



Effect of basicity on amination of activated carbon pellets modified for CO₂ adsorption

Adedeji A. Adelodun

Department of Environmental Science and Engineering,
Kyung Hee University,
Yongin, Gyeonggi-do, 446-701, South Korea

adedejiaadelodun@yahoo.co.uk

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ABSTRACT

Acid pre-oxidation was used on activated carbon (AC) pellets to increase the amount of oxygen complexes that could serve as sites for creating surface nitrogen functionalities (SNFs) during amination. Four acids with different basicity (HNO₃, H₂SO₄, H₃PO₄) and H₂O₂ were used as pre-oxidants. The study of pH_{pzc} showed that H₂SO₄ and H₃PO₄ induced highest acidity on AC whilst non-acidic H₂O₂ had the least effect. Results of textural examination indicated that H₂SO₄ brought about highest depreciation to the sample's textural properties whilst H₂O₂ somehow improved them. Upon amination, both the structural and basic properties were improved. Based on the amount of SNFs created, the efficiency of the oxidants follows this trend HNO₃ > H₃PO₄ > H₂SO₄ > H₂O₂. Pure CO₂ adsorption test revealed that adsorption capacity of the modified adsorbents depend largely on the available surface area and micropore proportion, while 10% CO₂ adsorption rely both on the proportion of micropores (V_{micro}/V_T) and the nature and amount of SNFs. Consequently, pre-washing with either H₂O₂ or H₂SO₄ is most efficient for pure CO₂ adsorption at ambient condition while H₂SO₄ or H₃PO₄ pre-washing seems more efficacious for selective CO₂ capture.

Keywords: Activated Carbon; CO₂ adsorption; Amination; Pre-oxidation; Surface chemical functionalities.

1. Introduction

In recent years, the global environment has been subjected to various degradation and discomfort caused majorly by anthropogenic activities. One of the major concerns of today is global warming, courtesy of the huge and incessant increase in the average concentrations of greenhouse gases, especially CO₂ (Plaza et al., 2008). Despite having the least global warming potential (GWP), CO₂ has attracted highest attention, being the one produced in largest amount worldwide. According to experts, to combat climate change, the total emission of CO₂ from various sources of fossil fuel combustion has to be significantly cut, else the CO₂ mitigation option for the already-in-use combustion designs that emit large quantities, is to capture and sequester (CCS) or capture and utilize (CCU) the gas after combustion (Arenillas et al., 2005; Xu et al., 2005; Plaza et al., 2007). Adsorption presents itself as one of the viable alternative CO₂ containment techniques to already established absorption technology, hence the development of an efficient, readily available, and low-cost with high reusability has become salient research interest of recent.

The use of activated carbon (AC) as an adsorbent in gaseous phase suffices when those aforementioned properties are considered and many works have been done to improve the selective dry scrubbing of CO₂ from flue gas (Radosz et al., 2008; Pevida et al., 2008; Plaza et al., 2009; Shafeeyan et al., 2011; Wan Daud et al., 2010). Being an adsorbent with numerous and readily available precursors (Zhu et al., 2000; Aksoylu et al., 2001; Houshmand et al., 2010; Adelodun and Jo, 2013), some surface modifications have been performed to improve its surface basic property, thereby enhancing its ability to discriminately attract CO₂ from flue gas matrix (Shafeeyan et al., 2010). Amination (thermal decomposition of NH₃ at high temperature to produce very reactive radicals ·NH_x) has been used in this respect and promising results have been reported (Shafeeyan et al., 2011; Pevida et al., 2008; Przepiorski et al., 2004). These radicals could replace thermally desorbed surface oxygen functionalities (SOFs) on the carbon surface to promote the formation of basic surface nitrogen functionalities (SNFs) which bear free pair of electrons for CO₂ attachment.

Many wet oxidants have been used for surface modifications of carbon materials depending on pre-determined purposes (Jaramilo et al., 2010; Otake and Jenkins, 1993; Adelodun et al., 2012). In order to provide sufficient SOFs on the AC surface, the use of mineral acids was experimented in this work. Here, monoprotic (HNO₃), diprotic (H₂SO₄), triprotic (H₃PO₄) acids were used and compared with a wet oxidant (H₂O₂) for the purpose of pre-oxidation.

The CO₂ level in flue gas is about 4-15 % depending on fuel type, fuel purity, combustion efficiency, presence of additives etc (Figueroa et al., 2008; Shafeeyan et al., 2012). In this study, 10 % CO₂ in a binary mixture with N₂ and pure CO₂ feeds were used for selective and capacity adsorption tests respectively.

2. Materials and methods

2.1 Materials

Raw activated carbon WSC-470 (R), a commercially available pelletized coconut-shell based AC, procured from Calgon Carbon Corporation USA, was used as starting material. It has average diameter of 4.05 ± 1.22 mm and different lengths, ranging from 5.4 to 10.8 mm.

Mineral oxidants and other reagents used in this study were procured from Daejung Chemicals Co. LTD, Korea. Samples' densities were measure with the aid of Micrometrics Accupyc 1330, Gas Pynometer (Model No 133/34012100), supplied by One Micrometrics, USA.

Surface and pore size distributions were examined using BelSorp II mini, supplied by BEL Japan, Inc. Ultimate analysis was carried out with an automatic elemental analyzer Flash EA 1112 (CE), while the nature of impregnated surface chemical functionalities was determined by X-ray photo-electron spectroscopy (XPS) with the use of K-Alpha (Thermo-electron) X-ray photoelectron spectrometer.

2.2 Method

2.2.1. Wet pre-oxidation

About 20 g of pre-cleaned RAC was placed into four identical 200 mL pirex bottle and 100 mL of 2 M HNO₃, H₂SO₄, H₃PO₄, H₂O₂, was added. The contents were gently agitated for 5 min and filtered. This was followed by thorough and copious washing with deionized until pH of the filtrate was approximately neutral, after which the carbons were collected and dried in a vacuum at 120 °C for 12 h. The oxidized samples were cooled in a desiccator and name-tagged accordingly. Prefix "O" indicates oxidation while N, S, P and H denoted HNO₃, H₂SO₄, H₃PO₄ and H₂O₂ respectively, hence four pre-oxidized ACs namely O-N, O-S, O-P and O-H were obtained.

