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Surface Amine Enrichment on Modified Microporous Carbon Spheres for Effective Removal of Contaminants of Emerging Concern (CEC)

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Abstract
Amine surface bonded microporous carbon spheres were previously synthesized from sucrose through hydrothermal reaction, KOH activation and amine-surface modification using 3-aminopropyltriethoxysilane (3-APTES)at room temperature. Results indicate the presence of Si-O-Si and -NH_2 groups on the surfaces of the synthesized material. In the present work, the amine groups were improved by further modifying the surface of the material with 2-methylaziridine which yielded more -NH_2 groups through hyper-branched polymerization. Evidences from SEM micrographs, FTIR spectra and TEM images indicate attachment of more amine groups to the product. The amine enriched product is envisaged to be more effective adsorbent for the separation of various contaminants of emerging concern (CEC) especially those that are nitrogen-containing from the environment.

Keywords: Amine, aziridine, carbon spheres, enrichment, modification.

Introduction
The use of chemical mixtures by the society keeps increasing and as a result, maintaining the environment clean becomes a challenging issue. Current studies have revealed the accumulation of used chemical substances in our water supplies, at home, work place and on the farm. These compounds are collectively referred to as contaminants of emerging concern (Díaz-Cruz *et al.*, 2009). The term contaminants of emerging concern do not mean that the contaminants are necessarily new, they may be contaminants that have been existing for a long time in the environment but whose appearance and effects are only recently identified. A number of definitions have been proposed to describe contaminants of emerging concern but until now, there is no single and internationally accepted definition for the contaminants. However, in most cases contaminants of emerging concern are considered to be those contaminants that have not been currently regulated but are subject to future regulation depending on their risks available data with regards to their occurrence (Barcelo´, 2003).

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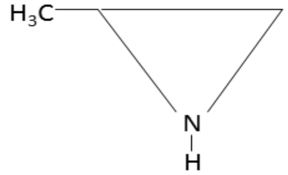
These compounds are collectively considered as a source of threats to the general environmental ecosystems as well as human health and safety (Farré *et al.*, 2008). Some examples of relevant contaminants that have emerged at present time include pharmaceuticals and personal care products (PCP), gasoline additives, nitrosamines and surfactants. Others include drugs of abuse, flame retardants, steroids and hormones, industrial additives and agents, together with their transformation products (TPs) and perfluorinated compounds (PFCs). Once introduced into the environment, these contaminants are passed through different degradation processes especially photo/chemical degradations and biodegradation which significantly play a role in their removal. Despite their high transformation or removal rates, these groups of contaminants still pose some threats because of their frequent exposure into the environment (Damià, 2003).

Carbon spheres (CSs) are spherical form of carbon having either semi-crystalline or crystalline structure with solid, hollow or core shell morphology. The spherical carbons include carbon blacks, carbon onions and carbon microbeads (Deshmukh *et al.,* 2010). Different techniques mainly high temperature pyrolysis, chemical vapour deposition (Auer *et al.,* 1998), hydrothermal treatment (Miao *et al.,* 2004), and arc discharge (Chen *et al.,* 2007) have been employed in the synthesis of carbon spheres.Activated form of carbon spheres were found to possess properties like high specific areas, uniformity, high thermal stability and excellent conductivities which make them useful as catalyst support (Qiao*et al.,* 2006), adsorbents and super capacitors (Li *et al.,* 2011), and also in hydrogen storage and drug delivery (Chua *et al.,* 2010; Rosenholm*et al.,* 2006).

In recent times, there has been a great interest in the synthesis, activation and surface modification of carbon spheres. The current synthetic techniques have given rise to spheres with diverse range of sizes and surface properties. A few findings were published in literature related to the synthesis, activation and modification of carbon spheres (Deshmukh *et al.,* 2010; Rodriguez-Rrinoso*et al.,* 2002). A wide range of carbon sources have been used to make CSs. These sources vary from methane to glucose and include PAHs, carbon oligomer and polymers. Typically, the carbon source is polymerized at high temperature and in the process smaller molecules such as water, carbon monoxide and carbon dioxide are eliminated. The sphere surface is non-ideal and consisted of graphite flakes that contain functional groups (COOH, OH, etc.). These groups can be converted or modified into other organic groups by conventional organic chemistry procedure (Deshmukh *et al.,* 2010).

