

Preparation and Characterization of a Hierarchically Porous Zeolite-Carbon Composite from Economical Materials and Green Method

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Abstract

A hierarchically porous structured zeolite composite was synthesized from NaX zeolite supported on carbonaceous porous material produced by thermal treatment for plum stones which is an agro-waste. This kind of inorganic-organic composite has an improved performance because bulky molecules can easily access the micropores due to the short diffusion path to the active sites which means a higher diffusion rate. The composite was prepared using a green synthesis method, including an eco-friendly polymer to attach NaX zeolite on the carbon surface by phase inversion. The synthesized composite was characterized using X-ray diffraction spectrometry, Fourier transforms infrared spectroscopy, field emission scanning electron microscopy, energy dispersive X-ray analysis, thermogravimetric analysis, N₂-adsorption/desorption isotherm, and point of zero charges. The results showed that the composite had a surface area of 208.463 m²/g, a pore volume of 0.122 cm³/g, distinct morphology, and functional groups. Also, its p*H*_{pzc} was 6.9 above which its surface has a positive charge and below 6.9 it is charged negatively. This property determines the composite sorption property in the removal of pollutants from wastewater.

Keywords: Green materials; hierarchical porosity; NaX zeolite; phase inversion; polymer; carbon.

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1- Introduction

Zeolites are crystalline aluminosilicates with interconnected microporosity, which is defined as pores of 2 nm or less in size [1, 2]. Zeolitic materials have a negatively charged framework because Si atoms have been replaced by Al atoms within the structure; this charge is typically balanced by extra-framework cations or protons [3]. Zeolites are utilized as ion exchangers in the detergent industry, purification, liquid waste treatment, radioactive waste storage, environmental treatment, catalytic cracking of petroleum, and refining petrochemical, coal, and fine chemical industries [4, 5]. Zeolites have features of uniform pore size and shape, the continuous mobility of their cations, and hydrophilic and/or hydrophobic nature to some solutes which allow them to accomplish all of these activities in a variety of industrial applications [6, 7]. Large molecules or dense fluids are unable to diffuse effectively into the micropores of zeolite powder, therefore, undesirable mass transfer restrictions and significant pressure drops can be resulted [8]. Poor diffusion minimizes the zeolite efficiency and limits the range of applications.

Hierarchically porous structured zeolites have recently gained attention due to their porous properties and potential applications in separation, life science, adsorption, and catalysis [9]. According to a general

definition, materials with two or more porosity levels, regardless of the pore uniformity in each level, are said to have hierarchically porous structures [10]. These hierarchically porous zeolites have larger pore systems than conventional zeolites, which improves access and transport and reduces mass transfer problems [11, 12]. The conventional microporous zeolites show problems of reduced reaction activity and low adsorption capacity due to the low effective surface area and narrow pore size which determines the diffusion and mass transfer of the bulk-size molecules [13]. Hierarchically porous zeolites can reduce mass transfer problems by offering the potential of increasing the intercrystalline diffusion rate, reducing steric restrictions for converting bulky molecules, maximizing the catalyst employment and selectivity towards target products, and inhibiting deactivation of catalysts because of coke formation [4].

The hierarchically porous zeolites can be obtained by depositing a thin layer of zeolite crystals over a meso/macroporous support with the option of removing this support after the preparation step. Also, they can be obtained in a destructive way in which some silicon or aluminum atoms are removed from the framework to enlarge the inherited pore size. It is critical to find an appropriate approach to tailoring different levels of porosity in order to reap the benefits of the produced



hierarchically porous structure and maximize zeolite activity [9, 14]. Many supports and templates have been used to create these materials, but they are usually expensive and are frequently removed by post-synthetic calcination, which is wasteful and costly [11, 15]. It has been essential to find a low-cost porous material to act as a support for a particular hierarchically porous structured composite. Fig. 1 shows the types of hierarchically porous zeolites revealing the difference among their structures. Fabricating an inexpensive and green hierarchically porous zeolite-carbon composite from economic precursors is important for the potential use of wastewater applications such as heavy metal ions or organic pollutants including dyes, antibiotics, etc.

