be assigned to C=C stretches due to presence of aromatic rings. The band at 3406 cm^{-1} indicates the function group O-H. The emergence of a new functional group follows the plasma treatment that increases wettability. At 776 cm^{-1} and 2796 cm^{-1}, the C-H group's peaks were found. The C-O group might have produced the peak ranges at 1069 cm^{-1} and 1109 cm^{-1}. Moreover, the aromatic ring bond has C=C stretch that varies between 1385 cm^{-1}, 1600 cm^{-1}, and 2344 cm^{-1}[18], while the, bend at 2869 cm^{-1} suggest C-H bending [19,20]. The band at 3406 cm^{-1} serve as a representation of the function group O-H [21].Around 2329 cm^{-1}, two different bands that represent the carboxylic group that can be found in the O-H band can be seen [22]. According to the results, activated carbon that has been treated with air plasma contains hydroxylic and carbonyl functional groups.

3.3. SEM Analysis

The porous structure of the materials can be seen in (Fig.5), together with morphological study of the MFPAC. The activated carbon that has undergone plasma treatment demonstrates that it has more porous structure [17], [23,24]. MFPAC that has been air plasma treated is quite porous than untreated and oxygen plasma treated activated carbon, which will lead to increase in surface area. EDX confirms the presence of oxygen and carbon in all EDX spectra.

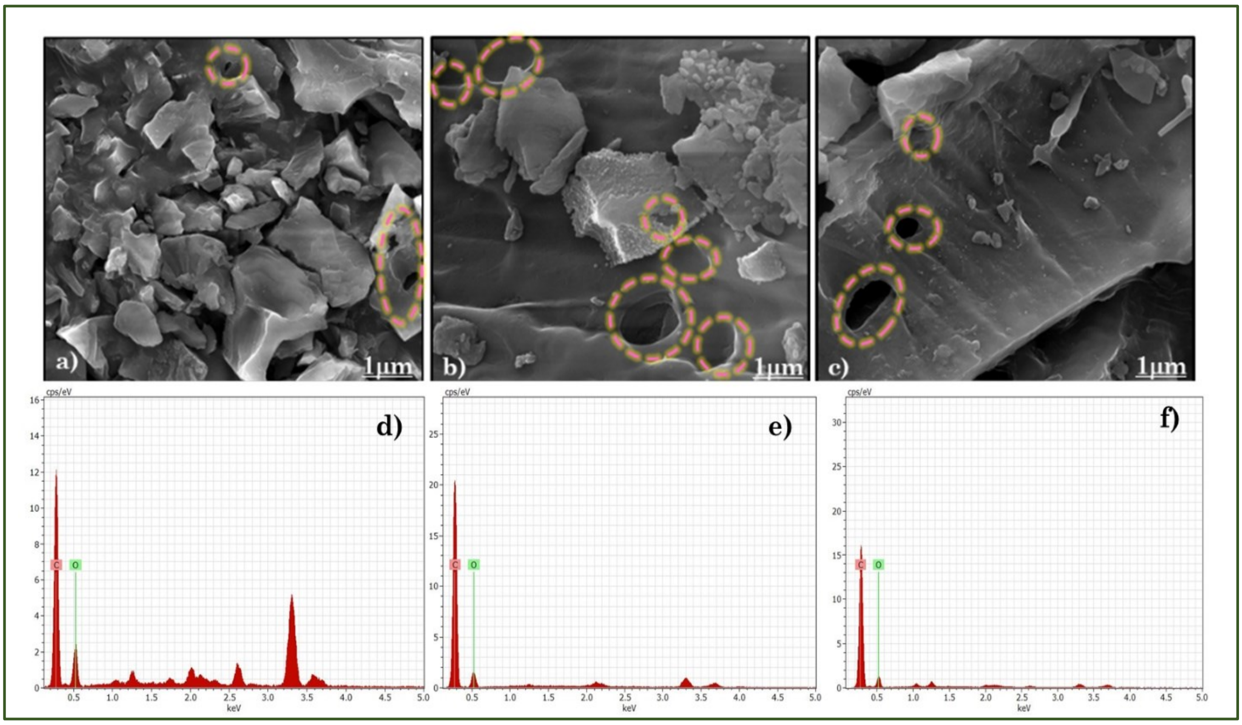

Figure 5. FE-SEM of a) Untreated, b) Air plasma treated, c) oxygen plasma treated MFPAC. d) EDX of Untreated, e) Air plasma treated, f) oxygen plasma treated MFPAC