2.2.2. Amination

About 10 g of pre-oxidized R was placed in a quartz reactor clamped into a vertical furnace (Fig. 1). N₂ was used to degas and subsequently decompose the SOFs on the pellets as the temperature was ramped up to 800 °C. At this temperature, the gas flow was switched to pure NH₃ and kept for 2 h, after which heat was retrieved by allowing the system to cool to 100 °C before the gas flow was changed back to N₂ while the reactor further cools to ambient temperature. The prepared adsorbents were name-tagged accordingly by substituting "N" for "O", indicating the replacement of SOFs by SNFs, i.e. N-N, N-S, N-P and N-H respectively.

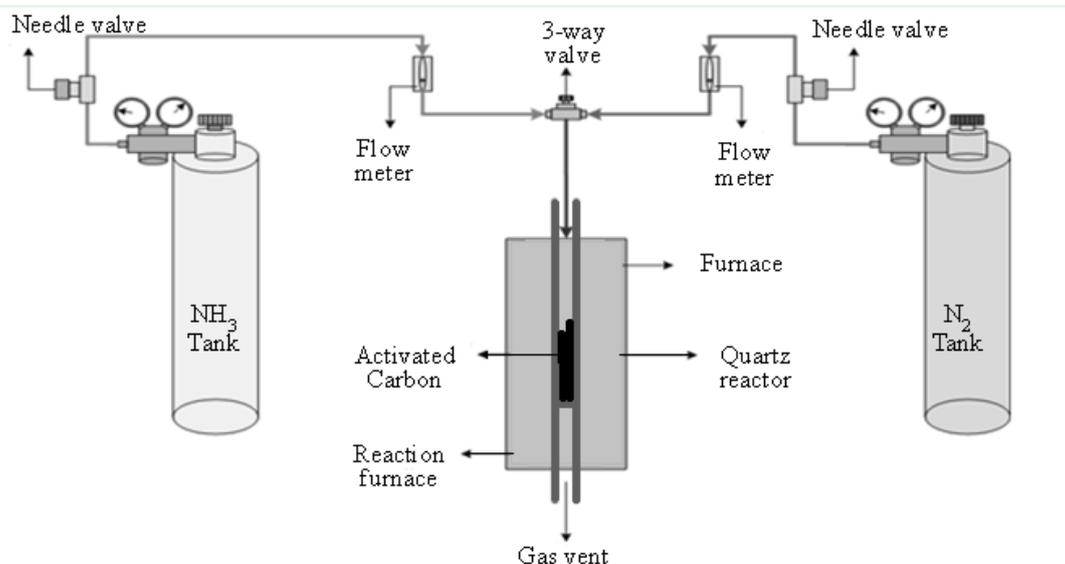


Fig.1. Amination setup

2.2.3. pH_{pzc}

In order to determine the samples' surface pH at point of zero charge, recent modifications made available to Noh and Schwarz's method (Noh and Schwarz, 1989) was studied. A proposed mass titration technique suggested was employed for this study (Fiol and Villaescusa, 2009).

2.2.4. Ultimate and X-ray photo-electron spectroscopic analyses

Ultimate analysis was carried out with an elemental analyzer in order to ascertain the effectiveness of both pre-treatment and amination by estimating respective changes in percentage % O and N. XPS results were processed with the aid of XPSPEAK41 software, using the assigned binding energies, given in the Table 1.

Table 1 Assigned binding energies for XPS spectra peak deconvolution (Biniak et al., 1997)

Sample	O 1s spectra	BE peak (eV)	N 1s spectra	BE peak (eV)
Peak 1	Carbonyl , quinone	531.1	Nitride-like/ aromatic N-imines	395.7
Peak 2	Hydroxyl, ethers	532.2	Pyridine type N	398.4
Peak 3	Lactone, ester and anhydrides	533.3	Pyrrole, pyridone N	400.1
Peak 4	Carboxylic acid	534.2	Quaternary-N	401.2
Peak 5	Chemisorbed H_2O or O_2	535.3-536.1	Pyridine-N-oxides	402.4

2.2.5. CO₂ adsorption test

Selective CO₂ adsorption capacity was obtained by weighing 2 g of test adsorbent into a stainless reactor which was placed in the set-up depicted in Fig. 2.

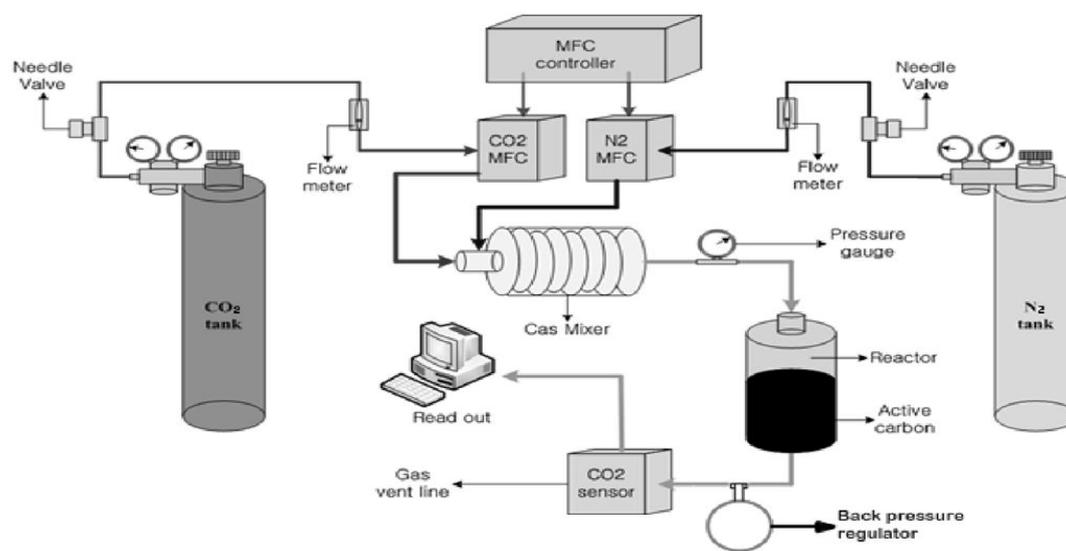


Fig.2. 10% CO₂ adsorption setup

The gas sensor (a product of SENSEair) was calibrated by a MFC controller as measurements were carried out at different temperatures (room 25 ± 2 °C (RT) and lowered temperature 0 °C (LT)) and pressures (1 and 6 bar). High pressure (6 bar) adsorption was achieved with the aid of a back pressure regulator which was read on a pressure gauge. The amount of CO₂ adsorbed (q), in mmol per gram of carbon was obtained by this mathematical expression:

$$q = \frac{Q \cdot C_0 \left(1 - \frac{C}{C_0}\right) t}{W} \quad (1)$$

where Q = the inflow rate of CO₂ (500 cm³), C_0 = CO₂ inflow concentration (100,000 ppm), C = CO₂ outflow concentration (ppm), t = CO₂ sensor intermittent read time (s) and W = mass of test sample (g). Since the amination conditions were kept constant for all the samples, observed significant differences in the CO₂ adsorption performances could be attributed to the efficiency of the oxidants. Pure (100 %) CO₂ adsorption capacity was measured with the aid of BelSorp II, calibrated for CO₂ adsorption test under specific conditions.

3. Results and discussion

3.1 Study of surface pH by point of zero charge

The pH_{pzc} of R was predetermined as 9.8, characteristic of carbons steam-activated at high temperature. Fig. 3 presents the pH_{pzc} profile of acid washed samples. It is apparent that H₂SO₄ incorporates largest number of SOFs as it reduces the surface pH of R from 9.8 to 2.1. Such acidification was closely achieved by H₃PO₄ which induced pH_{pzc} of 2.5 on the carbon. HNO₃ mildly increased the surface acidity to 6.3 whilst, as expected, H₂O₂ showed least impact.

After amination, the pH_{pzc} of prepared sorbents were also determined. The obtained profiles are depicted in Fig. 4. At a glance, there were no corresponding wide differences as it was observed after acid-washing (Fig. 3). Here, the pH_{pzc} were of close values, irrespective of the acidity achieved from the pre-oxidation step, with N-H, N-S and N-N having similar pH_{pzc} values of 10.5, 10.4 and 10.3 respectively while N-P has 9.7. This result indicates that some surface functionalities incorporated hugely by sulfuric and phosphoric acids might be insignificant in the amination process. Besides that, the carbon could have a limit at which it could be basified irrespective of the efficiency of pre-oxidation used.

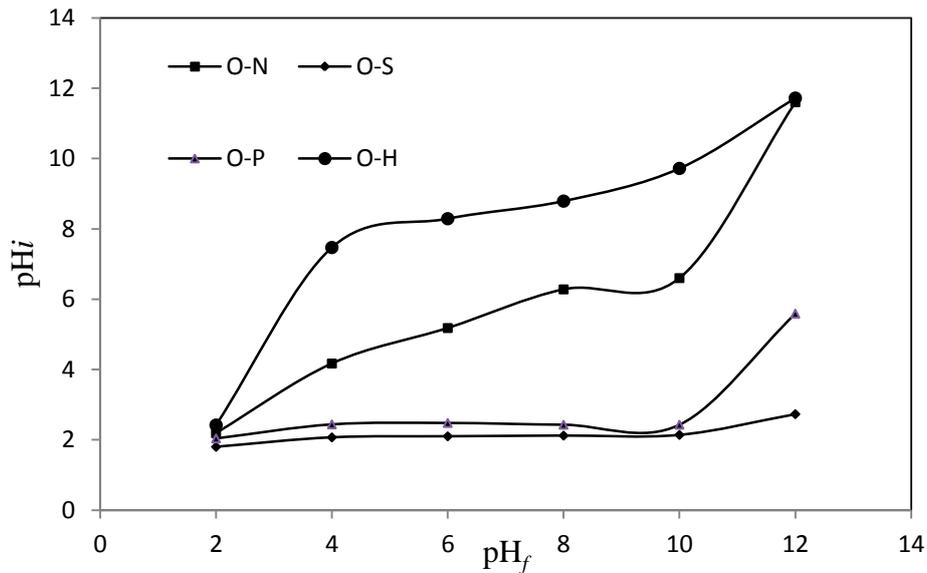


Fig.3. pH_{pzc} profiles for oxidized pellets.

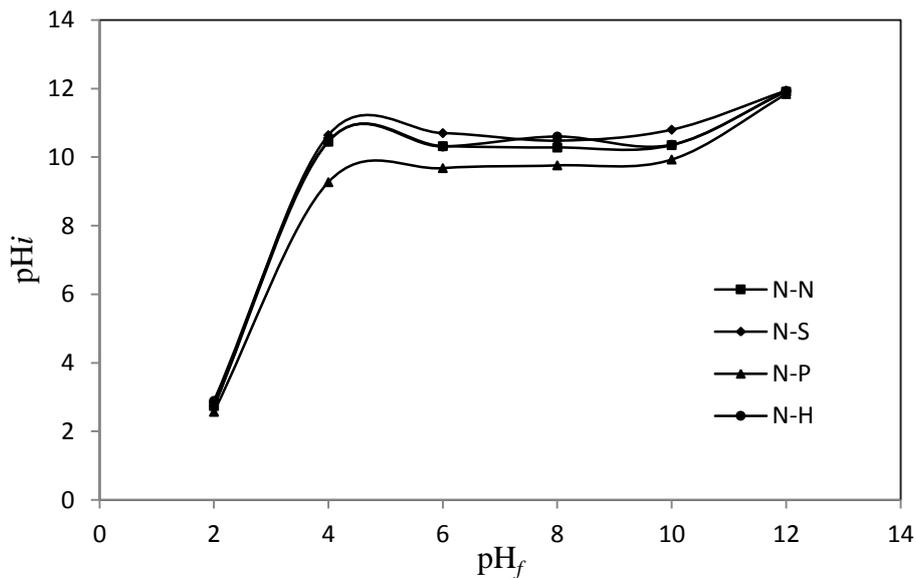


Fig.4. pH_{pzc} profiles for aminated pre-oxidized pellets.

