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Using Dates Leaves Midribs to Prepare Hierarchical Structures Incorporating Porous Carbon and Zeolite A Composites for Cesium¹³⁷Cs Ion Exchange

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Abstract:

This study synthesized zeolite 4A, and hierarchical composite structure consisting of zeolite 4A-carbon were successfully prepared. Hydrothermal method was used to grow a layer of zeolite 4A over porous carbon surfaces to enhance mass transfer and increase surface area of zeolite. The products then were used to remove radioactive cesium¹³⁷Cs from liquid wastewater. Iraqi dates leaves midribs (DM) were used as locally available agricultural waste to prepare low- cost porous carbon, using carbonization method in tubular furnace at 900C for two hours. Hierarchical porous structures including zeolite are prepared by mechanically activating the carbon surface via Ultrasonication nanoparticles suspension of ground zeolite type 4A. For preparing nanoparticles suspension, commercial zeolite has been milled using 0.3-0.4 mm diameter glass balls as grinding media. Nanoparticles of zeolite 4A acting as seeding (nucleation centers) increase the crystallization of amorphous aluminosilica gel on modification carbon surface. The products of the syntheses zeolite 4A and the hierarchical composite materials (DMZ) were characterized using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Nitrogen sorption (BET) and Energy dispersive X-ray spectrometer (EDX) to check the morphology, structure, surface area, and the chemical composition respectively. The products were used to treat radioactive wastewater contaminated with radioactive cesium¹³⁷Cs collected from destroyed building of the Radiochemistry Laboratories (RCL) in AL-Tuwaita Nuclear Site. The activity concentration for the contamination water pre and after the treatment were measured using gamma spectroscopy system supplied with a high purity germanium detector (HPGe) with 60% relative efficiency. The results showed that the radioactivity concentration after the treatment process decreased significantly from 4800 Bq/L to 186 and Bq/L, 121 Bq/L using 0.045 gm from synthesized zeolite 4A and DMZ respectively.

Key words: Cesium cs¹³⁷, Hierarchical structures, Liquid waste treatment, Porous carbon, Zeolite 4A.

Introduction:

Zeolite is among the most important classes of materials with various technical applications in the heterogeneous catalysts chemical industry, as sorbents or ion-exchangers (1). Zeolite is crystalline porous, three-dimension aluminosilicates of the alkali (primarily potassium and sodium) and alkaline earth (mainly calcium) metals. Zeolite's crystalline structures are based on 3-(SiAl)O₄ tetrahedra frameworks with four (O₂) atoms connected to the nearest tetrahedral(2). Zeolite's structure contains molecular cavities and ch

annels(3). The size and shape of the pores as well as the cavities vary depending on the type structure of zeolite.

Much of the commercial success of zeolites in many applications such as catalyst and ion exchange can be directly attributed to the presence of micropores in their structure. The major drawback in many industrial applications using zeolite can be represented by:

diffusion restrictions due to blocked access and slow mass transport to and from active sites within the microporous (4,5).

One way to solve this problem is via mixing the zeolites with binder material like clay or alumina to prepare shaped structure like beads, pellets, spheres, etc. This binder is usually low or non-adsorptive which causes block or/and cover the active adsorption sites (6).

Synthesis of nano zeolite crystals is often conducted in a clear aluminosilicate gel in the presence of organic template additives. A number of zeolites nanocrystals such as zeolite Z MS-5, sodalite and faujasite (X or Y) have been successfully produced. However the reduction of zeolite particle size from micro to nano leads to decrease in crystalline degree and the thermal stability and cause difficulties in separation and recovery (7). Hierarchical Porous Structures (HPS) refer to those materials with two or more porosity levels, modified for the sake of solving diffusion problems resulted from binding and pelletizing of catalysts or from the agglomeration of crystallite (8). Generally, (HPS) are made either by templating methods or by post-syntheses modification (delamination, desilication) and controlled crystallization (9). Many authors used different

kinds of zeolite to synthesize a variety of zeolitical hierarchical structures. Hernandez-Ramirez et. al. (10) designed hierarchical structures from faujasite zeolite Y crystallized on tow carbonized component, this was performed through seeding process coupled with ultrasonication. The addition of sonicated seeds from target zeolite to the carbon samples is required to increase the crystallization rate. Al-Nasri (11) and Sama M. et.al (12) studied the effect of nanoparticle seeds on the preparation of hierarchical porous structures, the authors found that the using of seeding on the temples surface induced crystallization of the amorphous aluminosilicat during the hydrothermal treatment.