Slika 5. FE-SEM od a) neobrađenog, b) tretiranog vazdušnom plazmom, c) MFPAC tretiranog kiseoničkom plazmom. d) EDX neobrađenog, e) tretiranog vazdušnom plazmom, f) MFPAC tretiranog kiseoničkom plazmom

3.4. Raman Spectroscopy

Both untreated and plasma-treated MFPAC were analyzed using the Raman spectroscopy, and the obtained spectra are presented in Fig. 6. Two bands are dominant: D-Band, at 1394cm^{-1} and the G-Band, at 1512cm^{-1}. The disordered carbon structure is linked to the D-Band. In contrast, the G-Band is connected to the graphitic or ordered lattice of carbon. The sp^3 hybridized disordered carbon phase appears by the D-band, whereas the sp^2 hybridized graphitic carbon phase is represented by the G-band. The defect with the sample's sp^2 carbon network, which may exist in either a C=C aromatic structure [24].

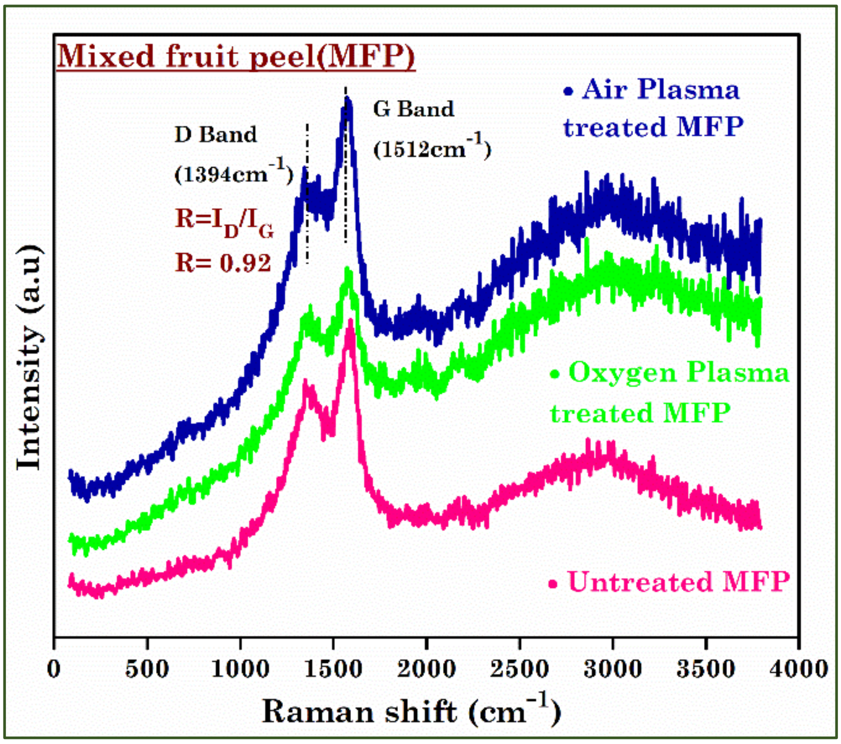

Figure 6. Raman spectra of Untreated, Air plasma treated and oxygen plasma treated MFPAC

Slika 6. Ramanski spektri netretiranog, obrađenog vazdušnom plazmom i MFPAC tretiranog plazmom kiseonikom

The MFPAC was subjected to the plasma treatment which result in the increases in the intensity which evidently shows by the intensity ratio (I_D/I_G)[25]. The Raman spectra characteristics that it has the amorphous nature with the intensity ratio of I_D/I_G for the untreated MFPAC is 0.82 and for Oxygen plasma treated MFPAC is 0.87, then for Air plasma treated MFPAC is 0.92. (Fig. 6) indicates the Raman shift of untreated, oxygen and air plasma treated MFPAC.

3.5. Impedance analysis

The MFPAC, EIS Nyquist plot in order to evaluate the conductivity performance over the frequency range of 1μHz to 10 kHz, measurements were used. For each sample, the EIS measurement reveals a semicircle shape. Which includes the real Z’ and imaginary Z” components. (Fig. 7) shows the characteristics of the Polarization Resistance (Rs) and the Charge-Transfer Resistance (Rct). According to the graphs, linear shapes display at low frequencies (Polarization Resistance) and semicircular shapes at high frequencies (Charge-Transfer Resistance). The diameter of the semicircle at high frequencies represents the charge transfer resistance at the electrode-electrolyte interface [26].

