Nitrogen Doped Activated Carbon Derived From Chitosan/ Hexamethylenetetramine: Structural and CO2 Adsorption Properties

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Research Article

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Abstract

Chitosan and chitosan/hexamethylenetetramine (HMT) macrospheres were prepared respectively by dropping chitosan and chitosan/HMT (in wt/wt ratios of 1:1 and 1:3) solutions in aq. NaOH solution. Here, HMT served as an additional nitrogen precursor for in-situ N-doping with chitosan derived activated carbon (AC). The as-formed macrospheres were impregnated using ZnCl$_2$, freeze-dried, and carbonized at 500°C under inert atmosphere to yield ACs of average size 2.6 mm. All the samples were characterized using SEM, EDS, CHNS Analyzer, TGA, FT-IR, Raman, XRD and BET surface area analyzer. All the samples showed mesoporous characteristics. The surface area of the AC without HMT, with 1:1 HMT, and 1:3 HMT were 391.502, 259.017, and 111.717 m$^2$/g respectively. Similarly, the pore volumes of AC without HMT, with 1:1 HMT and 1:3 HMT were 0.138, 0.095 and 0.075 cc/g respectively. The chitosan/HMT derived AC possessed higher N-content and better thermal stability, however exhibited lower surface properties with increasing HMT content. Deterioration in adsorption capacity of chitosan/HMT derived AC may be attributed to the physical cross-linking of chitosan polymer chains induced by increase in pH with addition of HMT and also the intermolecular H-bonding interaction between HMT and chitosan, which in turn reduces the surface area of as-formed N-doped ACs progressively.

Introduction

One of the major problems faced by mankind in the 21st century is global warming caused by an increase in concentration of CO$_2$. According to the recent studies, accumulation of CO$_2$ in the atmosphere has been increased up to 413 ppm by 2021 [1]. Researches suggest a wide range of processes for the CO$_2$ removal from the atmosphere, such as absorption, membrane separation, adsorption [2]. Among them the widely adopted method is adsorption, where different porous materials are used as adsorbents, such as activated carbons [3–5], mesoporous silica [6, 7], metal organic frameworks (MOFs) [8], covalent organic frameworks (COFs) [9], zeolites [10], zeolitic imidazolate frameworks [11] etc. Activated carbon with tuned porosity is of significant importance in the adsorption of CO$_2$ among the proposed adsorbent materials. The adsorption capacity of activated carbons could be increased by doping with nitrogen, as this approach improves the surface properties as well as the basicity of the carbon [12]. The improvement of basicity while providing electron donor moiety to the carbon network increases the adsorption of acidic CO$_2$ gas molecules. Basicity on the activated carbon can be improved either by in-situ nitrogen doping or amine functionalization. Shivadas et al. reported the synthesis of activated carbon using sucrose as the carbon precursor and urea as the in-situ nitrogen dopant. Degradation of urea during carbonization produced NH$_3$, which resulted in the doping of nitrogen on the carbon matrix [13]. Similarly, Liu et al. also reported the use of urea as an in-situ nitrogen dopant during the synthesis of activated carbon from furfural carbon precursors [14]. In another study, Wang et al. reported the synthesis of activated carbon using polyacrylonitrile (PAN), and the as-prepared activated carbon was functionalized using tetraethylene pentamine (TEPA) where the amine is adhered on to the support via a non-covalent attachment [15].
Chitosan is a potential precursor for activated carbon as it is the second most abundant polysaccharide next to cellulose [16] and second largest nitrogenous natural organic matter after protein. Chitosan is the de-acetylated derivative of chitin, which is obtained from the shells of crabs and shrimps [17] as well as cell walls of fungi. Also it is a highly cost-effective material with an ease in processability, which makes it a better carbon precursor. Several studies have been made previously on the preparation of activated carbon from chitosan. In 2013, Fan et al. reported the synthesis of chitosan derived activated carbon using K$_2$CO$_3$ as the activated agent, which possessed a CO$_2$ adsorption capacity of 3.86 mmol/g [18]. Similarly Lee et al. in 2017 synthesized activated carbon from chitosan using KOH as the activating agent and urea as the nitrogen dopant [19].

In the present study, chitosan was used as the carbon precursor and was mixed with hexamethylenetetramine (HMT) to prepare spherical N-doped activated carbon as HMT possess four nitrogen atoms in its structure and upon carbonization dopes nitrogen onto the carbon framework [20]. The surface properties as well as the CO$_2$ adsorption capacity of both undoped and N-doped ACs were compared.

**Experimental**

**Materials**

Chitosan (MW: 100-200 kDa, Degree of deacetylation: 90%) was purchased from Acros Organics. Lactic acid (90%), analytical grade ZnCl$_2$, hexamethylenetetramine and NaOH were procured from Merck India Ltd., and were used as received. High pure N$_2$ (99.99%) and CO$_2$ (99.99%) gases were supplied by Chemix Specialty Gases and Equipments, Bangalore.