In this study novel structures consisting of porous carbon prepared from Dates leafs midribs (DM) coupled with Linda type 4A zeolite were synthesized to enhance separation process and recovery from solution and increase surface area. Zeolite 4A is chosen in this study because it has high cation exchange capacity CEC and high adsorption selectivity for ¹³⁷Cs.

Materials and Methods:

In order to prepare the synthesis material of zeolite A, the following raw materials were used without any addition for purification, sodium metasilicat ($\text{Na}_2\cdot\text{SiO}_3\cdot 9\text{H}_2\text{O}$, BDH) as a silica

source, Sodium Aluminate(50% Al_2O_3 , sigma Aldrich) as alumina source, and sodium hydroxide (99.9%) as mineralizing agent, while carbonaceous supports were prepared from locally available agricultural waste by a hydrolyses method.

Zeolite 4A synthesis

A combination of silica and alumina, which are dissolved in alkaline solution, was used to prepare zeolite 4A. The dissolving process was performed according to the formula $(13):3.1\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:1.9\text{SiO}_2:12\text{H}_2\text{O}$. A (0.94g) NaOH was added to (30g) deionized water, this solution was split into two equals halves. To the first half (3.22g) sodium aluminate was added and mixed until clear solution was obtained, to the second solution (2.43g) sodium silicate was added and mixed for 15 min, both precursors were mixed together and stirred for 30 min, aluminosilical gel then transferred to stainless autoclave lined with Teflon land. Zeolite 4A was crystallized at 100°C for 2 and 4 hours. After that the powder was separated by filtration and washed with D.W till the pH of the outer water became below than nine, and then dried at 80C for 6 hours. The powder then was collected and checked by (SEM), (XRD), N_2 -Adsorotion / desorption isotherms and EDAX in order to measure morphology, structure, surface area and the chemical composition for the product.

Iraqi Dates leaves midribs (DM) have been chosen as raw material to prepare carbon because they are locally available, plant waste. The (DM) Fig. 1 was cleaned, cut, dried and the prepared carbon was weighted before entering a tubular furnace at 900C for 2 hours. (N_2) gas was flowed through the furnace; the prepared carbon was weighted, and then manually ground to get carbon powder with particle size with range of (60-600 μm). Scanning Electron Microscopy (SEM) image was taken to this sample to illustrate the morphology structure of porous carbon.



Figure 1. Dates leaves midribs(DM)

Nanoparticles Suspension Preparation

Commercial zeolite 4A (supply by BDH) was used to prepare nanoparticles suspension as seeding on carbon surface to increase crystallization rate. 0.3-0.4mm diameter glass beads were used as grinding media according to the following weight ratio: 1H₂O: 1zeolite 4A: 2 grinding media. The product was finally characterized by Dynamic Light Scattering (DLS) to measure the particle size of suspension.

Preparation of Hierarchical Structures

Ultra sonication path was used with samples consisting of (carbon: suspension nanoparticles with mass ratio 15:1) for 6 hours to modification of carbon surface.

Hierarchical composite of zeolite 4A over date midrib (DMZ) carbon was hydrothermally made via mixing carbon with aluminosilical gel. The carbon powder was added as 2:1carbon to silica found in the silica source and mixed for 10 minute. After that, the gel was transferred in Teflon – lined autoclave and entered in an electricity oven for 4 hours. After that, the product composite was filtered, washed with D.W. till the acidic function became less than nine and measured by XRD,SEM, EDAX, and N₂- adsorption/desorption isotherm.

Results and Discussion: Characterization

Among all characterization techniques of X-ray, diffraction is the most important technique used to identify the zeolite structure and the phase purity of zeolite. X-ray diffraction instrument model shematzo /Jaban ,with CuK α radiation source ,the x-ray wave length = 1.541 \AA was used in this study to examine the synthesized materials.

Figure 2 illustrates the X-ray diffraction peaks of the synthesized zeolite 4A and commercial zeolite 4A, the pattern shows the plot the intensity of X-ray diffraction from the sample with the angle of diffraction (2θ).

