



COMPARATIVE STUDY BETWEEN REMOVERS AGENTS OF SILICON INTO THE SYNTHESIS OF MICRO/NANO-STRUCTURED PYROLYTIC CARBON FROM REFINED SUGAR

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Abstract

The present study deals with a comparison between HF and NaOH with different concentration, as removers agents of silicon into the synthesis of micro/nano-structured pyrolytic carbon (MNC) via nanocasting method, using SBA-15 as hard template. SBA-15 was prepared through sol-gel using pluronic P-123 as surfactant and tetraethoxysilane as a silicon precursor. MNC was synthesized by the nanocasting method and anhydrous pyrolysis at 800 °C using SBA-15 as structure directing agent and refined sugar as a carbon precursor. Testing six samples of MNC, the silicon removal was carried out employ solutions 1M NaOH, 2M NaOH, 4M NaOH, 8M NaOH, 8.6M HF and 28.9M HF by 24 h. The prepared materials were characterized by means of N₂ physisorption analysis, SEM, EDS, FTIR and Raman spectroscopy. EDS analysis revealed that 8.6M HF and 8M NaOH had the highest removal efficiency of silicon, detecting 0.21% wt Si and 0.32% wt Si respectively versus 23.8% wt Si before this process, however, using solutions of a low concentration of NaOH, a silicon weight percentage lower than 0.6% is detected. Therefore, the HF could be replaced by NaOH avoiding possible damage to the structure of MNC due to the effect of HF and contributing to the safety of researchers and the environment.

Introduction

The manufacturing process called molding dates back approximately 6000 years. This process, in broad strokes, consists in pouring a fluid material into a mold whose cavities have the desired shape, as the material solidifies, the mold is subtracted or broken to finish the process. This procedure is widely used in the industry until now. With the appearance of carbon nanotubes [1], a large number of investigations related to nanostructured materials have been carried out. Regarding the porous materials and according to IUPAC, a microporous material has pores with diameters less than 1 nm, mesoporous materials, diameters between 2 and 50 nm and a macroporous material, diameters greater than 50 nm [2]. The molding method on a nanoscopic scale properly called the nanocasting method and that essentially uses the same procedure described above, in 1997 was used for the first time, to manufacture microporous carbon materials using zeolites as a mold [3]. In 1998 the term nanocasting towards the synthesis of mesoporous materials is proposed [4]. At the end of the 20th century, Korean researchers synthesized a new species of micro and mesoporous carbon materials, using mesoporous silica materials (SBA-15, SBA-16, MCM-41) as a mold or template [5-6], which was removed or destroyed, using hydrofluoric acid (HF), a chemical compound at high risk and potentially lethal to humans. While it is true, the efficiency of removal of the mold by HF is high; its handling requires special care because it is a flammable reagent, very active, colorless and odorless. On the other hand it has been demonstrated that alkaline solutions with pH greater than 10 can completely dissolve silica-based vitreous materials [7]. In this research work, in order to determine the possibility of hydrofluoric acid replacement, a comparative study between HF and NaOH reagents, a strong acid and a strong base as silicon removal agents in the synthesis of micro/nano-structured pyrolytic carbon is proposed, which due to its physical, electrical and chemical properties has important applications as absorbents, electrodes for fuel cells and supercapacitors [8-9].



Materials and Method

Chemicals

Pluronic P-123 (non-ionic triblock copolymer, $\text{EO}_{20}\text{PO}_{70}\text{O}_{20}$), tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$, 98%), were obtained from Sigma-Aldrich. Deionized water, hydrofluoric acid (HF, 40%), hydrochloric acid (HCl, 37%), sulfuric acid (H_2SO_4 , 98%), sodium hydroxide (NaOH, 97%), were supplied by Fermont and refined sugar were obtained by Del Marques S.A.