Aziridines have recently attracted considerable attention in synthesis as they are reactive intermediates which can be opened with a variety of nucleophiles such as amines, alcohols, thiols or carbanionic species (Josiane and Vincent, 2004).Several workers have reported the use of aziridines to functionalize carbon and other materials. Few of these findings include aziridine-functionalized graphene (Sanjeev *et al.,*2019) and aziridine-functionalized mesoporous silica membranes(Hyung *et al.,* 2015).

The hydrophobic nature of the most commonly used adsorbent (activated carbon) results into low recoveries of highly polar contaminants of emerging concern (Nawrocki and Andrzejewski, 2011). Therefore, development of novel materials with suitable structure and better adsorption properties is highly important. Previously, no exact work on modification of microporous carbon spheres using 3-APTES coupled with aziridine was reported. The present work focuses on the enrichment of amine groups onto amine-modified microporous carbon spheres using2-methylaziridine. The resulting product is anticipated to have high affinity for nitrogen containing contaminants of emerging pollutants such as the nitrosamines due to similar surface groups interactions. Future studies will involve application of the modified material as an adsorbent in environmental analysis.



The structure of 2-methylaziridine

Materials and Methods

Reagents

All reagents (trichloromethane and 2-methylaziridine) were of analytical grade supplied by Sigma Aldrich (Madrid, Spain) and used without further purification. High purity deionized water was obtained from a Milli-DI water purification system (Molsheim, France).

Synthesis of Amine Surface Bonded Microporous Carbon Spheres using 3-APTES

The synthesis of amine surface bonded microporous carbon spheres using3-aminopropyltriethoxysilane (i.e. MCSs-3-APTES)was carried outin our previous studiesaccording to stages A, B through C as in Figure 1(Musa *et al.*, 2015a; Musa *et al.*, 2015b).

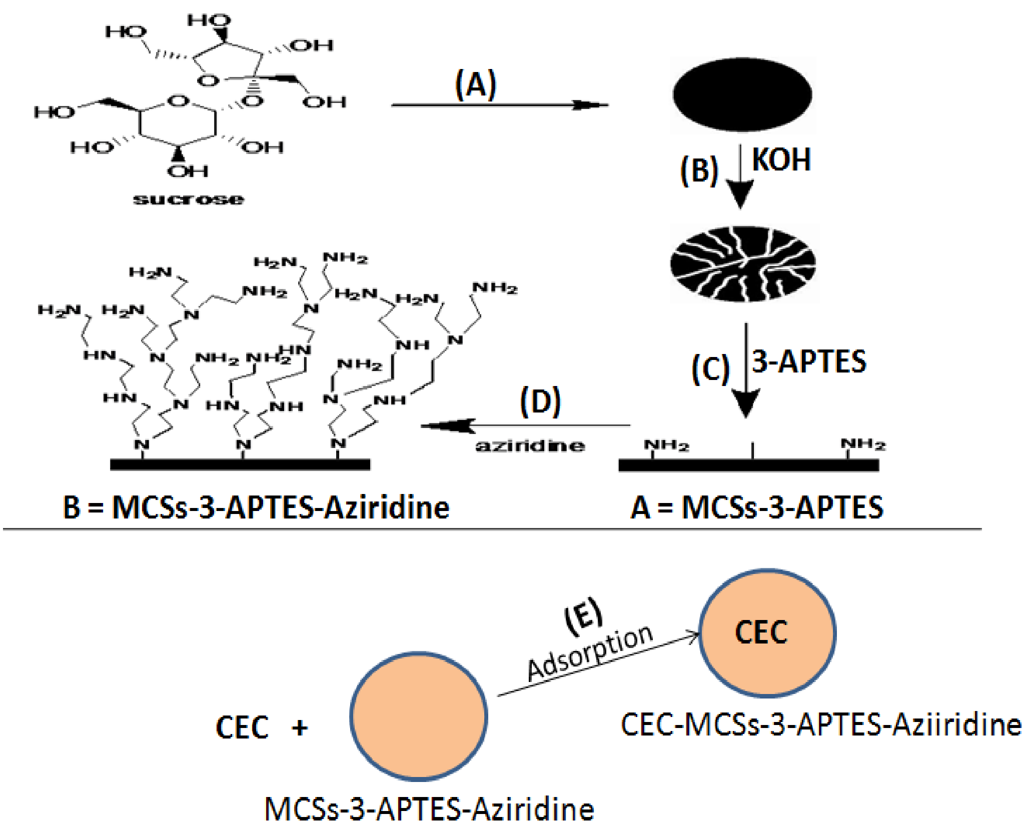


Figure 1: General approach for the synthesis, modifications and application of MCSs