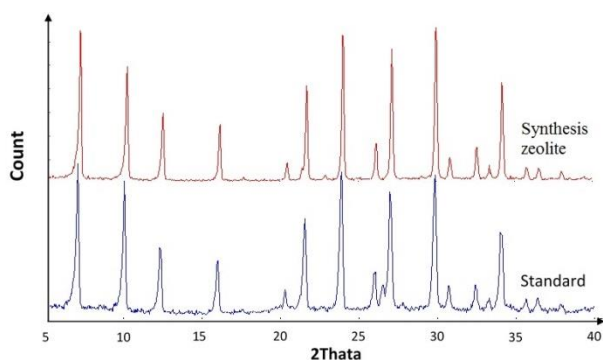


Figure 2. X-ray diffraction of the prepared Zeolite 4A

From the X-ray diffraction patterns, it can be seen that the prepared zeolite has a good crystallinity and nearly has the same crystalline structure as the standard type. The X-ray diffraction of prepared 4A has small peak at angle ($2\theta = 7^\circ$), ($2\theta = 10^\circ$), put the characteristic angle at ($2\theta = 30^\circ$) (14).

The comparison between The X-ray peaks from heretically composite sample with that from Synthesis zeolite 4A sample, Fig.3 shows that the presence of carbon powder as scaffold does not affect the preparation process of zeolite.

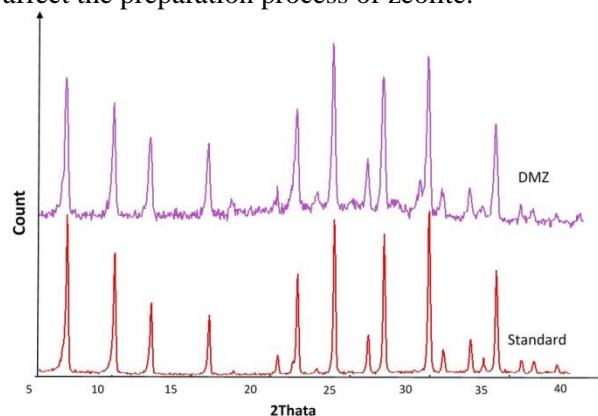


Figure 3. XRD patterns of synthesized zeolite 4A and zeolite 4A composite prepared using date palm leaves midrib (DMZ)

Scanning electron microscopy (SEM) image can provide information about the surface texture, morphology and size of sample. The material that will be analyzed in SEM must be electrically conductive, therefore the zeolite sample was coated with a thin layer of gold.

SEM images of the carbonized materials illustrated the morphology structure of prepared carbon Fig.4 date palm leaf midrib (a), (b) show the typical honeycomb structure generally observed in plant steams. The good crystallization of prepared zeolite 4A with cubic shape, approximately 2 μm particle size is shown in (c), (d).