Synthesis of SBA-15 (hard template) and SiO_2 -MNC nanocomposite

SBA-15 sample was synthesized according to the standard procedure [10] with some modifications. In a typical synthesis, 2.0 g Pluronic P-123 were dissolved in 14 mL deionized water and 60 mL of 0.6 M hydrochloric acid by stirring at room temperature for 5 h. Afterwards, 4.3 mL of tetraethoxysilane (TEOS) were added dropwise and the mixture was stirred (700 rpm) at 45 °C for 24 h. After, the mixture was aged in oven at 90 °C for 24 h. The white powder was obtained through filtration, washing and drying under vacuum. Finally, the sample was calcined at 550 °C for 6 h under air to obtain the silica template. SiO_2 -MNC nanocomposite was synthesized using a nanocasting pathway using SBA-15 as hard template and refined sugar as carbon precursor according to the procedure reported in the literature [11] with some modifications. In brief: 2 g of refined sugar and 2 g of SBA-15 were dissolved in 10 mL of deionized water by stirring at room temperature for 30 min, during this time 0.1 mL of sulfuric acid was added. The mixture was heated in an oven at 100 °C for 6 h, and subsequently 160 °C for another 6 h. The silica sample, containing partially polymerized and carbonized refined sugar and denoted by SiO_2 -MNC, was carbonized in a quartz furnace at 800 °C for 1 h under N_2 flow.

Silicon removal and obtaining MNC

The silicon removal was carried out under vigorous stirring using solutions 1M NaOH, 2M NaOH, 4M NaOH, 8M NaOH, 8.6M HF and 28.9M HF by 24 for each concentration. Finally, the carbon materials were obtained through filtration, washing with deionized water and drying in an oven at 80 °C for 12 h. The resulting carbon materials are denoted by MNC-1MNaOH, MNC-2MNaOH, MNC-4MNaOH, MNC-8MNaOH, MNC-8.6MHF and MNC-28.9MHF respectively.

Characterization and measurements

Textural properties (surface area, pore volume and average pore diameter) of the samples were determined by N_2 physisorption at 77 K, using a Quantachrome Autosorb-iQ equipment. The specific surface area was calculated according to the Brunaur- Emmet-Teller (BET) equation, while pore volume and average pore diameter, pore size distributions (PSDs) were obtained from the desorption branch of the nitrogen isotherm using the Barrett-Joyner-Halenda method. Before N_2 physisorption measurements, samples were desorbed at 623 K for 2 hours. The study of functional groups of the samples was made by means of infrared spectroscopy (conventional transmittance). The FT-IR spectroscopy study of samples has been realized in mid-IR region (4000-650 cm^{-1}) with a Nicolet iS 50 FT-IR spectrometer from Thermo Fischer Scientific. The morphology, particles size and composition (topography characteristic) were obtained in a microscope JEOL model JSM-7100F operating at 20 KeV and an EDS detector from Oxford Instrument. This microscope allows the superficial characterization of inorganic and organic materials (no conductive materials); in this case, the image is formed using an electron beam at 25 kV to low pressure (0.0012 bar) in the sample zone. Raman spectra were recorded on a LabRAM HR Raman spectrometer equipped with a 633 nm excitation red laser and an InGaAs detector. For each spectrum, an average of 10-50 scans were obtained with a laser power of 40-300 mW in the 1500-100 cm^{-1} range, with a resolution of 2-4 cm^{-1} in a LabRAM HR Raman spectrometer equipment. The conditions were: a resolution of 4 was used for the catalysts, and a laser power of 200mW and 20 scans; for the supports, a resolution of 8 and a laser power of 2000mW and 20 scans.

Results and discussion

BET Characterization

Fig. 1 shows the isotherms of adsorption/desorption of the SiO_2 -MNC nanocomposite and SBA-15 hard template, which present typical type IV isotherms with a significant H1 hysteresis (Fig. 1a), in addition to the carbon materials MNC-8.6 MHF and MNC-1MNaOH (Fig. 1b) which present type IV isotherms with a H4



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hysteresis [12]. The textural properties such as the specific surface area SA, pore volume PV and pore diameter D_p , for the materials SiO_2 -MNC, SBA-15 and all the carbon materials are shown in Table 1.