The Polarization resistance is 0.2 ohms and the charge transfer resistance is 1.76 ohms for the untreated MFPAC and for air plasma treatment the polarization resistance and the charge transfer resistance are 0.2 and 1.43 ohms thus for Oxygen plasma treatment the polarization resistance and the charge transfer resistance are 0.2 and 1.43 ohms. Thus due to the hydrophobic nature of the plasma treated materials the resistance is lowering due the surface modification[27].

3.6. Contact angle analysis

The surface wettability of MFPAC is assessed using contact angle measurement. The wetting angle of MFPAC is shown in (Fig. 8). The MFPAC that has been plasma treated is hydrophilic in nature, while the untreated MFPAC has an angle of 114°, which is hydrophobic. When comparing the air and oxygen plasma treated MFPAC, the air plasma treated carbon has a higher level of wetness and has an angle of 16° and 61° for oxygen plasma treated carbon. This demonstrates that air plasma treated MFPAC has higher wettability than oxygen plasma treated and untreated MFPAC[28].

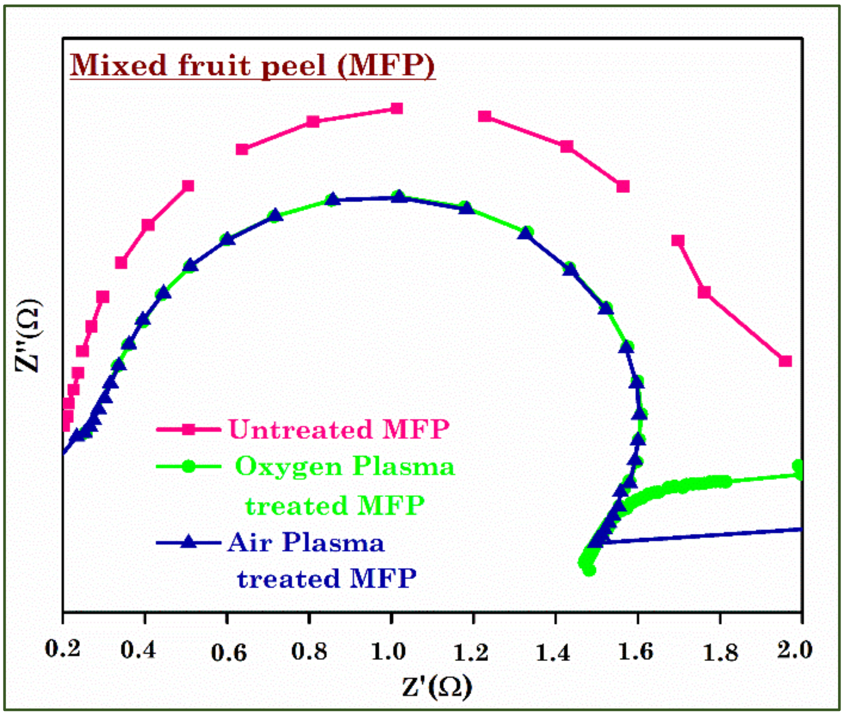

Figure 7. EIS of Untreated, Air plasma treated and oxygen plasma treated MFPAC

Slika 7. EIS netretiranog, vazdušnom plazmom tretiranog i MFPAC tretiranog plazmom kiseonikom

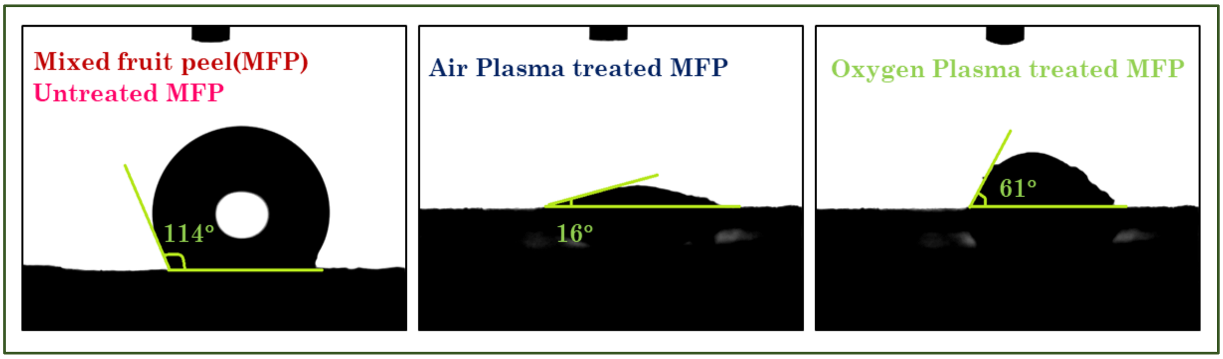

Figure 8. Contact angle of Untreated, Air plasma treated and oxygen plasma treated MFPAC