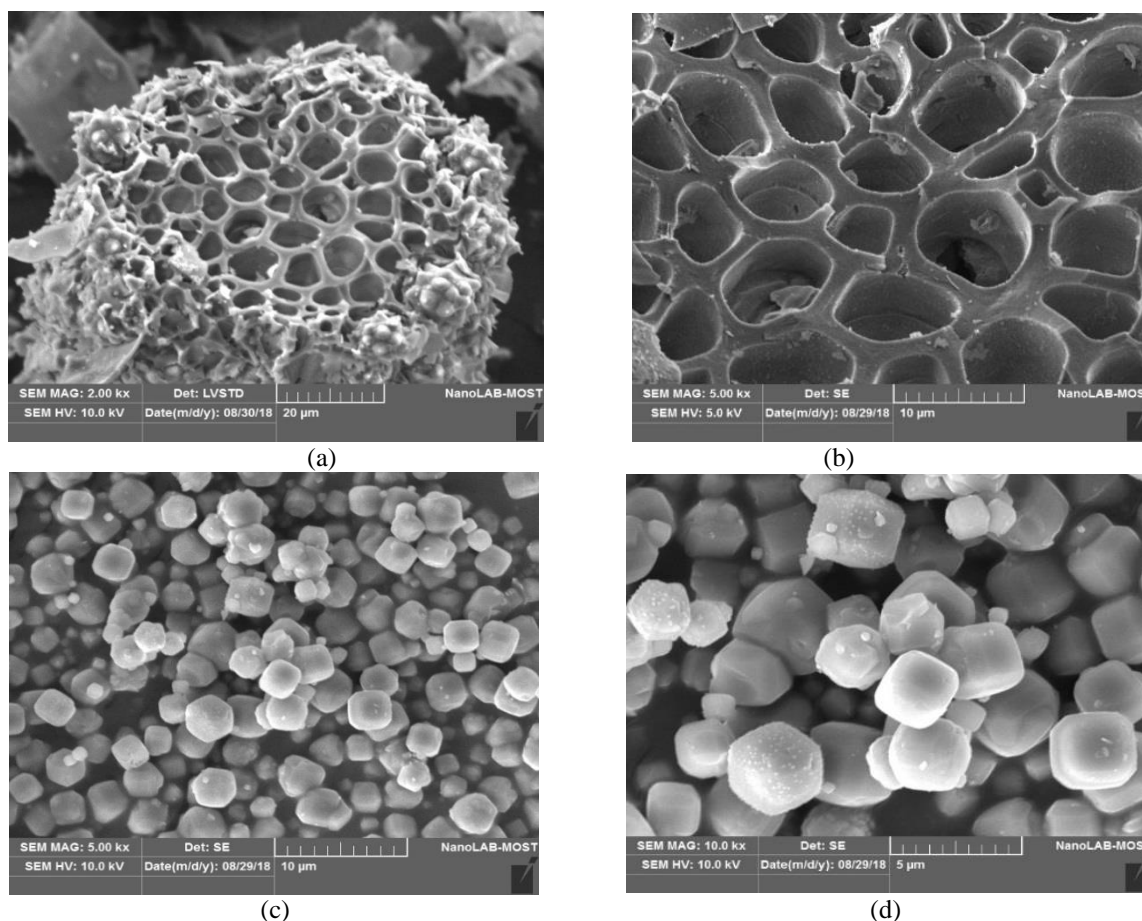


Figure 4. SEM images (a), (b) (DM.) carbon in different magnification, (c), (d) Synthesized zeolite 4A in different magnification.

The SEM pictures of synthesized composites zeolite 4A prepared using DM carbons ultrasonicated in the colloidal of zeolite A nanoparticles are given in Fig. 5. The SEM images

demonstrate the full crystallization and uniform shaping of crystals which are well distributed over surface of the carbon.

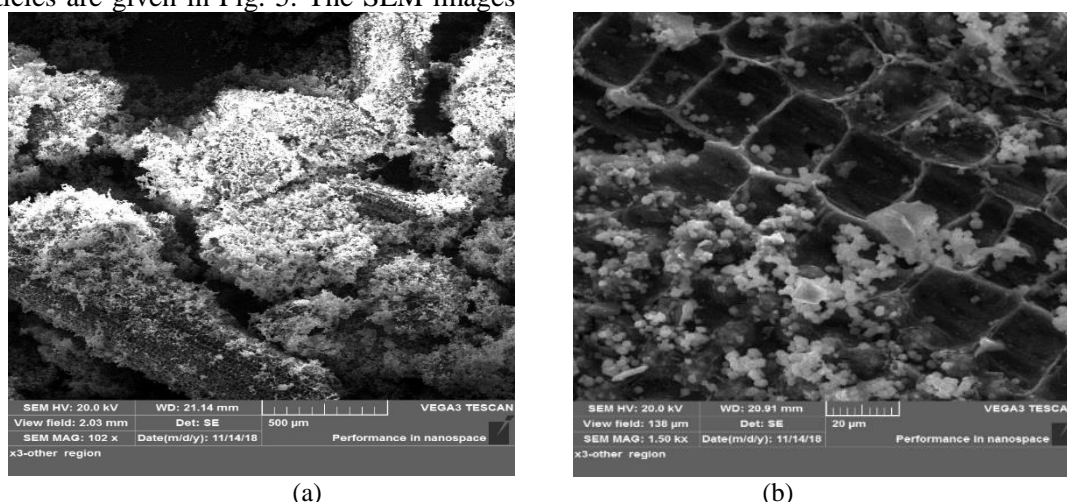


Figure 5. The SEM images (a), (b) of prepared hierarchal composites (DMZ) in different magnification.