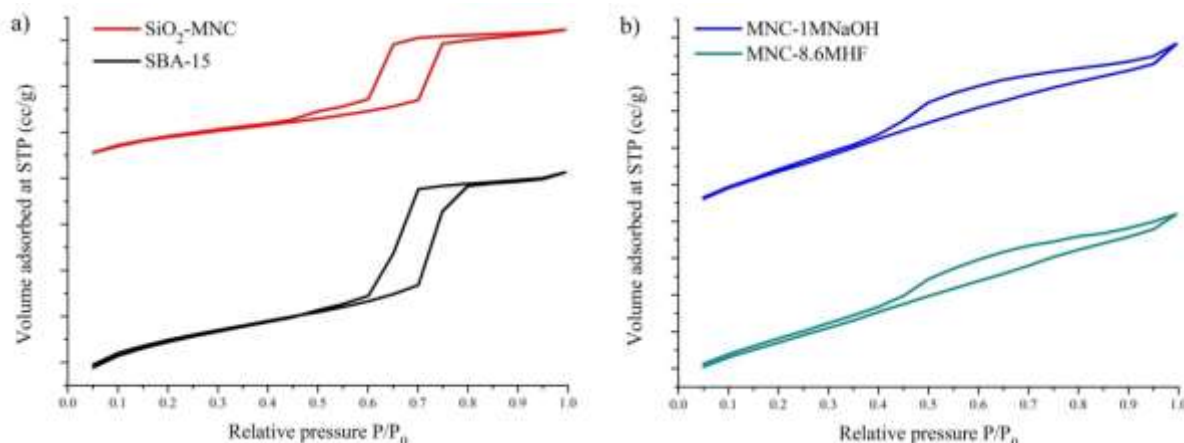


Figure 1: Nitrogen adsorption/desorption isotherms of a) SBA15 and SiO_2 -MNC, b) MNC-1MNaOH and MNC-8.6MHF

Table 1. Textural properties of hard template, SiO_2 -MNC nanocomposite and the micro/nano-structured carbon serial materials

Sample	SA (m^2/g)	PV (cc/g)	D_p (\AA)
SBA-15	872	0.96	78
SiO_2 -MNC	560	0.85	27
MNC-8.6MHF	1280	1.14	38
MNC-28.9MHF	1198	1.05	38
MNC-1MNaOH	1130	1.01	38
MNC-2MNaOH	1090	1.07	39
MNC-4MNaOH	1201	0.99	38
MNC-8MNaOH	1170	1.10	38

According to IUPAC, all the analyzed materials have a mesoporous structure. The decrease of specific surface area for the nanocomposite SiO_2 -MNC can be explained by the alteration of the pore diameter size of the SBA-15 template due to the inclusion of the carbon precursor (refined sugar in solution) within the channels or pseudo-cylindrical pores of the hard template [13]. On the other hand, the high specific surface area of all the micro/nano-structured carbon samples is characteristic of the mesoporous carbon materials, which is due to the fact that they are negative replicas of the SBA-15 mold, producing clearances between the fibers and carbon nanotubes that are formed during the pyrolysis process and by the presence of sheets with turbostratic carbon caused by excess of carbon that cannot penetrate into silica pores, and that is located on the surface of rope-like silica [14-16].

FTIR Analysis

The infrared spectrum in the average range of $4000\text{--}650\text{ cm}^{-1}$ of the SiO_2 -MNC nanocomposite is shown in Fig. 2 where it can be observed, the absorption band at 1048 cm^{-1} corresponding to the antisymmetric vibration in the group Si-O-Si that overcomes the possible bands due to the stretching vibrations of the Si-O-C, -C-O-O and Si-C groups, the absorption band at 807 cm^{-1} corresponding to the stretching vibration of the Si-O group [17] and a narrow band can be visualized in 1591 cm^{-1} corresponding to the symmetric vibration in the C = C double bond of the aromatic ring that forms the carbon hexagonal lattice.

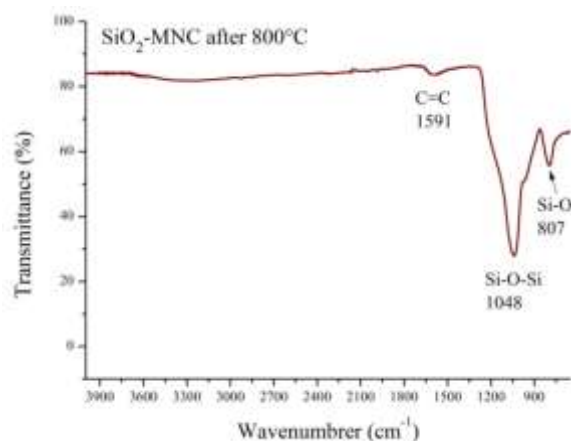


Figure 2: FT-IR spectrum of SiO₂-MNC nanocomposite

For the micro/nano-structured carbon serial materials, the functional group C=C appears at around the bands 1714 y 1557 cm⁻¹ (Fig. 3) in addition to a weak band around to 1019 cm⁻¹ due to the stretching vibrations of the C-C group that overlaps the carbonyl group C-O [18]. It is notable that in these last six materials the absorption bands corresponding to the Si-O-Si and Si-O groups no longer appear showing the efficiency of the hard template removal process.