In this study, a green hierarchically porous zeolite-carbon composite sorbent will be synthesized using an eco-friendly method. The synthesized composite will be tested by X-ray diffraction spectrometry, Fourier transforms infrared, field emission scanning electron microscope, energy dispersive analysis by X-ray, thermo gravimetric analysis, nitrogen adsorption/desorption, and by measuring the point of zero charges.

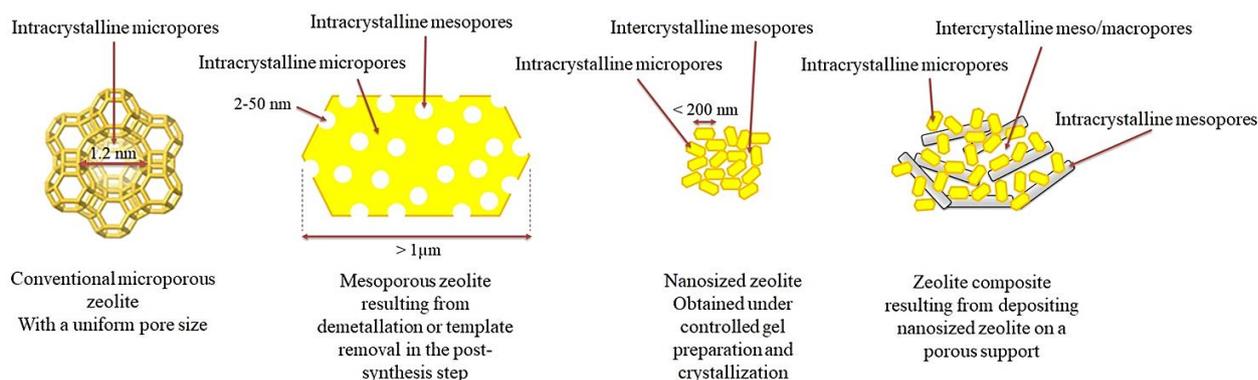


Fig. 1. The Types of Hierarchically Porous Zeolites

2.2. Synthesis of NaX zeolite and zeolite-carbon composite

According to the synthesis process described in Alfalahy and Al-Jubouri, 2022 [16], NaX zeolite was created from the gel formula represented by Eq. 1.



Preparation of carbon support commenced by cleaning and washing the shells of plum stones with distilled water. After drying for 24 h at 70 °C, the shells were crushed, heated to 250 °C at a constant rate of 10 °C/min for 20 min, ramped up to 650 °C for 3 h, then cooled to room temperature. The carbonization process was conducted in an airtight stainless-steel container with a tiny opening in the top cover that served as a working environment. Sieving the product of the carbonization process resulted in carbon particles ranging in size from 2.35 to 4.5 mm.

2- Material and Methodology

2.1. Materials

Plum stones shells were gathered from a local plum fruit as a carbon precursor due to their low cost and approachability. Sodium aluminate (55–56%wt. Al_2O_3) bought from RiedeldeHaen and sodium silicate (32–33%wt. SiO_2) acquired from Lab-UAE Company were both used for preparing NaX zeolite. N, N-Dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, M.wt. =73.09 g/mol) acquired from Central Drug House(P) Ltd. Polyacrylonitrile (PAN - $(\text{C}_3\text{H}_3\text{N})_n$, M.wt. =150000 g/mol) bought from Hangzhou Sartort Biopharma Co. Ltd. and Polyvinylpyrrolidone (PVP - $(\text{C}_6\text{H}_9\text{NO})_n$, M.wt. = 40000 g/mol) were used to prepare the composite. Sodium hydroxide (NaOH, 97%wt.) purchased from HIMedia Laboratories Pvt. Ltd. was used for zeolite synthesis and changing the solution pH. Hydrochloric acid (HCl, 35–38% Vol.) supplied by Central Drug House(P) Ltd. was used for changing the solution pH. Sodium chloride (NaCl, 99.9%wt.) obtained from CDH was used for preparing the background electrolyte.

