



“STUDY OF ADSORPTION OF AMMONIA WITH
HARDNESS BY ACTIVATED CARBON USING NESSLER
REAGENT METHOD”

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Abstract

Researchers examined the effects of various kinds and quantities of even more oxygen groups discovered on the surface of activated carbon based for resin on its ability to absorb ammonia. Experimentally employing NH_3 breakthrough columns, nitric acid modifications of such original activated carbon, also recognized as at ambient temperature, the adsorption characteristics are vastly enhanced by the presence of oxygen-containing surface groups. Adsorption capability appears to be proportional to the number more acidic, lesser permanent oxygen surface groups present. Reliable results from studies conducted in humid circumstances demonstrate that the effect of moisture is particularly sensitive towards the surface properties of materials, such as carbon. The inclusion of water greatly improves the absorption action of substances with low oxygen functional concentrations. This is most likely because ammonia is preferentially adsorbed by water due to its ability to dissolve in water. On the other hand, samples that have a rich surface chemistry show only a minor effect from the presence of moisture. This is because there is a preferred adsorption pathway on the carbon surface that travels across Bronsted then Lewis acid centres. This is the reason why this occurs. Moreover, Bronsted acid sites directly communicate with NH_4^+ species, FT-IR measurements of depleted and oxidized samples also indicate the existence of NH_3 individuals that also are directed with Lewis acid domain on the graphene layers, all the way down to the lone pair electron. These findings are supported by the fact that the graphene layers are acidic. The discovery that the layers of graphene contain lone pairs of electrons is the foundation for these findings.

Keywords: - Activated carbon, Ammonia, FT-IR, BET, Adsorption

Introduction

In order to meet the requirements of the new emission standards for air quality, the various governments are being forced to establish new rules to limit pollutant emissions. Of them, ammonia is regarded as one of the most significant dangers to human health. This is due to the fact that it can be fatal if taken in high amounts via the respiratory system, and even in lower concentrations, it can irritate the eyes, throat, and nose [1]. The production of fertilizer and coke, the burning of fossil fuels, the management of livestock and poultry, and the use of refrigeration systems are the primary sources of actual ammonia emissions. The management of animal waste and the production of fertilizers are responsible for approximately 90 percent of the total ammonia emissions from all of these sources combined [2] The removal of NH_3 from industrial effluents has been the subject of numerous research articles, each of which proposes a unique method. These include ion exchange employing polymeric resins, separation utilizing membranes, absorption by solution, heat treatment, catalytic breakdown, reactivity with the other gases, adsorption by porous materials, and heat treatment [3]. When used to waste streams with low concentrations of contaminants, certain of these processes, including such thermal combustion, provide economic benefits; but, when applied to waste streams with high contaminants, these processes become economically unviable. Adsorbed on porous solids, like activated carbons and zeolites, for example, as well as other similar substances, can be an effective strategy for dealing with the specific circumstances described above [4,5] Activated carbons have certain benefits that set them apart from other permeable solids that are described in the scholarly research. The ability to tailor the porous structure and the surface characteristics towards the requirements of a certain application are among these benefits. The advantages also provide a high "apparent" volume of water, a highly advanced porous structure, as well as, most importantly, the ability to do so. [6] Surface changes are required in order for activated carbons to adsorb polar gases like NH_3 ; this is due to the fact that activated carbons normally have non-polar surfaces. Because surface alterations are required in order to adsorb polar gases like NH_3 , these modifications, utilizing both before and after synthesis treatments are quite advantageous when trying to absorb these gases. Research that was conducted not too long ago and published in scholarly journals has demonstrated that the chemical nature of carbon materials is probably the single

most important factor that determines the total adsorption capacity of carbon materials for basic molecules like ammonia [7]. This discovery was made possible because the surface chemistry for activated carbons is now so complicated. Researchers found that the overall amount adsorbed is dependent on both the number and type of oxygen surface substituents on the carbon surface [8]