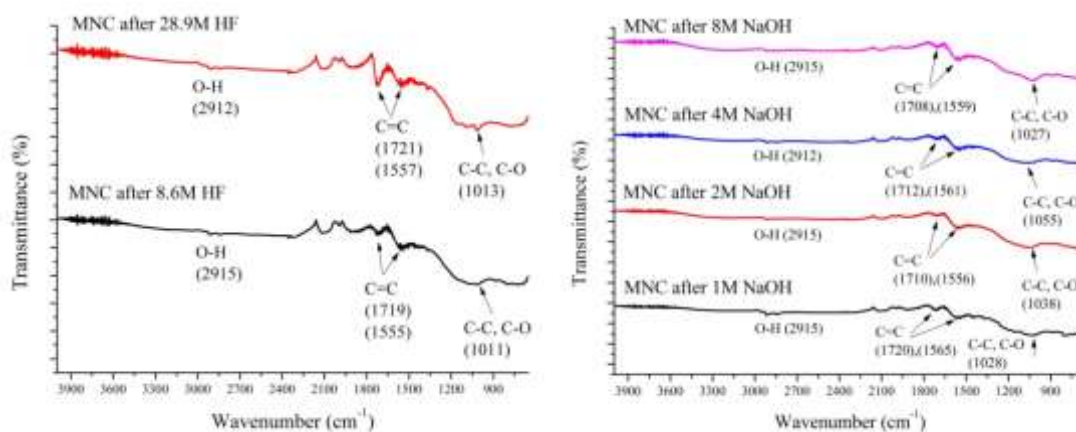


Figure 3: FT-IR spectra of the micro/nano-structured carbon serial materials

Raman spectroscopy

In the Raman spectra of the SiO₂-MNC nanocomposite (Fig. 4) and of all the carbon materials of the present comparative study (Fig. 5), the band G (narrow) can be seen in the range 1592-1600 cm⁻¹ corresponds to the Raman active mode of vibration E_{2g} of the movement in opposite directions of neighboring carbons in the hexagonal crystalline structure of the graphite, this indicates that the given materials achieved a crystalline phase, that is, a degree of graphitization. Also for all cases, the band D of medium amplitude but with different intensities can be seen in the range 1318-1340 cm⁻¹, which corresponds to the defects in the hexagonal mesh of the carbon graphitized by the sp³ hybridization [19], such defects can be attributed to the turbostratic carbon structure [20] and to the oxygenated groups that were formed after the hard template removal process [21].