Synthesis of Amine Enriched Microporous Carbon Spheres
The amine enrichment carried out in this study was a continuation of stage C to D of Figure 1. To2 g of MCSs-3-APTES in $CHCl_3$, 2 mL of 2-methylaziridine was added. The mixture was heated mildly at 45ºC for 4 hr. After cooling to room temperature, the product was washedwith$CHCl_3$. Using the same solvent, the washing was continued daily for 2 days to remove any unreacted aziridine. Finally, the product was dried under vacuum andheatedat120ºCfor20hrpriorto characterization (Britt *et al.,* 2010).

Characterization
Characterizations of the amine enriched product were carried out on version 5.3 Perkin Elmer FTIR spectrometer, JEOL JSM6390LV scanning electron microscope (SEM) andJEOL-JEM-2100 transmission electron microscope (TEM).

Results and Discussion
The synthesis of MCS-APTES-Aziridine was believed to proceeded through hyper-branched polymerization (Figure 1). This is in agreement with Chang *et al.* (2004) who reported the achievement of surface modification of indium-tin oxide with aziridine to have occurred through facile ring-opening and hyperbranching polymerization initiated from the reactive group on the surface which yielded a surface with high amine density.

Figure 2 provides the FTIR spectra of amine bonded microporous carbon spheres modified using 3-APTES only (MCSs-3-APTES) and that of amine enhanced microporous carbon spheres modified with both 3-APTES and aziridine (MCSs-3-APTES-Aziridine). Both spectra appeared very similar to each other probably because the aziridine modification did not significantly change the structure of the MCSs-3-APTES. The strong and broad band at 3789 and 3401 cm^{-1} are attributed to the presence of hydroxyl groups (-OH) on the surfaces of the CSs, which presumably resulted from atmospheric moisture. This indicated that a large number of -OH groups are found on the surfaces of CSs. Another band appeared at 2923 cm^{-1} giving information on C-H groups which is consistent with Deshmukh and co-workers where they reported that CSs show a major band between 2850 and 2920 cm^{-1} indicating C-H groups (Deshmukh *et al.,* 2010).The band at 1558 cm^{-1} in two spectra are assigned to NH_2 scissors frequencies (Lin-Vien*et al.,* 1991).

Comparing the band intensity for the NH_2 groups, it will be observed that the NH_2 band in the case of MCSs-3-APTES-Aziride is more intensethan that in MCS-3-APTES signifying more of the NH_2groups attached to the surface of MCSs-3-APTES-Aziridine.

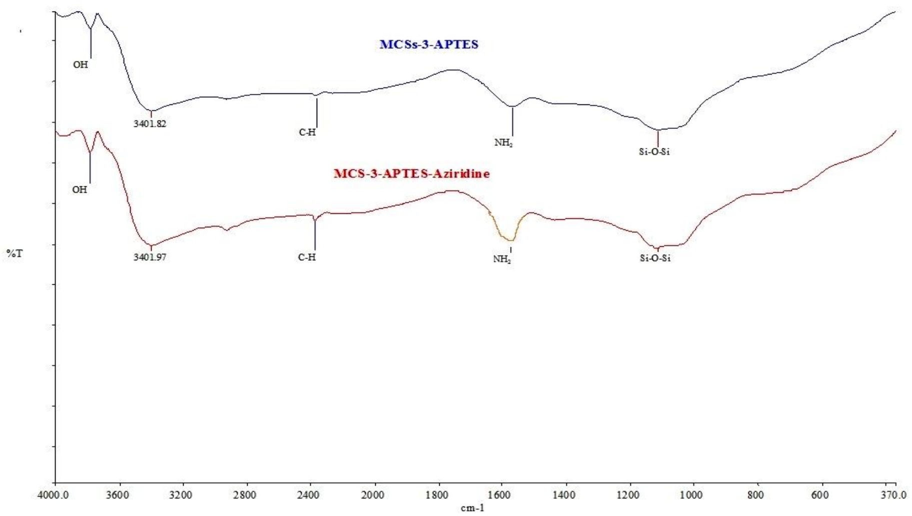


Figure 2: FTIR spectra for MCSs-3-APTES and MCSs-3-APTES-Aziridine.