Moreover, a material's NH₃ release capability is proportionate to the total of its own acidic groups [9]. Existing research indicates that metals (Fe, Co, Cr, Mo, and W) mediated photocatalysts have a similar favorable effect on ammonia elimination. [10] Several suggested reaction pathways have been postulated for the adsorption process, however the actual mechanism is still up for debate. However, It is challenging to determine how the adsorption mechanism relates to the carbon support's inherent characteristics [11] due to the fact that many of these research discussed in the literary works agreement with an extremely broad range of carbon specimens, all of which have unique textural and chemical properties. The significance of the presence of moisture in industrial streams has been the topic with little research. The purpose of this study is to examine the effect of oxygen surface areas on activated carbons during ammonia removal under two conditions: both in and out of the moisture present. Activated carbon was made from such a resin precursor by oxidizing it with HNO₃, followed by a heat treatment at different temperatures to remove the oxygen surface groups [12, 13]. Modifying the surface chemistry under controlled conditions allows researchers to isolate the effect of ammonia adsorption's surface qualities in dry or humid conditions., as is particularly documented in the literature. This will be possible because, under close supervision, just the surface chemistry must be tweaked.

2. Experimental Section

2.1. Materials

Carbonization and the solvent-pore forming properties of ethylene glycol are employed to activate a porous resin made from the cross-linking of phenol-formaldehyde Novolac precursors with hexamethylenetetramine, was used to prepare a spherical charcoal filters which had a particle size of approximately 0.32 millimeters. This activated carbon had a spherical shape. This activated carbon had a particle size During the oxidation procedure, 25 grams of carbon were heated for one hour at 90 degrees Celsius with 250 milliliters of a six-millimolar solution of hydrogen peroxide (H₂O₂). The oxidized sample (MA₂ox) was next washed till the pH was neutralized, then finally dried at 85 degrees Celsius for one full day.

After that, a sample of MA₂Ox was heated with one hour inside a helium environment at temperatures of 300, 500, then 700 degrees Celsius while a flow at a rate of 50 ml/min was maintained. This was done with the intention of getting rid of surface functional groups in a selective manner. The samples were each given their own unique name, such as MA₂Ox300, MA₂Ox500, and MA₂Ox700.

2.2. Characterization

Isotherm measurements of N₂ adsorption and desorption were carried out in home-built volumetric apparatus with a high degree of accuracy at a temperature of -195 degrees Celsius. Before any experiments were performed, samples were degassed for four hours at 150 degrees Celsius under a vacuum of 10⁻³ pascals. After determining the "apparent" surface area by applying the BET formula to the data on nitrogen adsorption, the micropore volume (V₀) was computed with the help of such Dubinin-Radushkevich (DR) equation. This was done just after appropriate of trying to apply the BET formula to the data on nitrogen adsorption. The CO₂ capture isotherm that was measured at 0 degrees Celsius employed the same equipment and process as the one that was used for the previous measurement. The DR equation was used in conjunction with the data on CO₂ adsorption to determine the volume for narrow micropores (V_n). The width of a micropore is regarded to be thin if it is less than 0.7 nanometers. There were a total of 15 Temperature-programmed decomposition (TPD) tests that were carried out in order to describe the oxygen surface functionalities that were present on the different types of materials. After putting 100 milligrams of carbon in a reaction chamber with such a stream of helium at a percentage of fifty milliliters per minute, this same carbon was elevated to a temperature of one thousand degrees Celsius at a rate of ten degrees Celsius per minute. This process was repeated until the carbon reached the desired temperature [14]. An on-line mass spectrometer was utilized in order to perform analyses on the several gas species that were produced as a consequence of surface group decomposition (mostly CO and CO₂) (Omnistar™, Balzers). After the calibration was complete, quantitative studies were carried out with CaC₂O₄H₂O serving as the standard material. In order to generate FTIR spectra of the depleted materials, we made use of an energy dispersive FTIR spectrometer known as a Mattson Infinity Gold. The spectra were generated by adding together one hundred scans that had a resolution of five cm⁻¹ and were performed in the range of four thousand to seven hundred cm⁻¹. Before carrying out any kind of experiment, each and every sample was first diluted with KBr.