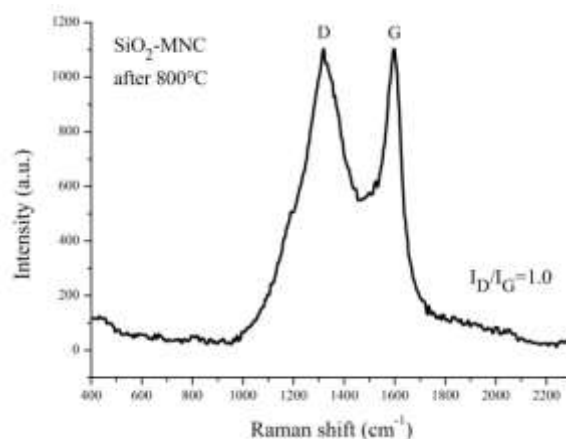


Figure 4: Raman spectrum of SiO₂-MNC nanocomposite

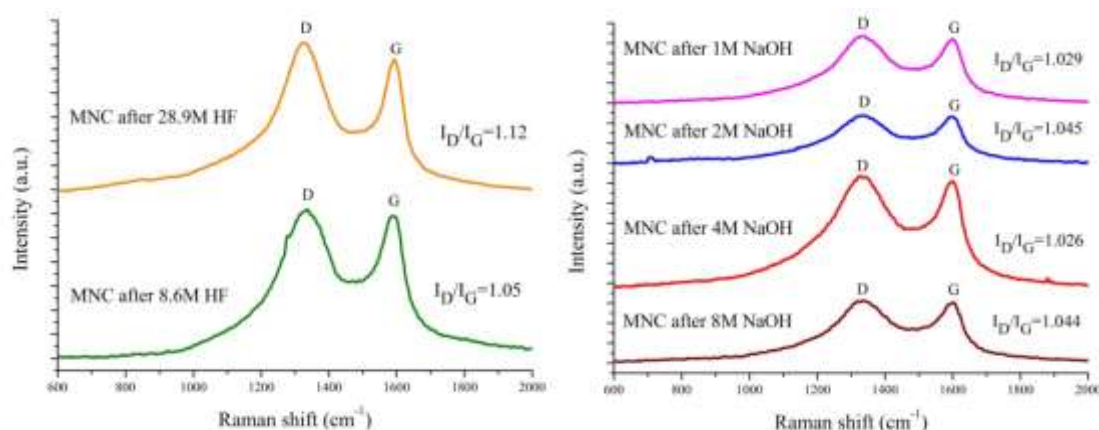


Figure 5: Raman spectra of the micro/nano-structured carbon serial materials

Taking the pristine structure of graphite as a base, the I_D/I_G ratio of the Raman intensities is proportional to the number of defects in the hexagonal carbon network and this is correlated to the degree of crystallinity of the same [22-24]. The Raman index for SiO₂-MNC was equal to 1, while for the carbon materials treated with HF and NaOH it was greater than 1, which indicates that they had a certain degree of disorder in the structure due to the rupture of the bonds between the carbonaceous fibers and a low composition of the oxygenated groups on their surface.

SEM and EDS analysis

The analysis of scanning electron microscopy using the GB-LOW mode at 2.0 keV and 9000 X of magnification, clearly shows the typical morphology of the SBA-15 mesoporous silica material consisting of elements micrometric with rope-like shape (Fig. 6a) of approximately 400 nm in diameter [25-26], likewise this analysis reveals the retention of this same morphology for the SiO₂-MNC nanocomposite (Fig. 6b) and the micro/nano-structured carbon materials MNC-28.9MHF (Fig. 6c) and MNC-8MNaOH (Fig. 6d) due to the nanocasting process. It can also be observed that these last two materials did not have structural alterations at the end of the silicon removal process, maintaining the aforementioned morphology. Similar results were obtained for materials MNC-8.6MHF, MNC-1MNaOH, MNC-2MNaOH and MNC-4MNaOH.

