Modification of Activated Carbon by Gamma Radiation - Removal of Acetic Acid

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Abstract:

The present paper deals with the removal of acetic acid using modified Norit Activated Carbon (NAC). Surface properties of NAC were modified by irradiating the sample with gamma radiations from Co-60 Source. Batch adsorption method was used to study removal of acetic acid by adsorption. Characterization differences in the Irradiated and Non-irradiated NAC surface were confirmed by different analytical techniques viz. FTIR, XRD, SEM, BET and EDX. Adsorption equilibrium study shows consistently higher capacities in irradiated adsorbent compared to the non-irradiated adsorbent for adsorption of acetic acid. The results show that the adsorption capacity of irradiated Norit activated carbon increases with increase in the amount of irradiation dose.

Key words: Adsorbent, Acid removal, Activated Carbon, Gamma irradiation, Separation

1. Introduction:

Organic pollutants are commonly found in sewage wastewaters, effluent streams of different industries and even in wastewaters generated in agriculture production due to the use of pesticides/ insecticides or chemical fertilizers[1]. Appropriate treatments are required for these different wastewater streams based on their organic/ toxic load; based on biologically degradable components in industries such as food processing, or industries generating streams containing refractory pollutants such as pulp and paper, dyes and pigments, specialty chemicals and so on. The degradation of organic

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pollutants requires oxygen and the dissolved oxygen in water bodies can at times get consumed at a rate higher than its replenishment, depleting oxygen levels having adverse impact on the stream biota. Coagulation / clarification is widely used to remove colloidal impurities by the charge neutralization process, and a large number of coagulants/ flocculants can be used including inorganic/ organic/ biocoagulants or using process integration with cavitation, a process modification in the form of cavigulation reported recently[2]. Many other conventional techniques apart from coagulation include ion exchange[3] advanced oxidation processes, cavitation, adsorption etc[1]. Nanomaterials or nanocomposites, biomass derived materials as adsorbents are also being investigated for effective removal of various pollutants[4,5]. In recent years, techniques such as cavitation, an advanced oxidation process is also considered environmentally friendly methodology for the destruction of pollutants[5-7]. Adsorption technique is one of the most widely used technique for the removal of organic compounds[1,8-10]. One of the major organic pollutants in waste water stream is organic acids such as acetic acid. Acetic acid is largely found in wastewaters of industries producing acids or using these acids as catalyst. Removal of these acids is an important operation in the industry for safety of the environment. Industrial effluents containing low concentrations of acetic acid are produced in large quantities by many industries manufacturing acetic acid and also petrochemical, process and fine chemical industries which are using acetic acid as a chemical reagent to produce many chemical compounds[3]. The treatment of wastewater containing acetic acid is a major concern to meet the discharge norms. Although many treatment methods are used for the removal of acids, adsorption is a common methodology for removing the traces of acetic acid. Adsorption is defined as selective removal of one or more components of either a gas or a liquid mixture on the surface of a material (adsorbent) through the application of the forces of attraction or chemical bonding. It is a reversible process and regeneration of adsorbent by desorption of the adsorbed species is also important. The most important parameters of the selection of adsorbent are its surface area, typically ranging from 100 – 1000 m^2/g, porosity, selectivity and adsorption capacity. Both microporous and macroporous carbon adsorbents are made or commercially available having different characteristics for the equilibrium capacity and improved kinetics[11]. The carbon adsorbents can be derived from a variety of natural materials/ bioresources such as wood, coal, lignin and coconut shell[12]. Typically, the selection of the source material, its characteristics and the processing dictates the pore size and pore distribution. Being

hydrophobic in nature, the activated carbons are considered to be suitable for removal of organic contaminants due to their affinity toward organic species. The adsorption capacity and selectivity can be further enhanced by modifying the surface of AC either through physical or chemical modifications. The conventional modifications include physical modifications (e.g. heat treatment) and chemical modifications (e.g. acid/ base treatment, surface functionalization etc.)[1,4,12]. Radiation treatment has been reported for altering the surface properties of carbon materials, such as films, fibers, powder etc.[13] An irradiation is known to induce chemical reactions at any temperature in the solid, liquid and gas phase without use of catalyst. It is considered as a safe method. The two main processes of irradiation in use are use of gamma rays and electron beam. Gamma rays from Co-60 source are highly penetrating because of its energetic photons (1.17 and 1.33 MeV).