3.2 Textural properties

Physical modifications made by the wet oxidants were assessed in terms of specific surface area (S_{BET}) and pore size distribution, as shown in Table 2. The acids generally showed depreciation in the S_{BET} but an enhancement was observed with the use of H_2O_2 . H_2SO_4 brought about highest textural degradation followed by H_3PO_4 . It was observed that acid washing tends to collapse some graphene sheets, resulting in decrease in pore diameter observed in the test carbons. Unlike the acids, H_2O_2 seems to improve the S_{BET} as well as the microporosity of the carbons.

Table 2 Results of textural properties of RAC and treated samples

Sample	S_{BET} (m^2/g)	BET Total pore volume V (cm^3/g)	Pore diameter (nm)	MICROPOROSITY		MESOPOROSITY	
				Pore volume v (cm^3/g)	Pore area (m^2/g)	Pore volume (cm^3/g)	Pore area (m^2/g)
R	1221.05	0.574	1.881	0.483	1123.9	0.091	97.1
O-N	1218.30	0.560	1.839	0.454	1104.7	0.106	113.6
O-S	779.88	0.337	1.732	0.297	741.4	0.039	38.4
O-P	864.55	0.388	1.795	0.323	798.8	0.064	65.7
O-H	1299.81	0.574	1.766	0.490	1211.9	0.084	87.8
N-R	1172.95	0.578	1.976	0.455	1037.9	0.123	134.9
N-N	1040.42	0.454	1.745	0.394	978.5	0.059	61.9
N-S	1146.66	0.506	1.746	0.436	1079.8	0.064	66.8
N-P	1174.05	0.514	1.751	0.442	1095.6	0.072	78.4
N-H	1168.01	0.501	1.689	0.433	1088.0	0.067	79.9

The microporosity of an adsorbent has been described as key in the physisorption of small size gas molecules such as CO_2 [8]. In this light, the proportion of microporosity is examined and reported (Fig. 5).

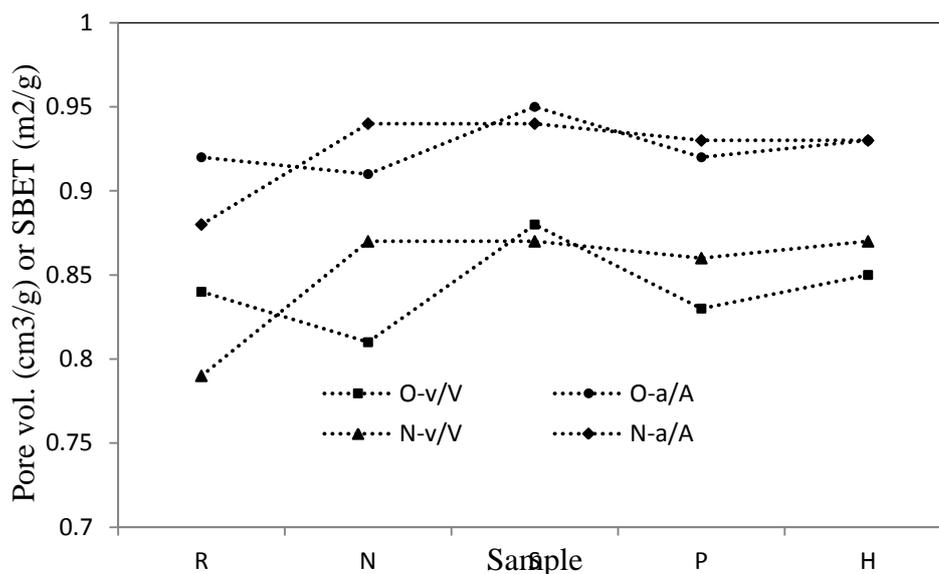


Fig. 5. Correlation between microporosity proportions of all test samples.

Note: O-v/V and O-a/A are proportions of micropore volume and surface area of oxidized samples respectively, while N-v/V and N-a/A represent those of prepared adsorbents after amination. Here and henceforth, broken lines will be used to enable easy correlation and NOT to indicate trend.

As lucidly shown, there was no huge discrepancy in the differences brought by amination to v/V and a/A amination (N-v/V and N-a/A). This could either indicate the redundancy of pre-oxidation or the reproducibility of the amination step.

3.3 Assessment of sample's density

The study of densities could indicate the extent by which the carbon structure has been distorted, either by collapsing the layers resulting in higher values or by enlarging the pore spaces, thereby lowering the density. Those of oxidized carbons, along with the aminated ones are reported in Fig. 6. All acid-washed carbons exhibited significant decrease in density. H₂SO₄ induced the largest depreciation as the density of R was reduced from 0.446 g/cm³ to 0.241 g/cm³, indicating that ca. 48% of the graphitic carbon was lost to the oxidation. Some fine carbon particles were left in the solution after the oxidative treatment, showing intense etching on the graphene structure. The highly exothermic oxidative power of H₂SO₄ could be attributed to its staggering effect on the carbon particles.