2.3 Innovative column experiments

Using an ammonia removal process at temperatures higher than ambient temperature (23 degrees Celsius), we studied the adsorption capability under dynamic settings and column with an internal diameter of one centimeter and a carbon bed height of two centimeters (less than 0.6 grams of sorbent). Air containing 1000 ppm of this type of ammonia was pushed at a rate of 300 ml per minute through the column that was holding the control sample (without any pre-treatment). A detector known as a Polytron 3000 (Drager) was utilized in order to monitor the ammonia concentrations at the outflow. Tests on adsorption were conducted either with air that was completely dry or air that had a humidity level of 70%. In order to imitate conditions in which there was a significant amount of moisture present a calibrated syringe was used to inject moisture into the NH₃/air flow. As the concentration of ammonia at the outflow reached 100 parts per million, the breakthrough experiment being abruptly terminated for no discernible reason. After taking into consideration the air intake concentration levels, Adsorption efficiency was determined by summing the area discovered with the area above the curve representing the breakthrough point for a given total flow rate and sorbent amount. This was done after taking into consideration the total flow rate. Further studies were carried out with pre-humidified samples, with relative humidity levels ranging from 20% to 70%, with the goal of better understanding the function that humidity plays. In order to accomplish this goal, First, a thermal treatment was performed on the carbon samples at such a temperature of 100 degrees Celsius for one full night in order to eliminate any remaining humidity. Subsequently, the samples were exposed to a specific mixture of water and hydrogen sulfide for twenty-four hours at room temperature while the humidity was kept under tight control. Experiments on breakthrough columns employing the pre-humidified samples have been invariably carried out under dry conditions [15].

3. Results and discussion

3.1. Sample characterization

The nitrogen desorption as well as adsorption equilibrium for the activated carbon as it was originally manufactured, along with the activated carbon after it was modified. As can be seen, the existence of a continuous knee in the nitrogen isotherm models indicates resin-based activated charcoal (MA2) may have had a more sophisticated microporous structure. This may be deduced from the fact that the models were run at low relative pressure. This is demonstrated by the fact that

the structure is present. In addition, capillaries condensation processes were seen to take place at p/p_0 ratios that were lower than 0.8, that corresponded to the material's huge mesopores being filled up. The oxidation process, which is predominately carried out using HNO_3 , brings about minute alterations in the porous structure, the principal impact of which is the blocking off of some of the microporosity. This occurs as a result of the formation by polar oxygen surface communities just at entrance of tiny pores, which, in turn, results in a slight reduction in the adsorption of molecules such as nitrogen. It's due to the fact that this carbon structure can only burn partially, the preexisting micropores and mesopores expand when a high temperature thermal treatment is applied (700 degrees Celsius) in the context of a flow of helium. Table 1 summarizes the results from the analysis of N_2 and CO_2 adsorption data, which reveal the textural characteristics of this type of modified activated carbon. To determine these characteristics, the relevant equations were fitted to the data [16].

Table 1 presents the textural parameters again for various activated carbons that were derived from the N_2 as well as CO_2 adsorption statistics at temperatures of -195 degrees Celsius and zero degrees Celsius, respectively.

Samples	SBET (m ² /g)	V ₀ (cm ³ /g)	V _{meso} (cm ³ /g)	V _{t(0.97)} (cm ³ /g)	V _n (cm ³ /g) *
MA2	1550	0.61	0.68	1.29	0.55
MA2 _{ox}	1470	0.61	0.63	1.24	0.53
MA2 _{ox300}	1570	0.63	0.67	1.30	0.54
MA2 _{ox500}	1580	0.64	0.67	1.31	0.54
MA2 _{ox700}	1700	0.69	0.74	1.43	0.61

Researchers have used temperature-programmed decomposition (TPD) to compare the surface chemistry of undamaged activated carbon to that of activated carbon that has been modified. An investigation of the amount of carbon dioxide (CO_2) and carbon monoxide (CO) that was generated at temperatures ranging from ambient temperature to one thousand degrees Celsius was carried out with the help of the methods described in the experimental section. The numerical method for all of the individual samples are compiled in Table 2, which may be found below. CO_2 groups have a propensity to evolve at lower temperatures, and their appearance correlates with the biodegradation of oxygen surface groups that are more acidic and significantly less dependable. On the other hand, CO evolution is

generated by the biodegradation of oxygen groups that are more stable and much less acidic and it occurs at such a higher temperature. This process takes place in the atmosphere [17].