The present paper deals with a new strategy for the removal of pollutants using gamma irradiated NAC and non-irradiated NAC. Batch adsorption method was used for removal of acetic acid and modified NAC was characterized using different characterization techniques.

2. Experimental

All chemicals, Ferrous ammonium sulphate, Sodium Chloride, Acetic Acid, Sodium hydroxide, hydrochloric acid, Norit activated carbon, phenolphthalein indicator, acetone, methanol were of analytical grade (MERCK).

2.1 Sample Collection and Preparation

The Norit Carbon was ground to fine powder with pastel and mortar. Activation was done by placing the carbon in furnace for 8 h at 500-600 ˚C temperature, this was then cooled and stored in an airtight container for further use.

2.2 Determination of dose rate of gamma source

For gamma irradiation of NAC, Co- 60 Source (Gamma Chamber 900) was used. Its dose rate was measured by Fricke dosimetry. Fricke solution was prepared by dissolving 0.4 g ferrous ammonium sulfate and 0.06 g NaCl in 22 ml of 95-98% H_2SO_4 and diluting it to one liter with distilled water.

5 ml of the solution was taken in 5 tightly capped tubes and then irradiated in Co-60 gamma source, at various time intervals. The dose rate was calculated by plotting a graph of absorbance versus time of irradiation (Fig.1) and using the following equation

$$\text{dose rate} = (\text{slope} \times 10^7 \times 0.965)/(\varepsilon \times \text{d} \times \text{L} \times \text{GFe}^{+3}) \text{---(1)}$$

Where ε is molar absorption coefficient of Fe^{3+} ions (2174 lit $mol^{-1}cm^{-1}$), d is density of solution, l is path length and $GFe^{+3} = 15.5$

The absorbance of the ferric ions, was measured with a spectrophotometer at 304 nm. The dose rate was found to be 52.92 Gy/min

2.3 Sample irradiation

NAC was tightly capped in a test tube and then irradiated in Co-60 irradiator (Gamma Chamber- 900) for a pre-determined time with a dose rate of 52.92 Gy/min. The total dose absorbed was 0, 2,4,6,8 and 10 KGy.

2.4 Batch adsorption method

The batch adsorption method was used to determine the adsorption capacity of NAC for removal of acetic acid. For this purpose, six glass flasks containing known concentration of acetic acid and fix amount of NAC were agitated at constant speed using a shaker and after certain time interval, solution was withdrawn and filtered, the aliquot was titrated with standardized NaOH using phenolphthalein indicator. The adsorption process was carried out at ambient temperature and varying concentrations of acetic acid and amount of NAC. The obtained data was used to calculate adsorption capacity of NAC.

2.5 Characterization studies

Irradiated and non-irradiated samples of NAC were characterized by FTIR, SEM, XRD, BET and EDX techniques

3. Results and Discussion

3.1 XRD analysis

XRD Patterns of non-irradiated and irradiated NAC are shown in Fig. 7 and 8 respectively. The 2Φ value for Non-irradiated NAC was found to be 26.4 and 44.7 which show that crystallite size of carbon was 2.34 A^0 and 2.02 A^0 respectively.

3.2 Scanning electron microscope analysis

Scanning electron microscopy is one of best technique to study topology and morphology of sample. SEM can be used for studying Pore distribution and extent of porosity etc. Irradiated and Non-irradiated NAC samples were observed under electron microscope.

As can be seen from Fig. 9 and 10, pore distribution is getting affected due to gamma radiation, more uniform distribution is observed for irradiated sample so consequently surface area also increases due to high energy radiation.

3.3 BET Surface Area Analysis

Specific Surface area for Non-irradiated NAC was found to be 731.59 m^2/g and for Irradiated carbon it was found to be 847.32 m^2/g so approximately 16% increase in surface area was observed for irradiated NAC.