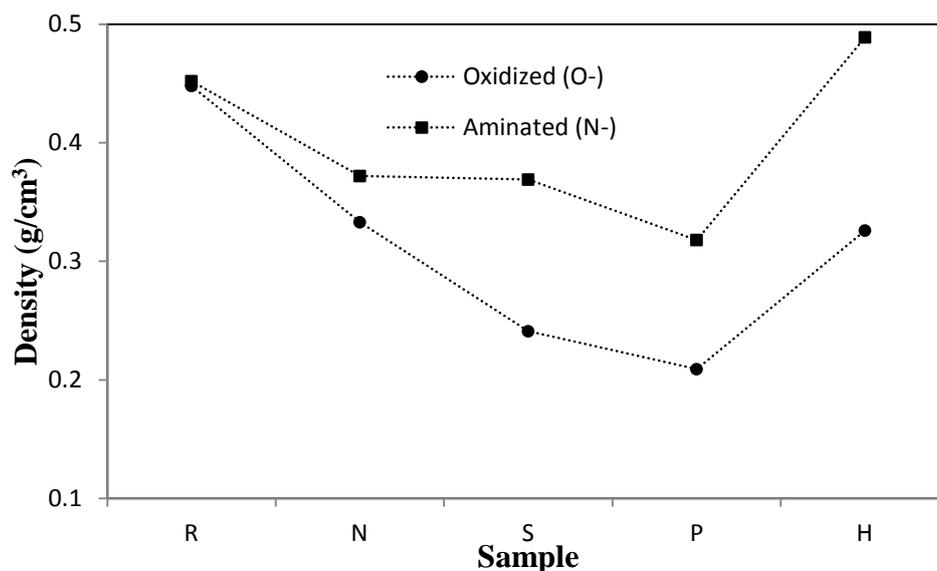


Fig. 6. Comparison between densities of pre-oxidized and aminated samples

However, after amination of R showed no significant change in density as a negligible increase of 0.034 g/cm^3 was achieved, whereas those acid-pretreated exhibited significant increase in densities (Fig. 6). One could infer that amination was able to tether more SNFs which increased the weight composition of the carbons. All except HNO_3 showed huge improvement in density. When compared with R, H_2O_2 was the only oxidant that induced any increase in density after amination.

There seems to be a correlation between the results of pH_{pzc} study and density analysis. H_2SO_4 and H_3PO_4 with the least values for pH_{pzc} (i.e. highest acidity incorporated on the carbon surface) have ensured carbons with least densities as this means intense etching by wet oxidation has occurred.

3.4 Elemental analysis

The purpose of this ultimate analysis is to determine the possible increase in the amount of SOFs indicated by increase in % O on the carbon surface as an indication of extent of oxidation. Looking closely at the line graphs, the “M” and “W” shaped-correlation amongst the samples’ elemental compositions obviously showed high discrepancies in the effects of the oxidants, underlying their chemical differences (Fig. 7). Although all the oxidants increased the %O of R, this was accompanied by various degrees of surface etching which was evident in the huge decrease in % C. However, the intense the etching (i.e. decrease in % C), the more the surface oxidation (i.e. increase in % O). And it is obvious that HNO_3 and H_3PO_4 exhibited the highest oxidizing efficiency while H_2O_2 had trivial effect in this respect. In this light, one could conclude that without considering the nature of the SOFs incorporated by the oxidants, neither the basicity nor the amount of oxygen atoms of in a molecule of an acid determines its efficiency as an oxidant for activated carbon. However, XPS analysis was further used to investigate the natures of the SOFs tethered.