Table 2. Total amount of CO₂ and CO groups evolved in the TPD experiment

Carbons	CO (mmol/g)	CO ₂ (mmol/g)
MA2	0.837	0.18
MA2ox	2.800	1.770
MA2ox300	2.820	0.862
MA2ox500	1.822	0.245
MA2ox700	1.048	0.093

Activated carbon (MA2) seems to have poor surface chemistry when first received, with a higher concentration of acidic groups relative to those that developed when CO₂ (a CO/CO₂ proportion of 4.6) and a lower concentration of oxygen surface groups. As received charcoal filters (MA2) has a higher concentration of such fewer acidic groups compared CO₂ did throughout its evolution. After being exposed to oxidizing agents like nitric acid, the CO₂ surface functional group abundance is predicted to skyrocket while the CO functional group increase will be considerably more modest (resulting in a CO/CO₂ ratio of 1.6). That this finding agrees with established findings is hardly shocking. The less stable oxygen groups, such as those that have evolved as CO₂, are greatly diminished by a second thermal treatment at such an incredibly low temperature (300 degrees Celsius), while oxygen groups, which are more stable, are mainly unaffected. Both of the highly acidic oxygen surface group and a significant fraction of the most stable oxygen surface group were removed specifically requires temperatures greater than 300 degrees Celsius. These clusters emerged as critical ones during the TPD experiment [18].

3.2 Column experiments breakthrough

The glass tubular reactor used in the breakthrough column tests had a maximum flow rate of such 300 ml/min either either wet or dry air with 70% humidity levels with 1000 ppm NH₃. Each sample's total adsorption (mg/g) is listed in Table 3. Whether or not moisture was present, dynamic adsorption experiments revealed statistically significant variations across the test samples. In general, the samples all exhibit unique breakthrough saturation profiles, showing that now the

adsorption process is not constrained by any kinetic barriers. This result is probably due to the high absorption kinetic model with NH_3 through the highly porous networks on such carbon materials, as mesopores provide the pathways to interconnect with inner microporosity of the these carbon materials. The total adsorption capacity in dry conditions is improved by an order of magnitude once the initial carbon has been oxidized with HNO_3 . In accordance with the data given in the science publications about oxidized activated carbons, this oxidized sample (MA2ox) has an overall adsorption rate of up to 17.5 mg/g. Its resale value drops below what it would have been had it not been subjected to further heat treatment from both hot and low temperatures. Notably, the adsorption capacity declines considerably following low-temperature thermal treatment (sample MA2ox300), but then only slightly after that (up to 700°C). This finding suggests that oxygen surface groups will play a significant role in gas-phase ammonia removal, and more specifically, acidic and far less stable surface oxygen communities (mainly carboxylic groups) will have an important effect during the adsorption process when moisture is absent [19]. With respect to the surface chemistry, the effects of adding 70% relative humidity to the input sequence will vary. The adsorption efficiency of the oxidation sample (MA2ox) somewhat increases when it is wetted. This points to the importance of oxygen surface groups in the adsorption process, while water is likely to play a secondary role. If we consider the heated samples, There is a consistent and substantial increase in the adsorption process in all thermally treated samples as compared to the oxidized sample because of the incorporation of moisture, independent of the temperatures where the heat degradation was performed. These thermally treated samples, i.e., where the oxygen surface groups, which were more acidic but considerably less stable, have been eliminated, demonstrate the crucial role water plays in the adsorption mechanism. The condition of numerous additional surface characteristics or their precise composition determine if this is actually the case. Yet, carbons with such a wide range of surface chemistry may have their entire adsorption capacity dictated by the interface ammonia prefers to form with the carbon surface, with the assistance of oxygen surface group and, in particularly, by means of more acidic groups. It's possible regardless of the relative humidity outside. The significant adsorptive capacity obtained in the two-phase oxidized sample (MAox) during dry circumstances as well as the minimal improvement that was discovered after moisture inclusion was somewhat puzzling when comparing to what has been documented in the literature. According to these results, water is crucial in creating NH_4^+ ions, which interact with Bronsted acid groups on the two carbon surface

and are required for the adsorption mechanism. MAox's high adsorption capability in dry environments accounts for its widespread application here [20].