Slika 8. Kontaktni ugao netretiranog, obrađenog vazdušnom plazmom i MFPAC tretiranog kiseoničkom plazmom

These qualities have led to the high intensity of air plasma treated (MFPAC), which has been detected in XRD analysis. According to IR spectroscopy, MFPAC that has been treated with air plasma has improved bonding, which results in better pore structure. Additionally, the air plasma treated MFPAC has a more increased porosity structure in comparison to oxygen plasma treated and untreated mixed fruit peels. Raman spectra reveal that MFPAC treated with air plasma has the highest ratio of intensity. EIS explains the benefits of good conductance for MFPAC treated with air plasma. The wettability of MFPAC treated with air plasma has increased. According to these findings, air plasma treatment of MFPAC improves its surface characteristics, making it suitable for electrode in energy storage applications.

4. CONCLUSION

The emergence of Air plasma treated MFPAC presents a sustainable and eco-friendly solution to energy storage applications. By harnessing the inherent value of discarded fruit peels, this material offers good porous properties for air plasma exposed activated carbon that can be harnessed across various industries, from water and air purification to energy storage remediation. MFPAC shows promise in energy storage applications, particularly in supercapacitors, because of its large surface area and good electrical conductivity. As we strive for a greener and more sustainable future, MFPAC stands as a testament to the potential hidden within nature's bio waste, unlocking new possibilities for a circular economy and a healthier planet.

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IZVOD

OJAČANA POVRŠINSKA SVOJSTVA AKTIVNOG UGLJA IZ KUĆNOG OTPADA POMOĆU PLAZME NISKE TEMPERATURE KOJA SE KORISTI U APLIKACIJAMA ZA SKLADIŠTENJE ENERGIJE

Pošto je aktivni ugalj visoko porozan materijal sa značajnom unutrašnjom površinom, lako je adsorbovati širok spektar supstanci kada se koristi u uređajima za skladištenje energije, tretmanu otpadnih voda, prečišćavanju vode, katalizatorima, preradi hrane i drugim primenama. Ovaj rad se fokusira na održivost upotrebe mešanih kora voća kao prekursora za proces karbonizacije sa fizičkom aktivacijom za proizvodnju aktivnog uglja. Fazna potvrda je ispitana korišćenjem rendgenske difrakcije (XRD). Infracrveni spektrometar sa Furijeovom transformacijom (FTIR) zaključuje funkcionalne grupe prisutne u mešanom aktivnom uglju od kore voća. Skenirajuća elektronska mikroskopija polja (FESEM) je korišćena za analizu morfološkog sastava i teksturnih osobina aktivnog uglja koji je proizveden. Energetska disperzivna rendgenska analiza (EDX) pokazuje elementarni sastav nano praškastog ugljenika. Ramanova spektroskopija potvrđuje prisustvo grafena koji se pojavljuje na 1580cm^{-1}. Korišćena su elektrohemijska impedansna spektroskopija (EIS) i Nyquist-ovi dijagrami u cilju procene performansi provodljivosti u opsegu frekvencija od 1μHz do 10 kHz.

Sprovedena je i analizirana kolicina prinosa ugljenika. Vlaženje kore mešanog voća je ispitivano primenom kontaktnog ugla. Aktivni ugalj za mešane voćne kore je podvrgnut plazmi niske temperature da bi se povećala svojstva površine. Rezultati su procenjeni, a otpor prenosa naelektrisanja i otpor polarizacije za tretman vazdušnom plazmom je 1,43 i 0,2 oma. Hidrofilna priroda se javlja kada se tretira vazdušnom plazmom. Prema ovim nalazima, tretman vazdušnom plazmom mešanog aktivnog uglja od kore voća poboljšava njegove površinske karakteristike, čineći ga pogodnim za elektrode u aplikacijama za skladištenje energije.

Ključne reči: *Mešane voćne kore, fizička aktivacija, niskotemperaturna plazma, modifikacija površine, Nano prah.*

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