Preparation of a green porous composite (symbolled by DFZPC) was made by mixing 0.75 g of zeolite NaX with 10 ml of DMF solvent to promote particle mobility and solid retention. The step of zeolite dispersion in DMF was performed in a completely sealed container to avoid solvent volatilization. The zeolite-DMF mixture was heated over a hot plate magnetic stirrer at 50 °C for 10 min. Afterwards, 0.1 g of PVP was added to the zeolite-DMF slurry and mixed for 20 min. Next, 0.2 g of PAN was added to the zeolite-DMF-PVP mixture and mixed for 30 min. After that, 3 g of carbon (PSC) was added to the above mixture and mixed for 3 h. Eventually, the product was recovered by filtration simultaneously with washing with distilled water to achieve a phase inversion process of the polymer which cross-linking the zeolite with carbon. The produced solid was dried at 70 °C.

2.3. Characterization techniques

Detecting the phase of the prepared zeolite was conducted by an X-ray diffractometer (XRD, XPERT PILLIPS HOLLAND instrument with a radiation source

of $\text{CuK}\alpha$ with $\lambda = 1.5406 \text{ \AA}$, the voltage = 30 kV, the current = 30 mA, a scan speed = $3^\circ/\text{min}$, a step size = 0.05° and $2\theta = 5\text{-}50^\circ$. The functional groups and chemical bonds were detected by the Fourier-transform infrared (FT-IR) model Shimadzu IRAffinity-1 spectrophotometer within $4000\text{-}400 \text{ cm}^{-1}$ scan range. The morphology of NaX zeolite, PSC, and DFZPC was characterized by the field emission scanning electron microscope (FE-SEM, TESCAN MIRA3 FRENCH) with an accelerating voltage of 15 kV. The energy dispersive spectrometer by X-ray (EDAX) installed on the FE-SEM instrument was used to detect the element type and contents of the samples. The Thermo Gravimetric analyzer (TGA, Perkin Elmer) was used to identify the zeolite content in DFZPC. A sample of DFZPC was burnt at a rate of $10^\circ\text{C}/\text{min}$ at 900°C in the air atmosphere. The specific surface area of the sorbents was estimated by the Brunauer-Emmett-Teller (BET) procedures depending on the N_2 adsorption/desorption isotherms obtained using a MicroActive for TriStar II Plus, Version 2.03.

The value of the zero charge point (pH_{pzc}) of DFZPC was determined using the solid addition technique [17]. A 0.1 M NaCl solution was utilized as the background electrolyte. Thereafter, 0.1 M NaOH and 0.1 M HCl were used to change the initial pH of six specimen containers containing 25 mL of NaCl solution to (2, 4, 6, 8, 10, and 12). Afterwards, 0.1 g of DFZPC was added to each container and the containers were shaken at room temperature for 48 h. Subsequently, the pH of the solution was measured after DFZPC removal. The difference between the initial and final pH was calculated and plotted against the initial pH to identify the pH_{pzc} value.

3- Results and Discussion

3.1. XRD

XRD patterns of NaX zeolite and DFZPC are shown in Fig. 2. The pattern of DFZPC shows appearing peaks belonging to NaX zeolite at 2θ of 6.17° , 10.07° , 11.84° , 15.56° , 23.45° , 26.75° , 29.66° , 30.41° , 31.07° , 32.12° , and 33.08° . Also, it shows that the crystallinity of all peaks was lower than that of NaX zeolite due to dilution with carbon. Moreover, the presence of PSC in the content of DFZPC gave rise to the appearance of a ramp in the pattern of DFZPC at the regions of $5.2^\circ\text{-}8.9^\circ$, $13.5^\circ\text{-}35.12^\circ$, and $20\text{-}35^\circ$ due to the PSC amorphous structure.