Table 3 presents the total adsorption capability for ammonia in circumstances of air that are dry as well as moist (70% relative humidity).

Carbons	NH ₃ dried (mg/g)	NH ₃ 70% RH (mg/g)	m (mg/g) (0-70% RH)
MA2	4.7	5.3	0.6
MA2ox	17.5	20.1	2.6
MA2ox300	7.6	12.3	4.7
MA2ox500	3.4	7.6	4.2
MA2ox700	1.9	6.1	4.2

Wet and dry adsorption capacities are compared, and the total number for acidic oxygen surface groups (OSGs), which are defined as those that break down into CO₂ during normal TPD operation, is calculated. The goal here was to gain a better understanding of the role that oxygen surface groups play in the adsorption process. As we've shown, the introduction of humid air causes an increase in overall adsorption capacity from across board, irrespective of the surface chemistry, as we've discussed. Previous tests described in the study revealed that the presence of oxygen surface groups, normally acidic, would be important for the ammonia adsorption process even when the moisture content was low (for example, sample MAox). Adsorption efficiency is great when the oxidized sample is dry, whereas adding water has almost no effect. 8 The amount of ammonia adsorbed by a carbon surface is proportional to the total number of acidic groups present there, regardless of the humidity.

So the more oxygen surface groups there are, the less helpful water becomes. This points to a unique adsorption mechanism that is affected by the existence or lack of surface functions. (Especially acidic surface groups based on oxygen). Adsorption via separate oxygen surface groups is the preferred technique. The addition of oxygen functionality has only a little impact on moisture levels. Adsorption behavior for sample MA2ox700 was improved by 69% upon addition of water, demonstrating that carbon compounds exhibiting poor surface chemistry benefited considerably from the presence of moisture [21].

There are two distinct ways in which the adsorption behavior can be altered by introducing oxygen functions to the carbon surface: When species with a high electronegativity remove electron density from graphene layers, Lewis acid facilities can be built there. Ammonium ions (NH_4^+) are produced by a Bronsted acid-base reaction, which aids in NH_3 adsorption on the catalyst surface. These acidic oxygen groups occur towards the margins of the b - site. The addition of oxygen functionalities to the surface of the carbon promotes both processes simultaneously, thus a linear link by itself isn't necessary to rule out mechanism in favor of another. Studies have shown that when the Bronsted acid-base process is used to control the adsorption mechanism, the adsorption behavior rises exponentially below a certain pH (4.5), that corresponds to the pKa permitting groups containing carboxylic acids merely on the carbon surface to break apart. There is a wide range of maximal adsorption capacities for various sample types, and each is associated with the surface pH. Keep in mind that at the pH of 6.5, which is the range of all of the activated carbons utilized in this study, over 100% of the NH_4^+ you react it with will be converted to NH_3 . Regardless of humidity levels, below a certain pH value, NH_3 adsorption does not increase exponentially. This demonstrates that Bronsted acid sites on activated carbon surfaces are not the only factors regulating the NH_3 adsorption mechanism on these materials, as has been proposed in the literature. Both the Lewis and the Bronsted adsorption processes presumably occur on activated carbons, regardless of whether the carbon is wet or dry [22].