Maximum Volume of pores was found to be 0.4138 cm^3/g and 0.3791 cm^3/g for irradiated and Non-irradiated NAC respectively. Maximum diameter of pores was found to be 3.98 nm and 3.96 for non-irradiated NAC and irradiated NAC respectively.

3.4 Elemental analysis using Energy dispersive x-ray

Elemental analysis of irradiated and non-irradiated NAC is shown in Tables 1. The major constituent of Irradiated NAC is the carbon (> 90%). In addition, it also contains other atoms. These may be derived from the source of raw material or they may get associated during activation process or other preparation procedure[11,12]. The large difference in carbon and oxygen content in irradiated and non-irradiated NAC is surprising.

3.5 Functional Group Study

FTIR analysis was done using FTIR-84005 model. The obtained spectra are shown Figs. 5 and 6. As can be seen, there are two major absorption bands at 3500 cm^{-1} and 1500 cm^{-1}. The band at 3450 cm^{-1} is attributed to acetic acid adsorption on NAC (O-H stretching) while the band at 2930 indicates C-H interaction with carbon. Further, bands in the range of 3200-3650 cm^{-1} also can be attributed to the hydrogen-bonded OH group.

3.6 Measurement of equilibrium parameters, Effect of concentration and Adsorbent dose

The equilibrium studies were carried out by varying the acetic acid concentration, amount of NAC and contact time. The obtained data was used to study the adsorption capacity.

The effect of initial concentration on adsorption capacity of NAC was studied in the range of 20 to 150 mg/L by stirring 50 mL solution of acid for 20 h with a fix amount of NAC. Residual acetic acid concertation after filtration was determined as described above.

In order to study the effect of dosage of NAC on removal of acetic acid amount of NAC was varied between 0.2-1g and amount of sample solution (50mL) and time of stirring (120rpm) was kept constant

The results for the two adsorbents, irradiated and non-irradiated, are shown in Figs. 2 and 3. A comparative plot of equilibrium concentration versus adsorption capacity is depicted in Fig. 4.

3.7 Equilibrium study

Equilibrium studies were carried out at room temperature (25 ± 1ºC) by employing the batch adsorption technique. The data were analyzed in the light of adsorption isotherms. The sorption data (Fig. 4) shows that irradiated adsorbents have consistently high adsorption compared to the non-irradiated adsorbent, implying positive modification of the adsorbent using the suggested methodology and its practical utility. It is also observed that at higher concentration the capacity reaches a maximum value in the case

of both irradiated and non-irradiated adsorbents: the capacity of irradiated adsorbent is ~100% higher than that observed for the non-irradiated adsorbent.

4. Conclusion

Our study reveals that gamma irradiation of NAC increases its surface area and modifies pore size resulting into high adsorption capacity of acetic acid as compared to non-irradiated NAC

The specific surface area of Irradiated and Non-irradiated NAC were found to be 731.59 m^2/g and 847.32 m^2/g respectively. Since approximately 15% of surface is observed to be affected due to gamma radiation. Pore size of NAC was found to be 0.31 nm. Also maximum diameter of pore was of the range between 3.96-10.00 nm.

Adsorption capacity of irradiated NAC increases as amount of irradiation dose increases. BET analysis indicated that surface area of irradiated carbon increases with increasing dose. Further, the adsorption increases with an increase in the adsorbent dosage.