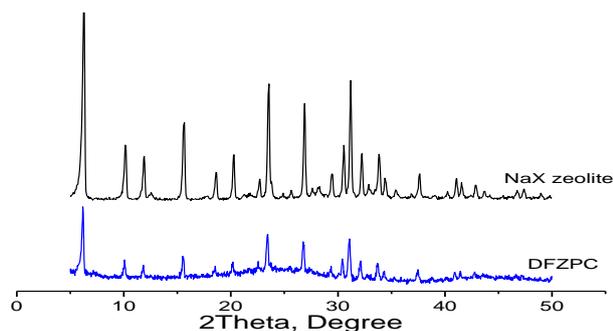


Fig. 2. X-Ray Patterns of NaX Zeolite and DFZPC

3.2. FT-IR

Identifying the functional groups present in the DFZPC surface due to incorporating NaX zeolite and PSC structures was conducted through the FT-IR test. Fig. 3 presents the spectra of PSC and DFZPC. The bands seen at 3873 cm^{-1} for DFZPC can be assigned to O-H stretching vibration. The bands seen at 3421 cm^{-1} for DFZPC (within the range of $3660\text{-}3100 \text{ cm}^{-1}$) showed a slight increase in the peak height and shifting from that appeared in the spectra of PSC at 3449 cm^{-1} which can be assigned to phenolic O-H bond stretching vibrations and N-H/C-H bond due to stretching of amines. A band present at 1643 cm^{-1} in the PSC pattern showed a high increase when present in DFZPC spectra at 1655 cm^{-1} , this peak can be assigned to C=C- stretching vibration due to the presence of alkenes. The band, which is assigned to primary amines (N-H), appeared at 1577 cm^{-1} in PSC and DFZPC spectra. The bands that appeared at 1454 cm^{-1} in the PSC and with less intense bands that appeared at 1458 cm^{-1} in DFZPC spectra are assigned to C-H bend stretching vibrations due to the presence of alkenes. The peaks that appeared at 1384 cm^{-1} and 1404 cm^{-1} in the PSC increased to appear obviously at 1381 cm^{-1} in the DFZPC spectra. This band is assigned to C-C stretching vibration due to the presence of aromatics. The bands that appeared at 1327 cm^{-1} in PSC spectra and at 1315 cm^{-1} in DFZPC spectra can be due to the nitroaromatic group ($-\text{NO}_2$). The bands that appeared at 1180 cm^{-1} in PSC and at 1168 cm^{-1} in DFZPC spectra can be assigned to alcohols (C-O stretch). Bands associated with Si-O-C deformation vibrations and esters (C-O stretch) can also be seen at 1103 cm^{-1} and 1010 cm^{-1} in the PSC spectra. But these peaks shifted and became one narrow and long peak that appeared at 1084 cm^{-1} in the DFZPC spectra. The peaks assigned to the alkyl halides (C-Br, C-Cl, C-I, and C-F) appeared with reduced height in DFZPC spectra at 583 , 640 , and $708\text{-}830 \text{ cm}^{-1}$. The peaks assigned to the presence of the C-OH group appeared at 875 cm^{-1} for PSC but shifted to 864 cm^{-1} for DFZPC.

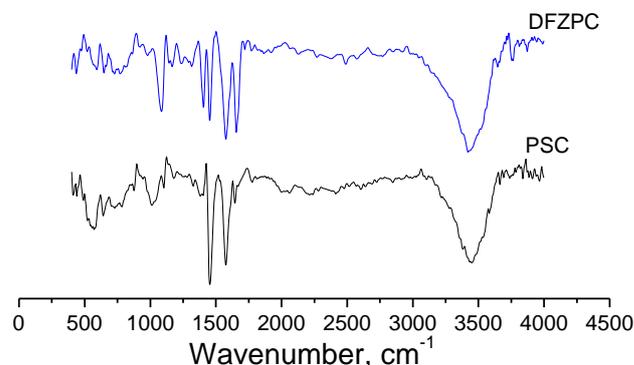


Fig. 3. FT-IR Spectra of DFZPC and PSC

3.3. FE-SEM and EDAX

The morphology of NaX zeolite, PSC, and DFZPC can be explained through FE-SEM images shown in Fig. 4.

NaX zeolite showed as assemblies of nanosized crystals with nearly spherical shapes as seen in Fig. 4 (a). A particle size software device was used to determine the crystal size depending on the FE-SEM images and it was 117.4 nm. Fig. 4 (b) shows the porous nature of the produced PSC from plum stones shells. The morphology of the produced DFZPC shown in Fig. 4 (c) can be described by a porous carbon surface fully covered by zeolite crystals. Table 1 shows the elemental analysis of NaX zeolite, PSC, and DFZPC based on EDAX. The

table shows that the Si/Al ratio of NaX zeolite and DFZPC was 1.2 and 1.3, respectively. The values of the Si/Al ratio of both NaX zeolite and DFZPC were close enough and the slight difference cannot be attributed to a reason associated with the structure properties because DFZPC was not subjected to harsh conditions or thermal treatment during the preparation. The variation simply can be attributed to a lack of uniformity in the physical manner of the characterization.