The fine particles size of zeolite crystals was prepared from a commercial zeolite 4A, ground using wet ball milling. The average particle size of the crushed zeolite 4A was measured using the Dynamic Light Scattering (DLS) technique. The (DLS) technique, also known as photon correlation

spectroscopy, is widely used for measuring size and size distribution of the particles presenting a suspension in liquid medium. Zeta plus instrument from (Brookhaven Company) in Ministry of Science and Technology, with particles size ranging from 10 nm to 30 μm and accuracy $\pm 2\%$ was used

to determine the average size of colloidal zeolite. It was found that the suspension of fine particles of zeolite with average particle size equal to 260 nm fixed fitted the carbon scaffolds using ultra sonication agitation for 6h.

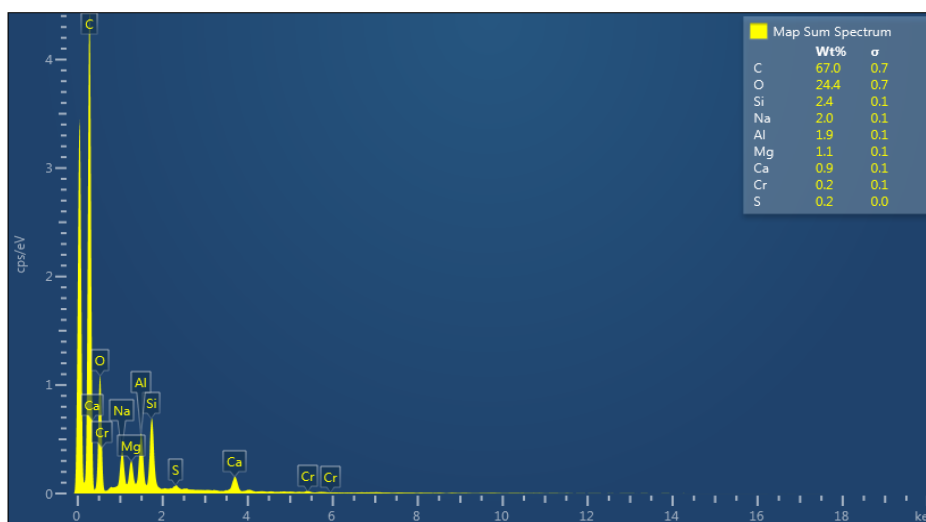
Energy Dispersive X-ray Spectroscopy (EDX) was used to determine the concentration of elemental species in a tested sample. EDX technique has been used for synthesized zeolite 4A and hierarchal composites samples to evaluate the ratio between silicon and aluminum as well as to measure the chemical composition for the samples. Figure 6 shows that the Si/Al ratio for synthesized zeolite 4A is 0.9 and for DMZ is 1.2. These

results are going with same tuning with (11, 15) in the range of about 1.

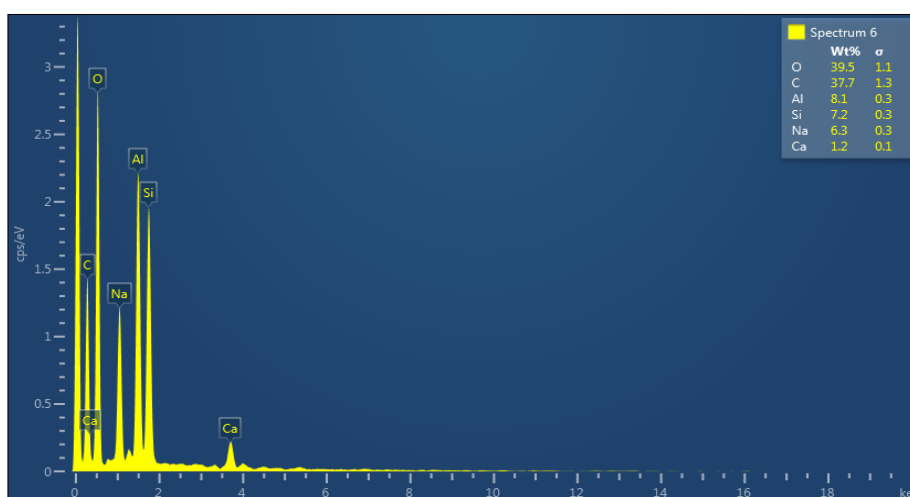
Determining the Surface area for different samples were done using BET Surface area analyzer in petroleum Research and development center / Ministry of Oil. The result of the BET surface area for both synthesized zeolites and composites samples are illustrate in Table 1.