Figures

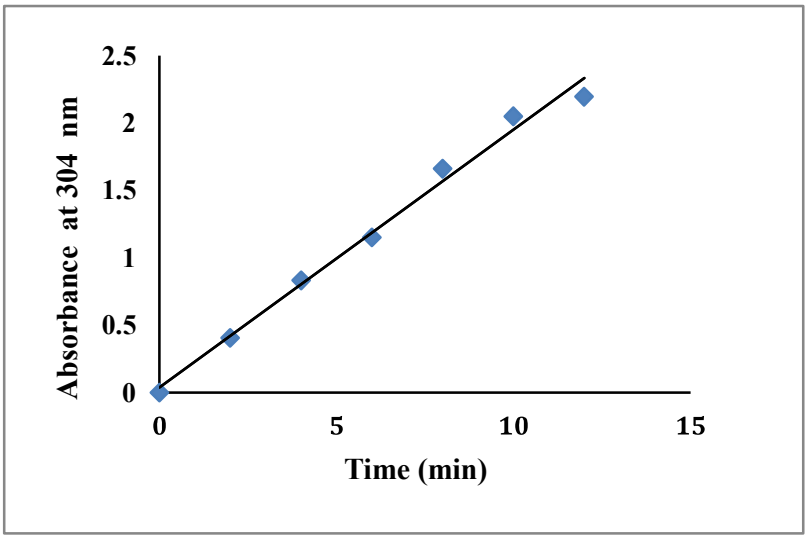

Fig.1 Calibration curve for Fricke dosimetry

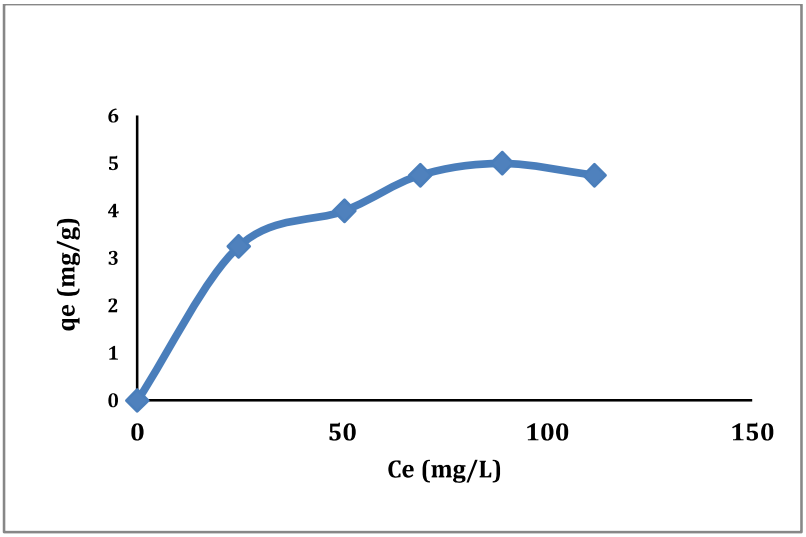

Fig.2. Equilibrium for Non-irradiated NAC