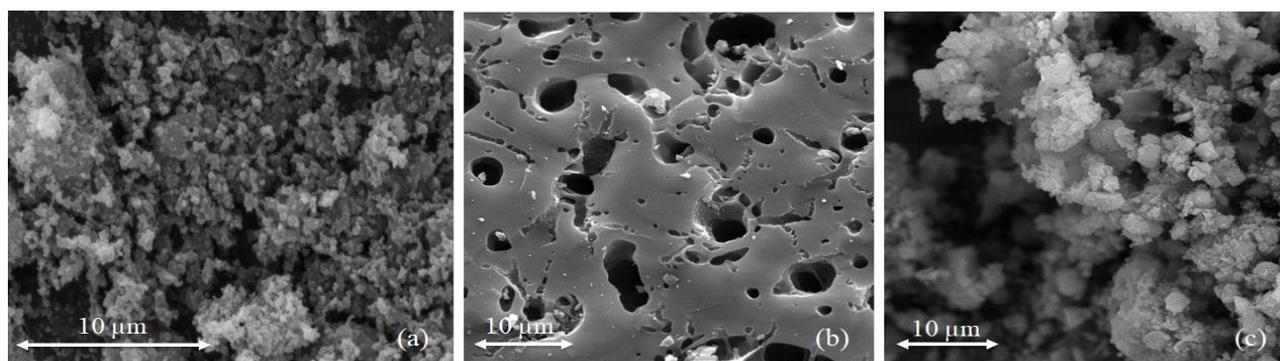


Fig. 4. FE-SEM Images for (a) NaX Zeolite, (b) PSC, (c) DFZPC

Table 1. Characterization Data of NaX Zeolite, PSC, and DFZPC

Sorbents	%Zeolite content based on TGA	Elemental analysis based on EDAX (wt.%)					Si/Al	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
		C	Si	Al	Na	O			
NaX zeolite	100	0	18.51	16.04	16.43	49.02	1.2	328.330	0.202
PSC	0	94.43	0.07	0.08	0.07	5.42	0	9.047	0.020
DFZPC	18.75	29.82	15.8	11.92	7.6	34.8	1.3	208.463	0.122

3.4. TGA and N₂ adsorption-desorption

The zeolite content in DFZPC according to TGA results shown in Table 1 was 18.75%. The N₂ adsorption-desorption isotherms of NaX zeolite, PSC, and DFZPC are shown in Fig. 5. This figure displays the isotherm of NaX zeolite is of type I which confirms the microporosity of the zeolite. Also, it confirms the mesoporosity of the PSC and DFZPC because their isotherms showed IV isotherm type. Also, Table 1 shows that the surface area for NaX zeolite was 328.330 m²/g, for PSC was 9.047 m²/g, and for DFZPC was 208.463 m²/g. The pore volume was 0.202 cm³/g for NaX zeolite, 0.020 cm³/g for PSC, and 0.122 cm³/g for DFZPC. The comparatively lower surface area of DFZPC can be attributed to incorporating carbon, which has a low surface area, in the content of DFZPC.

3.5. pH_{pzc}

Measurement of the point of zero charge (pH_{pzc}) of DFZPC resulted in the data presented in Fig. 6. The figure displays that the pH_{pzc} of DFZPC was 6.9 at which the DFZPC surface is neutralized (has zero charge). Also, Fig. 6 shows that at a very low pH medium (solution pH < 6.9), the DFZPC surface becomes positively charged with a low attraction tendency for cations. However, at solution pH > 6.9, DFZPC surface becomes negatively charged with a high attraction tendency for cations.