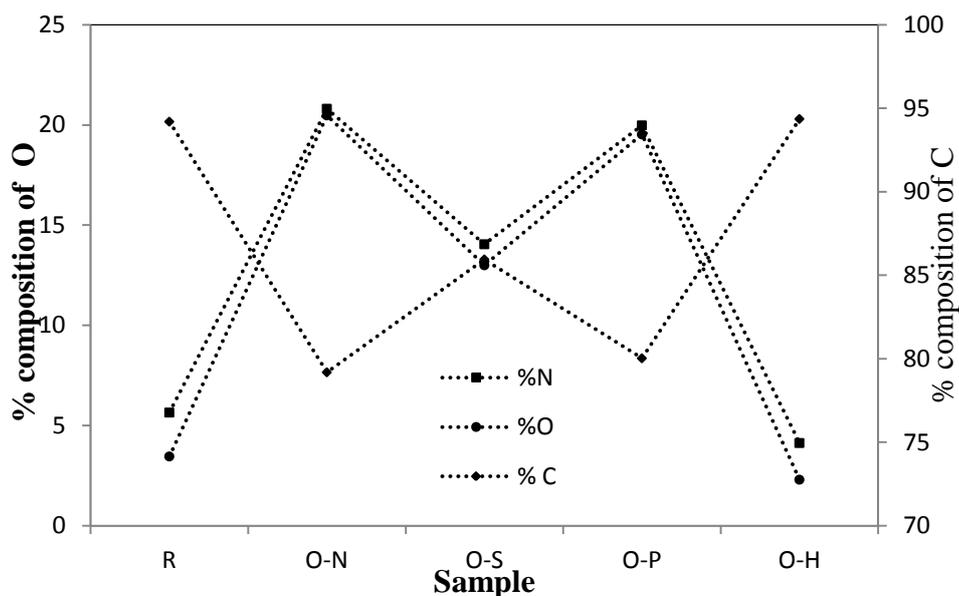


Fig. 7. Comparison of % N, %O and %C of O-2Ms

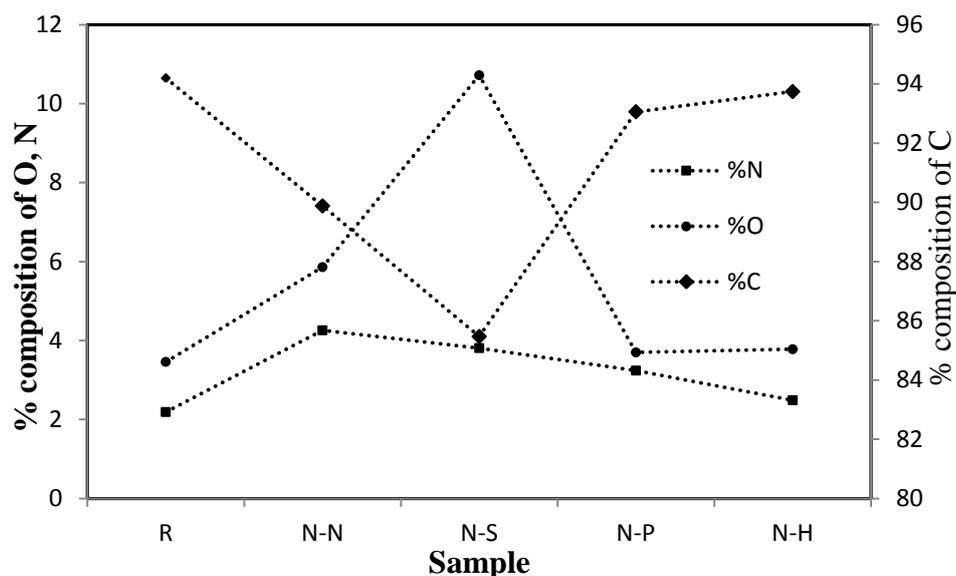


Fig. 8. Comparison of % N, %O and %C of N-2Ms

Note: The values of % N in Fig. 11 are 2.119, 0.33, 1.05, 0.45 and 1.33 for RAC, O-N following the same order of samples arrangement as present in the figure.

The elemental composition of aminated samples was also investigated and reported in Fig. 8. It was presumed that the “M” shaped dotted-line for % O in Fig. 6 would be closely maintained for % N in Fig. 7, if most of the SOFs were quantitatively converted by amination process. However, this was not the case. Focusing on the % N found in the aminated sample,

nitric acid pre-oxidation seems to provide highest amount of SOFs responsible for amination. H_2O_2 , although with an increased %N compared to R, gave the least.

3.5 Characterization of surface chemical functionalities

As it was found with elemental analysis, that nitric and phosphoric acids incorporated the largest amount of SOFs on the carbon particles, a similar observation was made when the total amount of SOFs was quantified by XPS O 1s peaks. Upon deconvolution, it was found that each acid induced similar SOFs but in different proportions. The amounts of these groups found on test samples were compared and represented in Fig. 9. Carbonyl and hydroxyl groups were both largely formed on the carbon surfaces, especially by HNO_3 and H_3PO_4 whilst H_2O_2 did reduce the ones inherently present on the pristine carbon. R possesses relatively low amount of acidic and easily decomposable carboxylic and lactonic groups, but upon oxidation by acid washing, the amount of these SOFs were increased significantly, except for O-H which showed less enhancement in this respect.

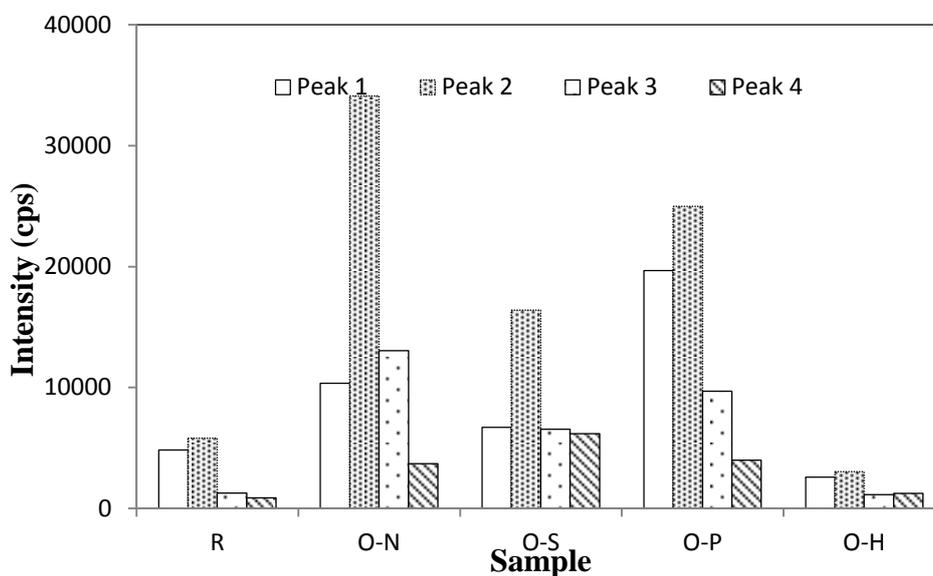


Fig. 9. XPS Peak area of O 1s peak oxidized carbons

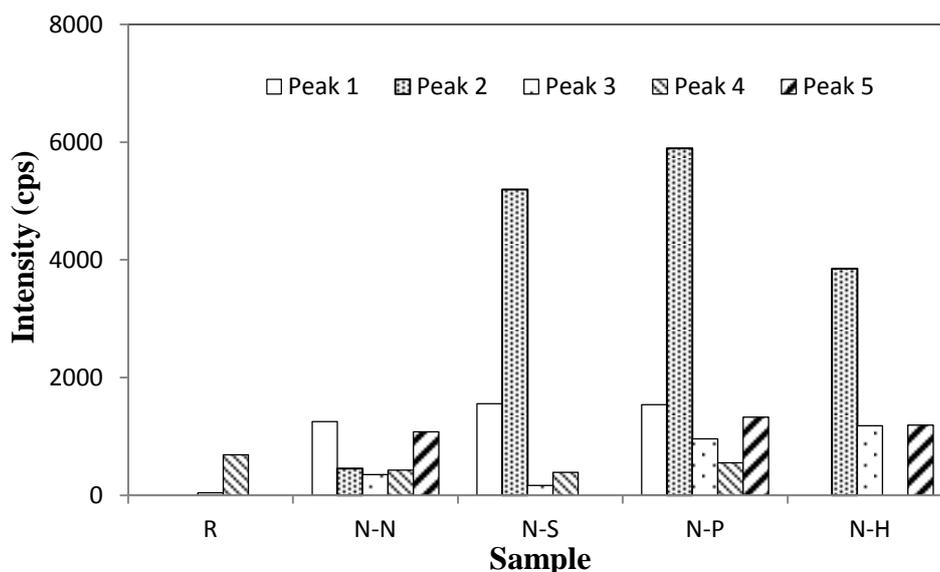


Fig.10. XPS Peak area of N 1s peak aminated carbons

After amination, XPS analysis was used to assess the nature and amount of SNFs on the sorbents. Deconvoluted N1s spectra peak areas were compared and reported in Fig. 10. Unlike the close values observed in that of O 1s amongst the samples, the discrepancies between the SNFs found after amination were much obvious. Pyridine-N (peak 2) which has been reported to favor the adsorption of CO₂ compared to other SNFs was found in abundant quantities in some pretreated samples. Other SNFs were present in relatively lower amount as some were found to be undetected. The significance of these SNFs on CO₂ adsorption was consequently investigated.