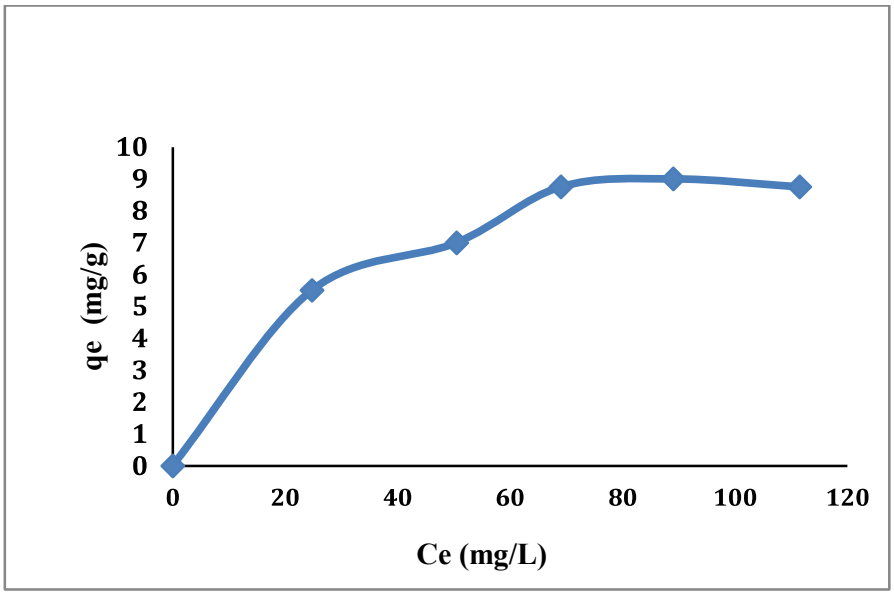

Fig 3.Equilibrium for irradiated NAC

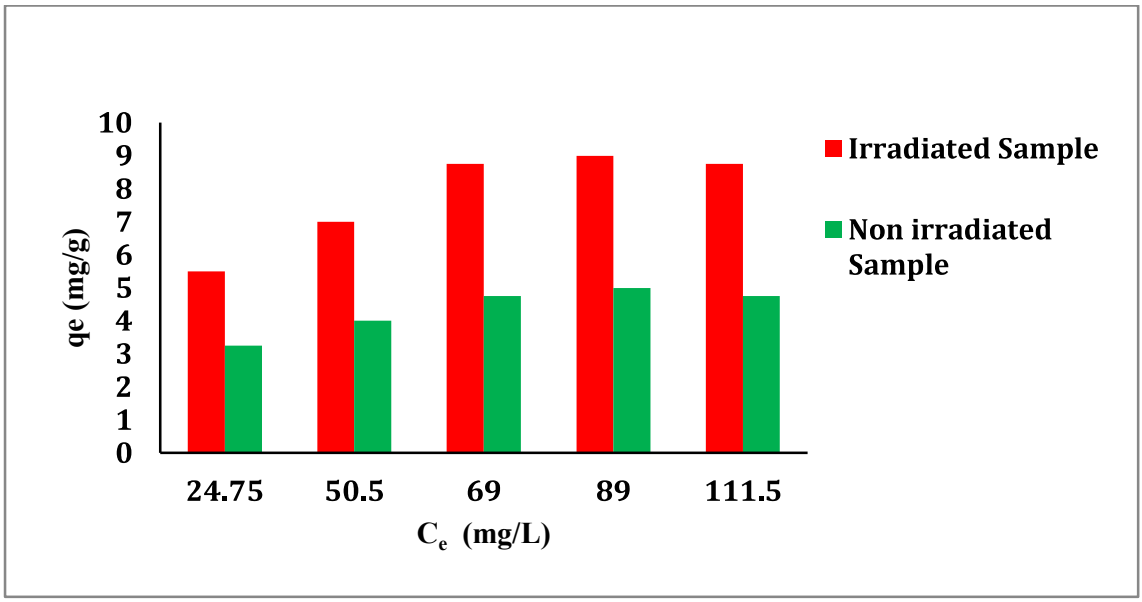

Fig.4. Comparative plot of equilibrium concentration Vs adsorption capacity of NAC