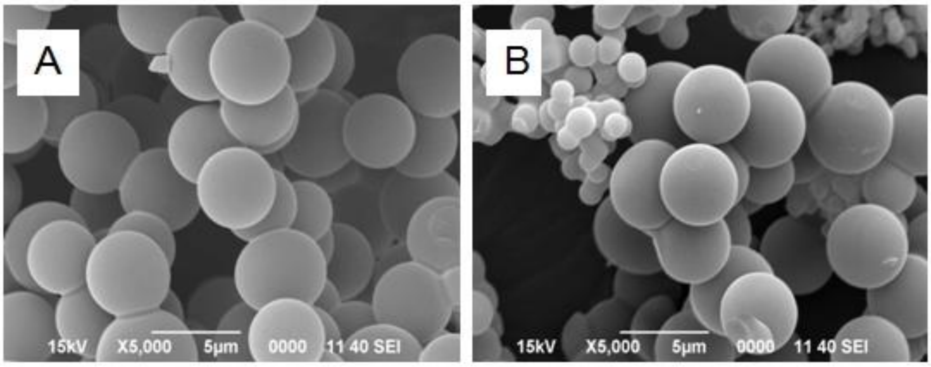


Figure 3: SEM micrographs of MCSs-3-APTES (A) and MCSs-3-APTES-Aziridine (B).

From Figure 3B, it can be observed that nodistortion of spherical shape was observed on MCSs-3-APTES-Aziridine after the modification and this infers that the MCSs-3-APTES (Figure 3A) are strong enough to withstand modification with aziridine.This is in line with Giulia *et al,*(2016) for their successful functionalization of multiwalled carbon nanotubes using aziridine without structural distortion. The insignificant change in morphology observed indicates that the functionalizing process does not play any obvious role in swelling or destruction of the MCSs-3-APTES.

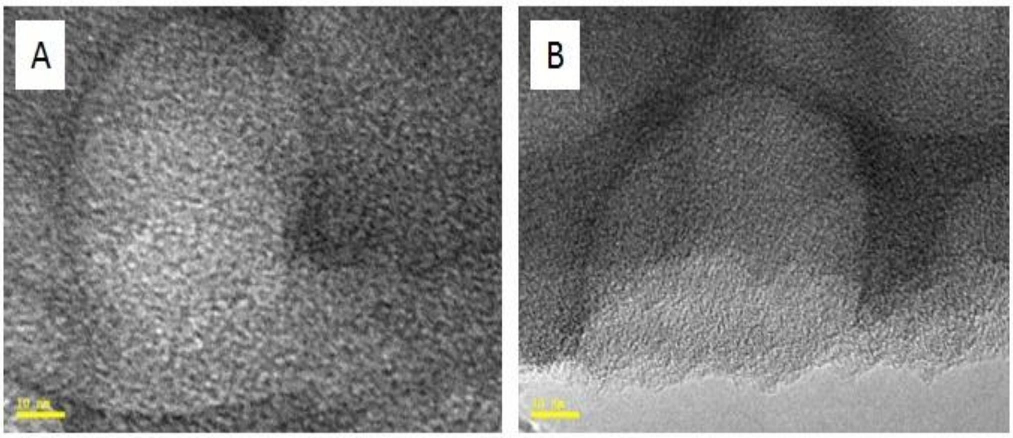


Figure 4: Magnified TEM images for MCSs-3-APTES (A) and MCSs-3-APTES-Aziridine (B)

Observing the magnified TEM images in Figures 4(A) and (B), it is clear that after aziridine modification of MCSs-3-APTES there is decrease in the porosity (Figure 4B)compared to MCSs-3-APTES(Figure 4A) which could be due to pore channels blockages by some of the functionalizing groups (Rodriguez-Rrinoso*et al.,* 2002), NH_2 in this case. Another evidence is from a study reported by Gibson *et al.* (2015) on microporous and mesoporous carbons which showed blocked fraction of the micropore volume for gas adsorption.

Conclusion

Attachment of amine groups on the surfaces of amine bonded microporous carbon spheres was successfully carried out using 2-methylaziridine. The morphology and attachment of the amine groups onto the surfaces of MCSs-3-APTES were confirmed by TEM and FTIR analyses. It is anticipated that the modified material will exhibit excellent extraction efficiency towards nitrogen-containing contaminants of emerging concern (CEC) due to its porosity and presence of more amine groups which may give rise to chemical similarities between the material and target analytes. Future studies will involve application of the modified material as an adsorbent in the extraction of contaminants of emerging pollutants (CEC) especially those containing nitrogen amine groups e.g. nitrosamines from the environment.

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