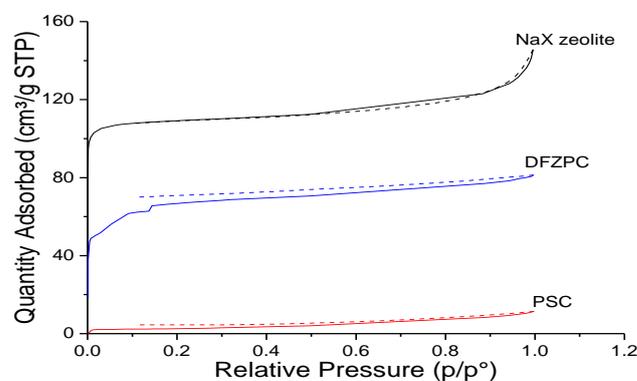


Fig. 5. N₂ Adsorption/Desorption Isotherms of NaX Zeolite, PSC, and DFZPC

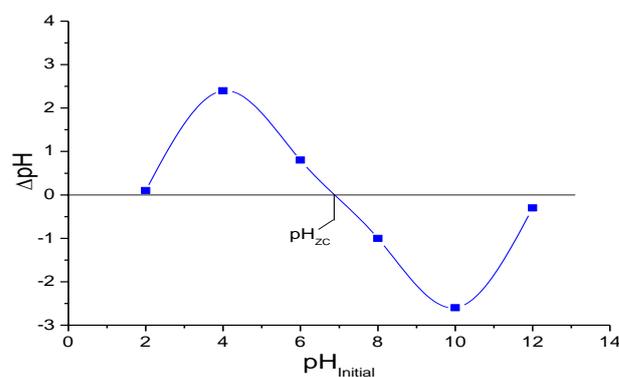


Fig. 6. Measuring of the pH_{pzc} of the DFZPC

4- Conclusion

A hierarchically porous structured zeolite-carbon composite was successfully synthesized by combining NaX zeolite on porous carbon support using PAN polymer in the phase inversion method. This method ensures no extra exposure of zeolite to high temperatures. The porous carbon support was obtained from agro-waste which was plum stones shells. The produced composite had promising structure properties such as a surface area of 208.463 m²/g, a pore volume of 0.122 cm³/g, and a relatively moderated zeolite content of 18.75%. Moreover, DFZPC has a pH_{pzc} of 6.9 at which its surface is neutral and does not show attraction or repulsion activity. Therefore, its surface has a positive charge below this value, but it is charged negatively above it.

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تحضير وتوصيف خليط زيوليت - كربون ذو المسامية الهرمية من مواد اقتصادية وطريقة صديق للبيئة

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الخلاصة

تم تصنيع خليط زيوليت - كربون الأخضر ذو المسامية الهرمية من زيوليت NaX مدعومًا بمواد مسامية كربونية ناتجة عن المعالجة الحرارية لغلاف نواة فاكهة البرقوق التي تعتبر نفايات زراعية. يتمتع هذا النوع من الخلائط العضوية - غير العضوية بأداء محسّن لأن الجزيئات الضخمة يمكنها المرور بسهولة في المسام الدقيقة إلى المواقع النشطة بسبب قصر مسار الانتشار مما يعني معدل انتشار أعلى. تم تحضير هذا الخليط باستخدام طريقة التوليف الخضراء بما في ذلك استخدام بوليمر صديق للبيئة لربط زيوليت NaX على سطح الكربون بطريقة انقلاب الطور. تم تشخيص الخليط باستخدام مطياف حيود الأشعة السينية، وتحويل فورييه الطيفي بالأشعة تحت الحمراء، والفحص المجهرى للانبعاثات الميدانية، وتحليل الأشعة السينية المشتتة للطاقة، والتحليل الحراري الوزني، N_2 -adsorption / desorption isotherm، ونقطة الشحنة الصفرية. أظهرت النتائج أن مساحة سطح الخليط المحضر هي $208,463 \text{ m}^2 / \text{g}$ ، وحجم مسام قدره $0,122 \text{ سم}^3 / \text{g}$ ، وشكل سطح متميز، ومجموعات وظيفية. وأيضًا، كان الأس الهيدروجيني لتعادل شحنة السطح هي 6.9 وفوق هذه القيمة يكون السطح له شحنة موجبة وأقل من 6.9 تكون شحنته سالبة. تحدد هذه الخاصية خاصية الامتزاز للخليط في إزالة الملوثات من مياه الصرف.

الكلمات الدالة: المواد الخضراء، المسامية الهرمية، زيوليت NaX، انقلاب الطور، بوليمر، الكربون.