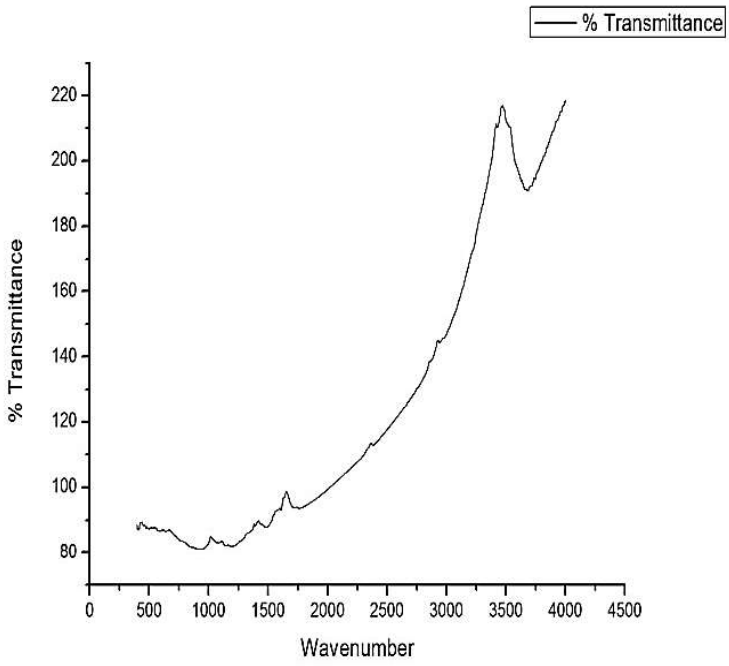

Fig. 5 FTIR of NAC before irradiation

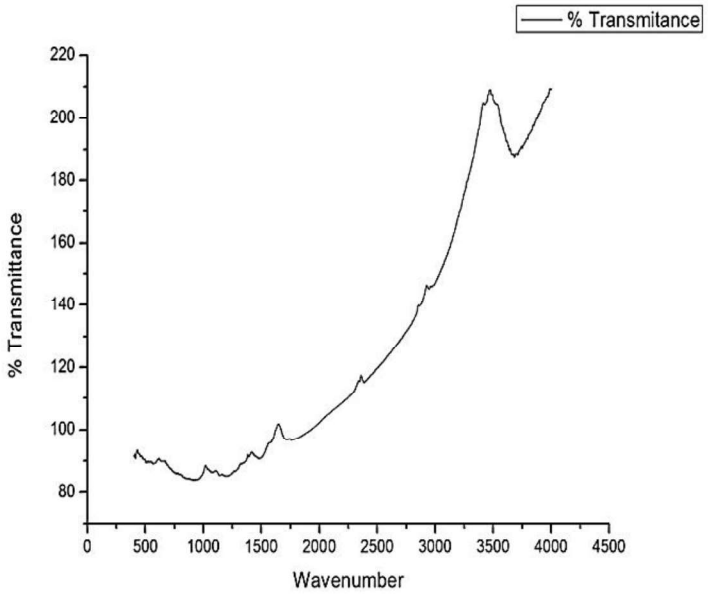

Fig. 6 FTIR of NAC after irradiation

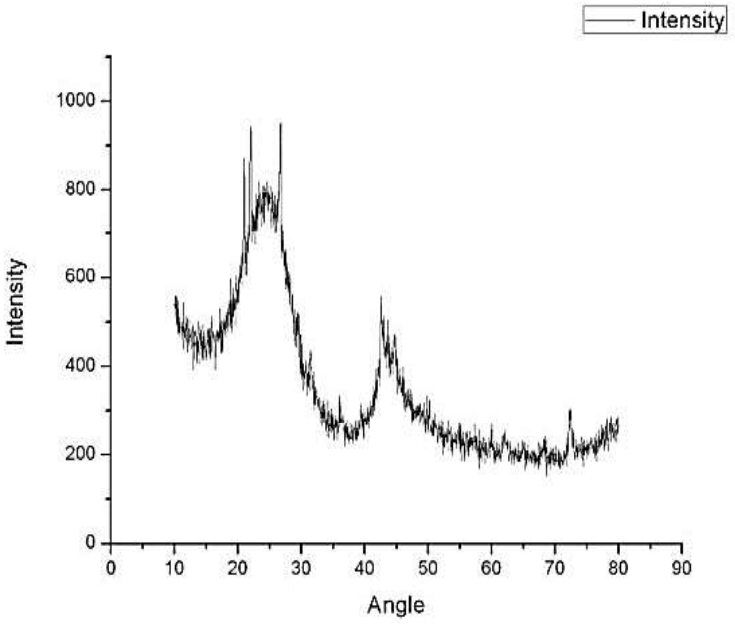

Fig. 7 XRD of Non-irradiated NAC

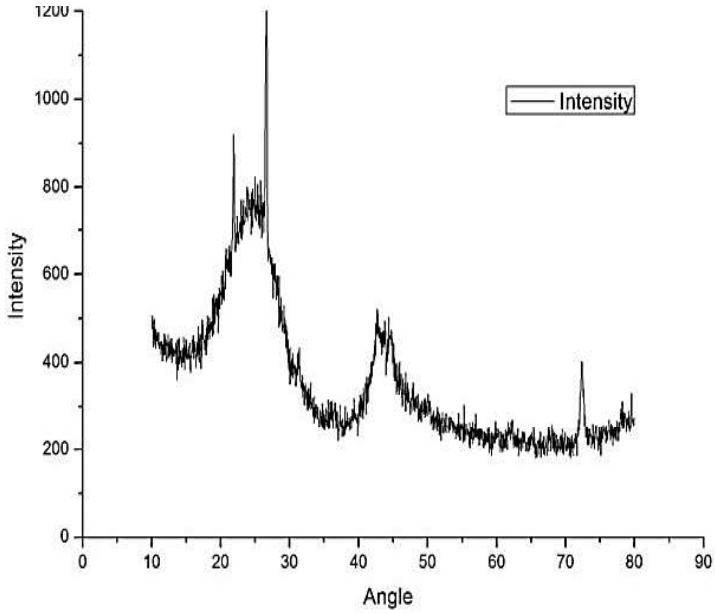

Fig. 8 XRD of Irradiated (10KGy) NAC

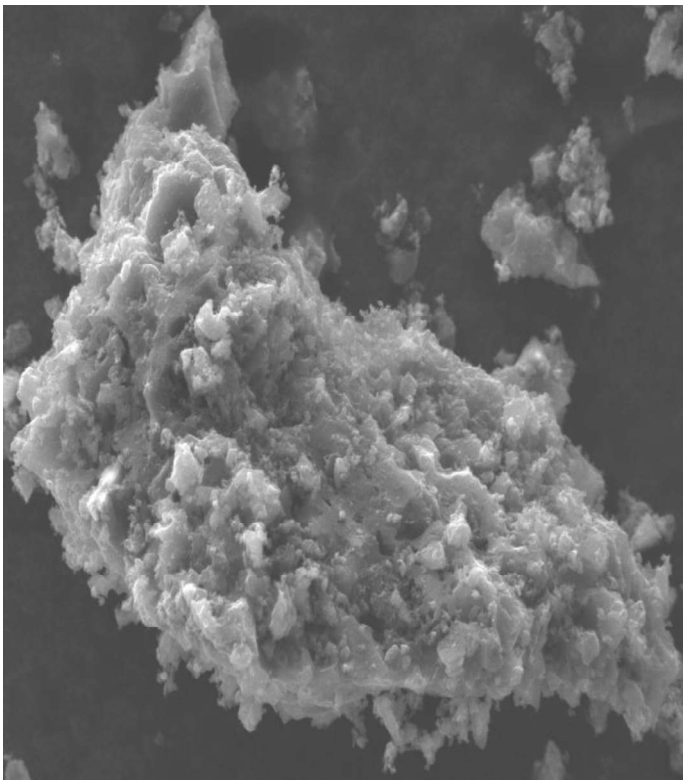