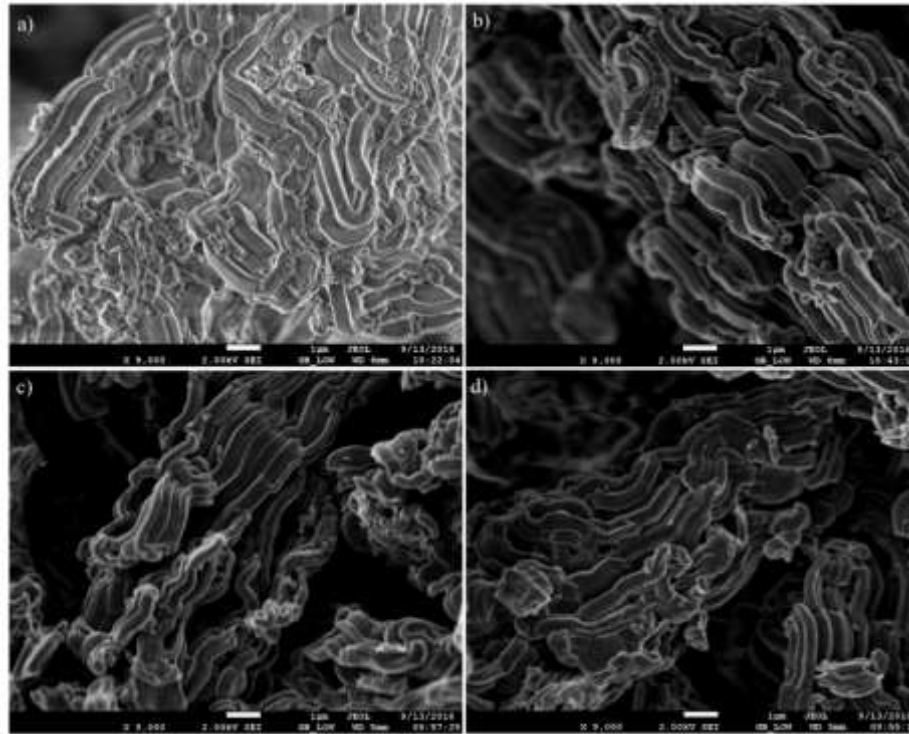


Figure 6: SEM images of a) SBA-15, b) SiO₂-MNC, c) MNC-28.9MHF and d) MNC-8MNaOH

The EDS spectra of all the samples are shown in Fig. 7, which determine the approximate elemental chemical composition. For the mesoporous silica material SBA-15, the presence of Si and O (typical components of this nanostructured material) can be observed [27], determining for silicon 32.39% wt. For the nanocomposite SiO₂-MNC, the carbon C signal appears due to the inclusion of refined sugar (95% C₁₂H₂₂O₁₁) in the pores of the SBA-15. The remaining spectra show the elemental chemical composition of the samples MNC-1MNaOH, MNC-2MNaOH, MNC-4MNaOH, MNC-8MNaOH, MNC-8.6MHF and MNC-28.9MHF subjected to the silicon removal process, in which it can be observed the presence of negligible amounts of F and Na as well as the decrease in the amount of oxygen.

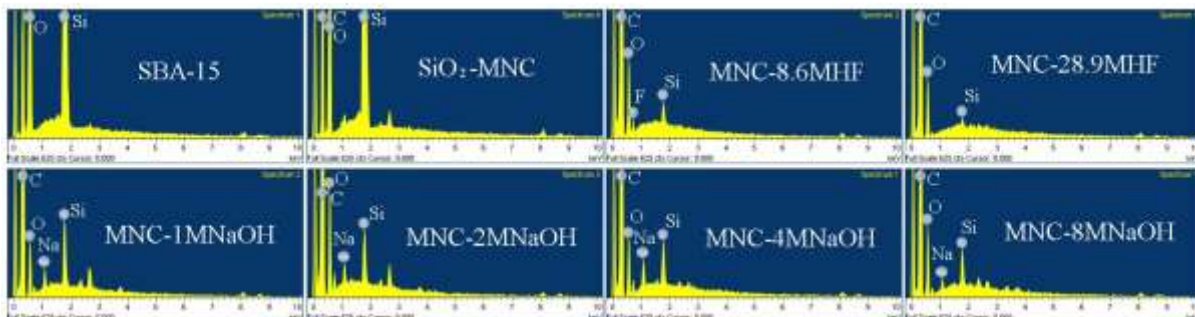


Figure 7: EDS spectra of SBA-15, SiO₂-MNC nanocomposite and the MNC carbon serial materials



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The quantitative results of the average elemental chemical composition of all the materials of the present study (Table 2) reveal a remarkable change in the weight percentage of silicon from the SBA-15 (32.39%) mold to the one obtained by the six samples after the silicon removal process, which at the most achieved 0.6% wt demonstrating the efficiency of the solutions of NaOH and HF that were used to remove the hard template [28], in addition to a notable decrease in the amount of oxygen according to the results of Raman spectroscopy.

Table 2: Average elementary chemical composition of all samples

Sample	EDS (% wt)				
	C	O	Si	F	Na
SBA-15	0	67.61	32.39	0	0
SiO ₂ -MNC	33.22	42.90	23.87	0	0
MNC-28.9MHF	86.11	12.48	0.22	1.19	0
MNC-8.6MHF	85.08	14.71	0.21	0	0
MNC-1MNaOH	87.41	11.63	0.42	0	0.54
MNC-2MNaOH	85.49	13.65	0.54	0	0.32
MNC-4MNaOH	86.64	12.07	0.57	0	0.72
MNC-8MNaOH	83.34	16.05	0.32	0	0.29

In accordance with the above analysis results and with respect to use of hydrofluoric acid [29] to silicon removal process, the possible pathway of this mechanism is shown in Fig. 8 in which the HF reacts with the silica (SiO₂) producing hexafluorosilicic acid (H₃O)₂[SiF₆] in vapour phase (1), besides causing the formation of oxygenated groups in the sp³ domain on the micro/nano-structured carbon surface, this agrees with the results of EDS and Raman spectroscopy.