Table 1. the Surface area results

Sample	Surface area m ² /g
synthesized 4A	19.1037
DM carbon	273.042
DMZ Composite	146.276



(a)



(b)

Figure 6. EDX analysis result (a) DMZ, (b) synthesized 4A

Application of Hierarchal with a real radioactive Solution

The prepared zeolite-4A and hierarchal composite DMZ were applied to remove radioactive ¹³⁷Cs isotope from radioactive liquid waste collected from Radio Chemistry Laboratories (RCL) in Al-

Tuwaitha Nuclear Site. The initial activity concentration for the ¹³⁷Cs radionuclide was measured by high purity germanium detector (HPGe). The activity concentration of the radioactive solution before the treatment was 4800Bq/L, batch mode have been carried out using

20 ml of contaminated solution mixed with different weights from absorbent materials. The contact time was two hours, while the pH of solution was 6.5 in room temperature. The result of removal is shown in Fig.7 The change of the radioactivity concentration after treatment versus weight of absorbent materials. It is clear that the radioactivity concentration after treatment decreased significantly from 4800 Bq/L to 186 Bq/L, 121 Bq/L using 0.045 gm from synthesized 4A and DMZ respectively .

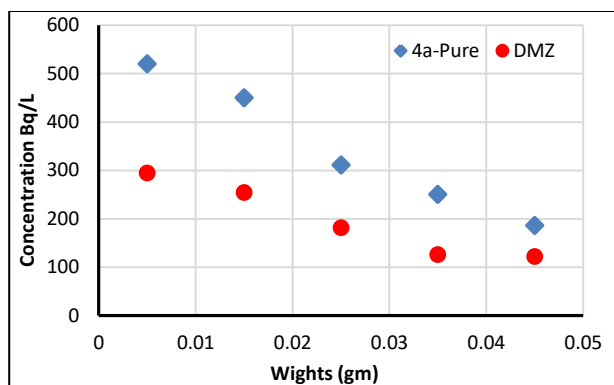


Figure 7. The Relation between the concentrations after treatment with absorbent Wight the initial concentration is 4800 Bq/L at room temperature

The effect of contact time on the final radioactivity concentration was studied using different time 15, 30, 60, 120, 180 min. The results show that the final radioactivity concentration of ^{137}Cs decreased rapidly with increasing the mixing time, after that it decreased gradually till reaching the equilibrium time at 120 minutes. This is due to the saturation process of the ion-exchange sites of the zeolite which contain exchangeable cation (sodium) with caesium ions as shown in Fig.8. This result agrees with A.M.El-Kamash who reported that for zeolite-A 80-90% of the sorption of Cs^+ and Sr^{2+} ions occurs during the first 30 min (16). In addition, it was noticed that the uptake of with ^{137}Cs from the contaminated liquids increase slightly by increasing the mixing time until reaching the equilibrium state.

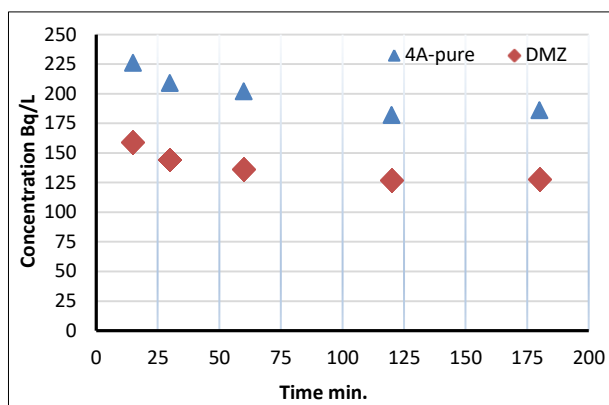


Figure 8. The relation between the concentrations after treatment with time the initial concentration is 4800 Bq/L.