New studies were conducted on previously dampened materials to better understand the effects of humidity. First, carbon materials were dried by heating them to 100 degrees Celsius for an entire night. Second, an $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ mixture was used to pre-humidify activated carbons at 20%, 40%, and 70% relative humidity. Finally, ground-breaking column investigations with dry air and ammonia were used to analyze carbon samples. The MA2ox versus MA2ox700 specimens, whose differ in their surface chemistry, show significant differences in the amount of NH_3 that they are able to adsorb. An indicator of how much moisture was retained in the sample, the weight gain following the pre-humidification stage. Due to its increased hygroscopicity, the oxidized sample (MA2ox) may be able to absorb more water from of the pre-humidification atmosphere. For carbon samples with weak surface chemistry, establishing a linear relationship between water retention and the sample's capacity to adsorb a basic molecule like ammonia is of utmost importance (sample MA2ox700). This strong

linear relationship between water content and adsorption indicates the importance of water in this sample. Materials with poor surface chemistry are likely to soak up ammonia (no acidic groups). This is because ammonia is soluble in water, and that the greater the amount of water, the further ammonia will be dissolved. Pre-humidification at 70% RH increased the concentration from 1.1 mg/g for just a drying to 5.3, a sample's total adsorption capacity might vary widely. For example, multiplying by 4.8. Nevertheless, the oxidized sample displays significantly distinct behavior. According to what has been stated up to this point, the adsorption rate of something similar to the untreated sample can reach as high as 15.6 mg/g in the absence of humidity. The adsorption of an elemental molecule like ammonia exemplifies the significance of oxygen surface groups. The fact that this number is lower than that shown in Table 3 (17.5 mg/g vs. 15.6 mg/g for the same sample) is relevant since it demonstrates that the sample's natural humidity is advantageous. Pre-humidification using 20% RH slightly increases the adsorption capacity (to 17.5 mg/g) but has no other effect (to 70% RH). Water absorption on sample MA2ox grows dramatically during the pre-humidification process (from 0 to 70% RH), whereas its adsorption rate hardly varies above 20% RH, demonstrating that the adsorption process takes a different course in carbons with such a high concentration of surface chemistry. The presence of moisture is of little consequence at this time. Surface oxygen groups, and in particular acidic ones, play a crucial role in the adsorption mechanism at carbon. Two different mechanisms have been postulated for the absorption of NH₃ onto oxidation materials. First, NH₄⁺ ions are formed when NH₃ combines onto acidic oxygen surface groups, while second, NH₃ interacts with Lewis acidic sites on graphene planes via lone-pair electrons. Both types of adsorption appear to occur in oxidized materials, whether or not moisture is present. The Lewis acid-base pathway, on the other hand, appears to be more common [23].

Conclusion-

Treating activated carbon using nitric acid at room temperature greatly improved its adsorption behavior, with the overall adsorption capacity relating linearly to the number of oxygen surface groups. Moist conditions have a minor suppressive effect on ammonia adsorption, but a rise in oxygen-rich surface groups considerably reduces this effect. Functionality as well as oxygen atoms may affect active sites, mainly acidic oxygen groups, around the edges of the basal planes on graphene layers, which are home to Lewis acid centers, which in turn may affect the adsorption characteristics of NH₃. Studies have demonstrated that when the

Bronsted acid-base procedure is strictly regulated at a pure pH of 4.5, the adsorptive propensity increases exponentially below that pH. Recent investigations showed that the amount of NH₃ adsorbed is proportional to the surface pH of the sample, Hence, NH₃ would've been protonated to NH₄⁺ at a nearly 100% ratio just at pH that includes every activated carbons employed in this work (pH6.5). This shows that activated carbons undergo the Lewis and Brnsted adsorption processes under both wet and dry environments. Adsorption mechanisms in carbons with such a lot of surface chemistry change depending on whether or not moisture is present. In the presence of moisture, NH₃ combines using acidic oxygen surface groups to form NH₄⁺ ions.