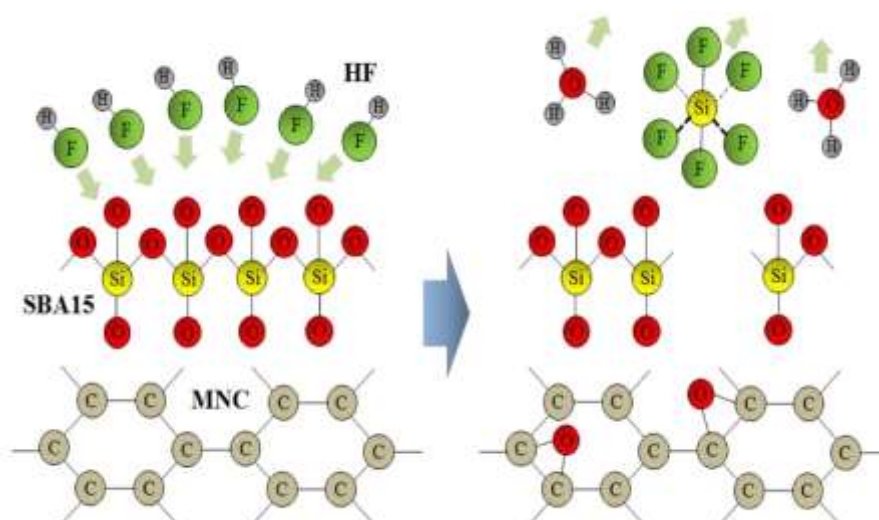


Figure 8: Possible pathway of silicon removal using HF solutions over SiO₂-MNC nanocomposite



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On the other hand, with respect to use of sodium hydroxide [30] to silicon removal process, the possible pathway of this mechanism (Fig. 9) involve the reaction of NaOH over the silica (SiO_2) producing sodium silicate (Na_2SiO_3) in aqueous solution (2) and besides causing the formation of oxygenated groups in the sp^3 domain on the micro/nano-structured carbon surface, in accordance with the results of EDS and Raman spectroscopy.

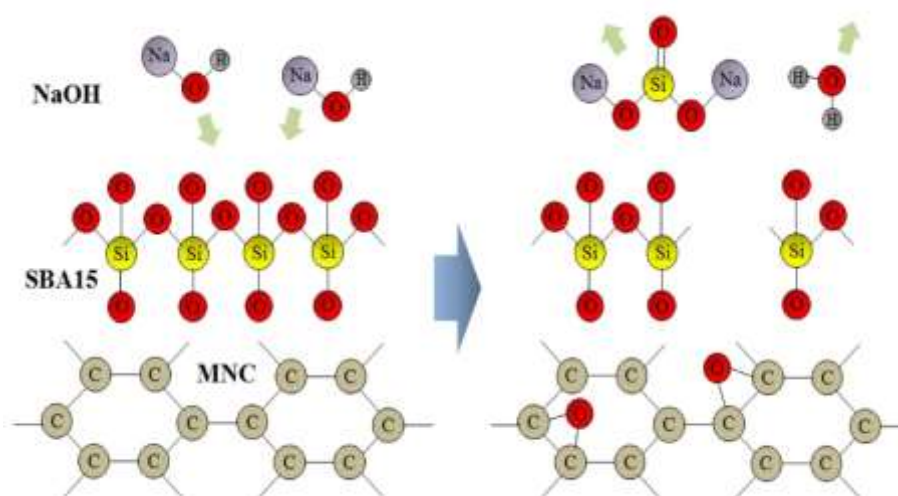


Figure 9: Possible pathway of silicon removal using NaOH solutions over SiO_2 -MNC nanocomposite

Conclusion

The results of the applied characterization techniques show that the solutions 1M NaOH, 2M NaOH, 4M NaOH, 8M NaOH, 8.6 M HF and 28.9 M HF applied to the six samples of the SiO_2 -MNC nanocomposite were able to remove the silicon from the hard template (SBA-15) at least 99%. It should be noted the independence of the concentration of NaOH producing all these, almost the same reduction in the percentage by weight of silicon in the process of removal of the mold. On the other hand, the micro/nano-structured carbon materials MNC-1MNaOH, MNC-2MNaOH, MNC-4MNaOH, MNC-8MNaOH, MNC-8.6MHF and MNC-28.9MHF had a rope-like morphology with a mesoporous structure and that did not suffer important alterations due to the corrosive nature of the mold removers used. Therefore, the HF can be replaced by low concentration NaOH solutions, considerably reducing the risks involved in hydrofluoric acid handling.

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