Conclusion:

Zeolite -4A, hierarchical structure incorporating zeolite and carbon have been successfully synthesized using hydrothermal method from amorphous gel.

Porous carbon surface is prepared using locally available agricultural waste (Iraqi Date leaves midrib) by carbonization method, then the carbon surface activated using ultrasonication in a suspension contain fine particles of commercial zeolite 4A to induce crystallization process.

The XRD diffraction pattern of the prepared zeolite and (DMZ) composite has the same crystalline structure of commercial zeolite A.

The porous carbon is withstanding and not affecting the structure of zeolite during hydrothermal method, that makes it be preferred as scaffold material in hierarchical structure.

The BET surface area increases from 19.103 m^2/gm to 146.276 m^2/gm for synthesized zeolite 4A and (DMZ) composite respectively.

The prepared zeolite A and (DMZ) composite are applied to remove the ^{137}Cs isotope from real radioactive waste water sample collected from Radiochemistry Laboratories in Al-Tuwaita nuclear site.

The radioactivity of ^{137}Cs decreases from 4800 Bq/L to 186 Bq/L, 121 Bq/L by using 0.045 gm from both materials.

The results show that the composed material could be used effectively as an eco-friendly to remove the radioactive isotopes from the contaminated wastewater.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours,

have been given the permission for re-publication attached with the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

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استخدام كرب سعف نخيل التمور لتحضير تراكيب سلمية تتضمن الكربون المسامي والزيوليت A لغرض التبادل الايوني مع السيزيوم 137

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الخلاصة:

تم في هذه الدراسة تحضير مادة مسامية سلمية تتضمن الكربون والزيوليت نوع 4A مع كفاءة عالية لإزالة السيزيوم المشع من مخلفات المياه الملوثة اشعاعيا. استعملت الطريقة الهيدروحراريه لأنماء طبقه من زيوليت نوع 4A على سطح الكربون المسامي لتحسين عمليه نقل الكتلة وزيادة المساحة السطحية للزيوليت استخدم كرب سعف النخيل العراقي (DM) كمخلفات زراعية متوفرة محليا لتحضير كربون مسامي واطى الكلفة باستخدام طريقة الكربنه في فرن انبوبي عند درجة حرارة 900C ولمدة ساعتين. التراكيب المسامية السلمية تم تحضيرها باستخدام التنشيط الميكانيكي لسطح الكربون باستعمال الموجات فوق الصوتية بوجود عالق يحتوي على دقائق نانوية للزيوليت المطحون نوع 4A. لتحضير عالق يحتوي دقائق نانوية للزيوليت تم طحن الزيوليت التجاري باستعمال كرات زجاجيه بقطر (0.3-0.4 mm) كوسط للطحن. تعمل دقائق الزيوليت النانوية كبنود (مراكز تنوي) لزيادة تبلور جل الالومينا سليكا العشوائي على سطح الكربون المعدل. تم تشخيص الزيوليت 4A المحضر و المادة المتراكبة المحضرة باستعمال المجهر الالكتروني الماسح (SEM)، جهاز حيود الأشعة السينية (XRD)، جهاز قياس المساحة السطحية (BET)، و (EDX) للتحقق من الهيئة، التركيب، المساحة السطحية، والتركيب الكيميائي على التوالي. استخدم المنتج لمعالجة المخلفات السائلة الملوثة اشعاعيا والتي تحتوي على نظير السيزيوم المشع Cs-137 تم جمعها من بناية مختبرات الكيمياء الإشعاعية المدمرة في موقع التويته النووي. قيس تركيز النشاط الإشعاعي للمياه الملوثة قبل وبعد المعالجة باستعمال منظومة أطياف كاما المزودة بكاشف الجرمانيوم عالي النقاوة (HPGe) ذي كفاءة كشف نسبيه تصل الى 60%. أظهرت النتائج ان تركيز النشاط الإشعاعي للسيزيوم 137 قد انخفض بصورة ملحوظة من 4800 Bq/L الى 121 Bq/L، 186 Bq/L باستخدام 0.045 gm من الزيوليت 4A و DMZ على التوالي.

الكلمات المفتاحية: سيزيوم ¹³⁷Cs، تراكيب سلمية، معالجة النفايات السائلة، كربون مسامي، زيوليت نوع 4A