Fig. 9 SEM image of Non-irradiated NAC

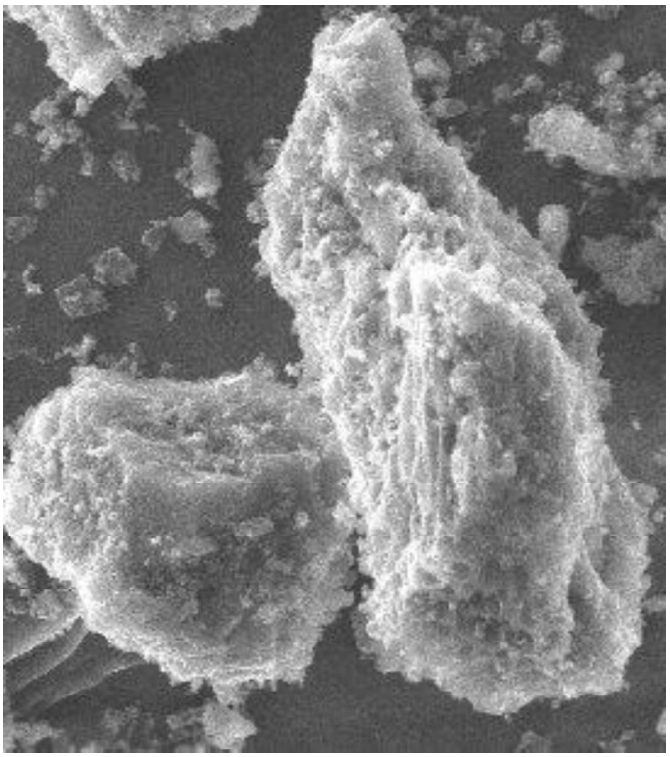

Fig. 10 SEM of Irradiated NAC

Tables:

Table 1. Elemental analysis for Non-Irradiated and irradiated NAC

Elements	% Weight	
	Non-irradiated	Irradiated
Carbon	56.30	93.58
Oxygen	34.89	4.93
Phosphorous	1.13	0.12
Magnesium	0.17	0.39

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