References-

- (1) Phillips, J. Control and pollution prevention options for ammonia emissions, EPA-456/R-95-002, 1995.
- (2) Calvert, S.; Englund, H. M. Handbook of Air Pollution Technology; Willey: New York, 1984.
- (3) Pez, G. P.; Laciak, D. V. Ammonia Separation using semipermeable membranes, US patent n 4,762,535, 1988.
- (4) Blonigen, S. J.; Fassbender, A. G.; Litt, R. D.; Monzyk, B. F.; Neff, R. Method for ammonia removal from waste streams, US patent n 6,558,643, 2003.
- (5) Blonigen, S. J.; Fassbender, A. G.; Litt, R. D.; Monzyk, B. F.; Neff, R. Apparatus and method for ammonia removal from waste streams, US patent n 6,838,069, 2005.
- (6) Huang, C.-C.; Li, H.-S.; Chen, C.-H. Effect of surface acidic oxides of activated carbon on adsorption of ammonia. J. Hazard. Mater. 2008, 159, 523-527.
- (7) Kim, B.-J.; Park, S.-J. Effect of carbonyl group formation on ammonia adsorption of porous carbon surfaces. J. Colloid Interface Sci. 2007, 311, 311-314.
- (8) Park, S.-J.; Jin, S.-Y. Effect of ozone treatment on ammonia removal of activated carbons. J. Colloid Interface Sci. 2005, 286, 417-419.
- (09) Petit, C.; Badosz, T. J. Role of surface heterogeneity in the removal of ammonia from air on micro/mesoporous activated carbons modified with molybdenum and tungsten oxides. Microp. Mesop. Mater. 2009, 118, 61-67.

- (10) Zawadzki, J.; Wisniewski, M. In situ characterization of interaction of ammonia with carbon surface in oxygen atmosphere. *Carbon* 2003, 41, 2257-2267.
- (11) Bernal, M. P.; Lopez-Real, J. M. Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. *Bioresource Technology* 1993, 43, 27-33.
- (12) Ahamadpour, A. and Do D.D (1997) “The preparation of activated carbon from macadamia nutshells by chemical activation”. *Carbon*,35, 1723 -1732
- (13) Cheremisinoff, P N. Ellerbusch, F .1979. *Carbon Adsorption Handbook*. Ann Arbor Science, Michigan USA.
- (14) Singhai et al.,2021. Preparation and characterization of pore structure by phosphoric acid activated carbon from unused wood of citrus shrub.*SciensageJ Adv Sci Res*, 2021; 12 (3) Suppl 1: 155-161 .
- (15) Bansal,R.C. Goyal. M., 2005. *Activated Carbon Adsorption*. CRC press, Florida.
- (16) Rodríguez-Reinoso, F.; Molina-Sabio, M.; Muñecas-Vidal, M. A. Effect of microporosity and oxygen surface groups of activated carbon in the adsorption of molecules of different polarity. *J. Phys. Chem.* 1992, 96, 2707-2713.
- (17) Badosz, T. J.; Petit, C. On the reactive adsorption of ammonia on activated carbons modified by impregnation with inorganic compounds. *J. Colloid Interface Sci.* 2009, 338, 329-345.
- (18) Molina-Sabio, M.; Muñecas, M. A.; Rodríguez-Reinoso, F. Modification in porous texture and oxygen surface groups of activated carbons by oxidation. *Stud. Surf. Sci. & Catal.* 1991, 62, 329-339.
- (19) Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Orfao, J. J.MModification of the surface chemistry of activated carbons. *Carbon* 1999, 37, 1379-1389.
- (20) Rolence C, Machunda RL, Bhau K N. Water hardness removal by coconut shell activated carbon. *Int J Sci Technol SoC.* 2014; 2: 97-102.
- (21) Rodrigues, C. C.; Moraes Jr., D. d.; da Nóbrega, S. W.; Barboza, M. G. Ammonia adsorption in a fixed bed activated carbon. *Bioresource Technology* 2007, 98, 886-891.

(22) Ngoc-Thuy Vu, Khac-Uan Do. Prediction of Ammonium Removal by Biochar Produced From Agricultural Wastes Using Artificial Neural Networks: Prospects and Bottlenecks. 2021, 455-467.

(23) Chu-Chin Hsieh, Jyong-Sian Tsai, Jen-Ray Chang. Effects of Moisture on NH₃ Capture Using Activated Carbon and Acidic Porous Polymer Modified by Impregnation with H₃PO₄: Sorbent Material Characterized by Synchrotron XRPD and FT-IR. *Materials* 2022, 15 (3) , 784.