3.6 Determination of CO₂ adsorption tendencies of aminated samples

The pure CO₂ adsorption capacity (q, in mmol/g of carbon) of test carbons was determined at 25±2 °C (room temperature, RT) and 0±1 °C (lowered temperature, LT) using BEL mini sorp machine. Results are provided in Fig. 11. There was not significant improvement in the adsorbed amount of CO₂, as HNO₃ and H₃PO₄ seem to bring about negligible reduction in RT test. However, HNO₃, H₂O₂ pre-oxidation seem to show no difference to those of R and N-R. It was presumed that AC physisorption of CO₂ depends majorly on the available surface area and microporosity. Being exothermic, adsorption of CO₂ generally improved at lowered temperature. With this result, one could infer that the significance of the chemical species impregnated on the surfaces is not significant for pure CO₂ capture, especially when the measurement was done at subnormal pressure of 0-1 bar.

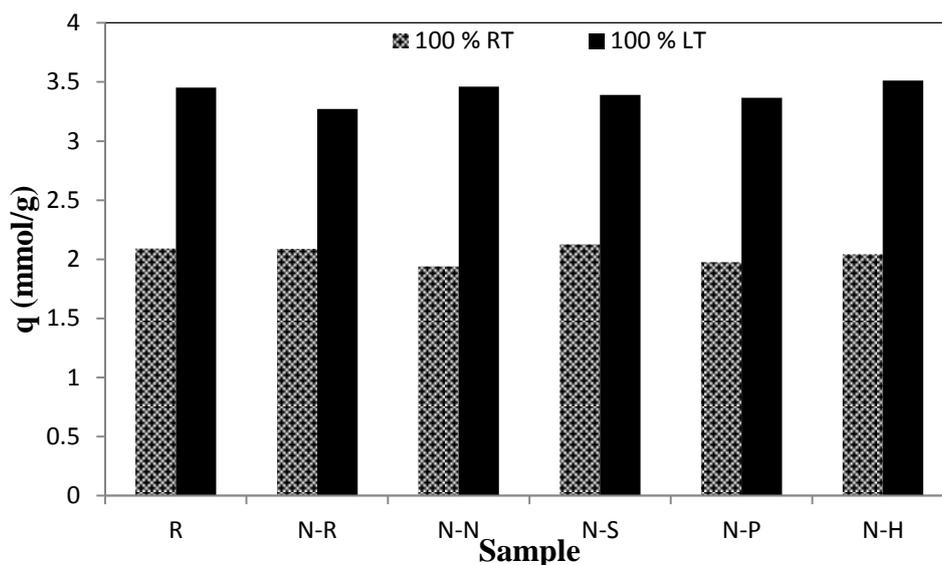


Fig.11. CO₂ adsorption capacity test at RT and LT

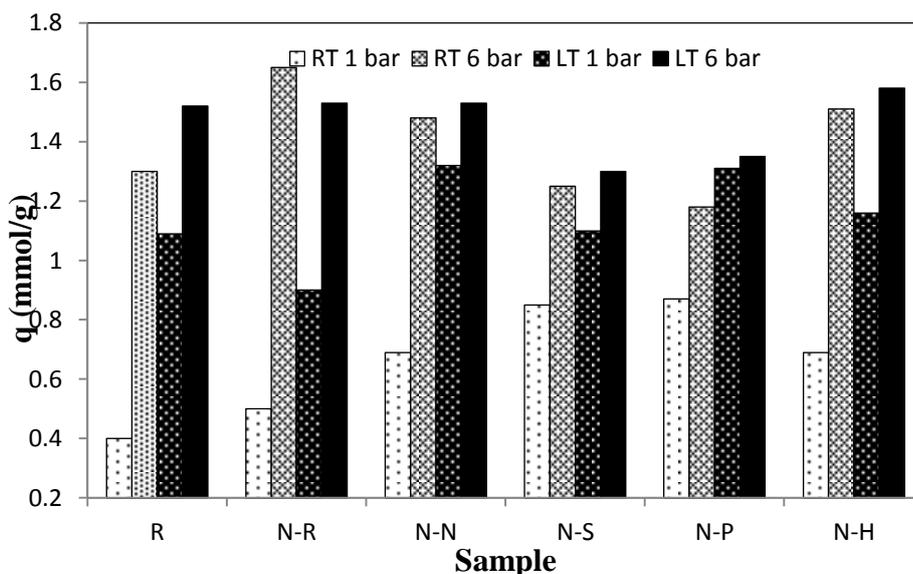


Fig.12. Results of CO₂ adsorption selectivity

With respect to selective test where the SNFs are expected to show some relevance, adsorption of 10% CO₂ was carried out at RT (25±2°C) and LT (0°C) and pressures of 1 and 6 bar, for both cases (Fig.12). At ambient condition, all acid pre-washed samples showed increased values for q . First, N-R indicated the positive impact of amination on CO₂ adsorption. This was further enhanced by pre-acid washing as q for N-2M N \approx N-2M H is higher than N-R, whereas the highest values were those of N-2M S and P which possess close values for q . With the use of acid-washing, one could infer that CO₂ adsorption selectivity at such a major level was improved upon, although not impressively significant. When the temperature was reduced

to 0°C at 1 bar, the observed simple trend with RT 1 bar became haphazard as some peculiar physical properties of each sample are believed to show significant impacts on the CO₂ adsorption.

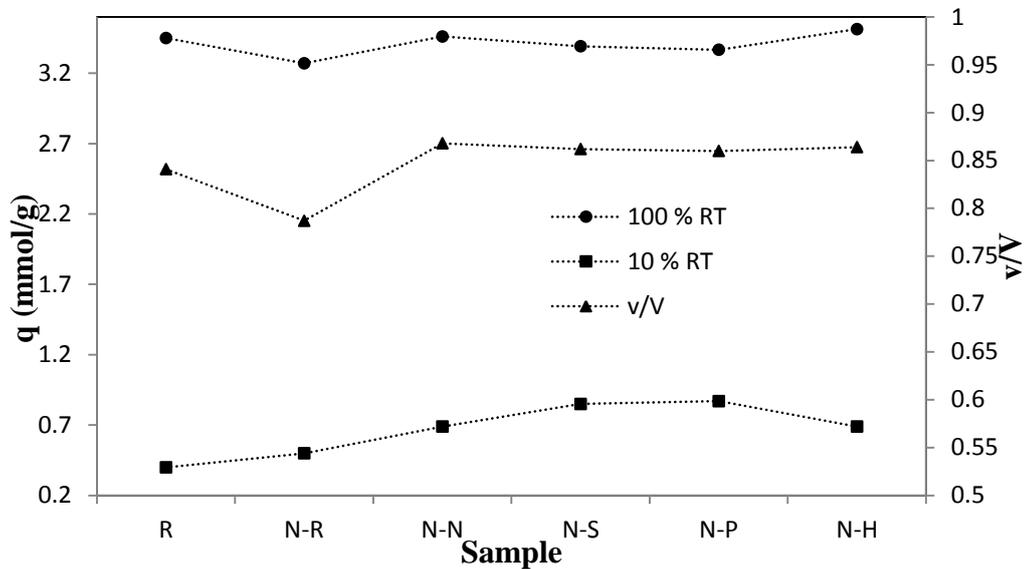


Fig. 13. Effect of v/V on ambient CO₂ adsorption

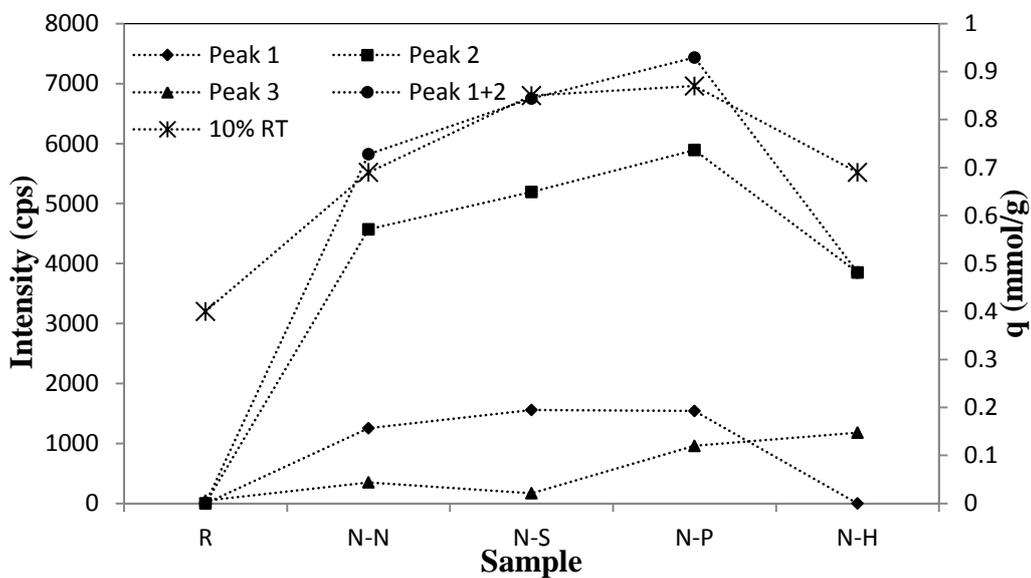


Fig. 14. Impact of SNFs on CO₂ selective adsorption.

Investigating the impact of micropore volume of CO₂ capture, the adsorption capacity and selectivity at ambient conditions were correlated with v/V (the ratio of micropore volume to total pore volume) and described in Fig 13. There was no direct correlation observed between v/V and CO₂ adsorption capacity of the samples. The increase in v/V observed after R was aminated (i.e. N-R) does not seem to correspond to an increase in the amount of CO₂ adsorbed.

However, there was an observed impact of v/V on the adsorption of 10% CO₂ at ambient condition.

Regarding chemical modification, the effect of some SNFs on the selective adsorption of CO₂ was examined and presented in Fig. 14. It is evident that there is close correlation between CO₂ adsorption capacity at this level and peaks 1 and 2 and NOT 3. It was also found that the total of peaks 1 and 2 showed less conformity with the selectivity test, while those of individual relationship was more accurate. This observation proves that not all SNFs have the propensity to attract CO₂ molecules. Results obtained showed that nitride, pyridine, pyrrole and pyridonic nitrogens are the useful SNFs with significant CO₂ affinity.

Hence one could infer that the pore size distribution and basic chemical nature of ACs both play significant roles in the selective capture of CO₂ from gas mixture while pure CO₂ adsorption largely, if not only, on the textural properties.

4. Conclusions

Efforts to curtail the incessant increase in the level of greenhouse gas CO₂ includes adsorption and modification of activated carbon prior its use to enhance its selectivity towards CO₂ were carried out in two ways viz pre-oxidation by acid-washing and amination, in other to increase the amount of N-containing basic complexes on the carbon surface. All the acids used enhanced the acidic properties of the sample in different proportions and eventual amination ensured better basic properties compared to those of pristine carbon and H₂O₂-washed. It was observed that the adsorption capacity of the prepared samples were dependent mainly on the microporosity while the selectivity, at major level of 10%, rely both on microporosity and the basic surface chemistry. Despite the huge reduction in surface area brought about by both H₂SO₄ and H₃PO₄, both are more efficient than HNO₃ and H₂O₂, judging by the eventual CO₂ adsorption. One could, therefore conclude that the basicity of an acid contributes to its pre-oxidation efficiency in the modification of AC for CO₂ adsorption.

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