**Preparation of activated carbon**

Chitosan solution (2% wt/Vol) was prepared in 5% aqueous lactic acid and was dropped into 2.5% NaOH solution using a peristaltic pump with a flow rate 3mL/min (nozzle size: 5 mm) in order to prepare chitosan macrospheres. Similarly, chitosan solution was mixed with hexamethylenetetramine in different ratios (wt/wt) and dropped into NaOH solution to form chitosan-HMT macrospheres. The macrospheres were allowed to stir for one hour, filtered, washed with distilled water and impregnated with ZnCl$_2$ (1:1 ratio with respect to the weight of chitosan) followed by drying by freeze-drying method. Carbonization of the macrosphere beads were carried out in a tubular furnace at 500 °C for 1h. 30 mins. under a nitrogen atmosphere. The carbonization temperature of chitosan was chosen from previous literatures, which showed a temperature between 300 °C to 600 °C yielded an improved surface characteristics for the chitosan derived activated carbon [21]. The resulting activated carbons were washed with dil. HCl and hot distilled water to remove excess ZnCl$_2$, until the negative result for Cl$^-$ ion with AgNO$_3$. The samples before carbonization without HMT was named as CB-0, while the samples with 1:1 HMT and 1:3 HMT before carbonization were named as NCB-1 and NCB-3 respectively [Fig. S1 (a)]. The activated carbons
without HMT incorporation was denoted as C-0 while the activated carbons with 1:1 HMT and 1:3 HMT were denoted as NC-1 and NC-3 respectively [Fig. S1 (b)].

Characterization

Iodine values of the prepared activated carbons were determined following ASTM D4607-94. The surface morphology of the samples were studied using Scanning electron microscope (Vega3 Tescan). The N\textsubscript{2} adsorption-desorption isotherms were obtained at 77K using Quantachrome Nova 2200e system. From the isotherm, the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation, pore size distribution was obtained using Barrett-Joyner-Halenda (BJH) method and the total pore volume was calculated at 0.99 P/P\textsubscript{0}. X-ray diffraction studies for the samples were performed using PANalytical X'pert Pro. FT-IR studies were performed using ThermoNicolate Summit FTIR spectrometer. Raman analysis was executed using ReinshawinVia confocal Raman spectrometer. The elemental mapping was carried out by EDS method using EDAX Ametek, and the elemental composition by CHN using Elementar Vario EL III. TGA Q500 V20 was used to evaluate the thermal properties of the activated carbon samples.

CO\textsubscript{2} adsorption studies

1 g of activated carbon samples taken in a U shaped glass column were preheated at 110 °C for 1 h and cooled in a desiccator for complete removal of moisture. High pure CO\textsubscript{2} (99.9%) at a flow rate 100 mL/min was purged through the sample and change in weight was monitored for every 5 mins. at 25 °C until the adsorption profile reached saturation [22]. The CO\textsubscript{2} capture capacity of the activated carbon in mg/g was calculated using the following equation [23]:

\[
\text{CO}_2 \text{ capture capacity (mg/g)} = \frac{(\text{Final weight}- \text{ Initial weight}) \times 10^3}{\text{Initial weight}}
\]

The desorption of CO\textsubscript{2} was performed on the CO\textsubscript{2} adsorbed samples by heating them at 150 °C. The regeneration studies were performed on the samples by continuing the adsorption-desorption process up to 5 cycles.

Results And Discussion

Structure and Morphology

Figure 1 (a), (b), and (c) represents the SEM images of samples before carbonization at a magnification of 50x, which reveals that the samples are spheroid in structure with average diameter between 3.0 to 3.2 mm. The cross section of these samples [Fig. 1 (d), (e), (f)] showed an internal layered structure of CB-0,
while that of NCB-1 and NCB-3 showed a clogged structure indicating HMT induced more compact internal structures. The diameter of carbonized samples [Fig. 1 (g), (h) and (i)] were between 2.5 and 2.8 mm. The outer surfaces of samples exhibited irregular and heterogeneous porous structure. The higher magnification of carbonized samples showed that the incorporation of HMT caused a decline in the porous structure, which was observed to be the maximum in case of NC-3, followed by NC-1 and C-0 [Fig. 1 (j), (k), (l)]. The decline in the porosity may be ascribed to the hydrogen bonding interaction between nitrogen atoms of HMT and -OH groups of chitosan (Fig. 2). The hydrogen bonding interaction brings the polymer chains closer together resulting the hindrance for the evolution of volatile gases during thermal activation process, thereby progressively reducing the porous structure.

**Elemental Analysis**

EDS spot scan and mapping were used for the elemental composition survey of the activated carbon samples. The elemental mapping of the samples is shown in Fig. 3 (a), (b) and (c). The elemental analysis by EDS spot scan illustrate the distribution of C, N and O in all the samples that qualitatively confirmed the doping of nitrogen in the increasing order as the composition of HMT was increased [Fig. 3 (d), (e) and (f)]. The percentages of C, N and H in the activated carbon samples were quantitatively obtained using CHN analysis (Table S1). The elemental analysis of C-0, NC-1, and NC-3 obtained from EDS spot scan as well as CHN analysis confirmed an improvement in the percentage of nitrogen as the concentration of HMT was increased. Thus upon carbonization, nitrogen from HMT was effectively doped on to the carbon framework [20]. Therefore, HMT acts as a better nitrogen dopant as compared to other nitrogen dopants such as urea and ammonia reported by Liu et al. [14] and song et al. [24] respectively. The reported percentages of nitrogen obtained for N-doped activated carbon using urea as the nitrogen dopant was 7.5, while using ammonia as the dopant was 9.72 while that of HMT (present study) is 13.06.

**Thermal Analysis**

The profiles of thermogravimetric analysis (TGA) as well as derivative thermogravimetry (DTG) carried out at 20°C/min. ramping under N₂ atmosphere obtained for samples before and after carbonization are shown in Fig. 4 and Fig. 6 respectively. The TGA plot depicted the weight losses as a function of temperature, while the DTG plot portrayed derivative of weight loss as a function of temperature. From Fig. 4 (a&b), it is observed that the removal of moisture happened for CB-0 at 120°C, which is not prominent for the samples, NCB-1 and NCB-3. This may be due to the increase in the intermolecular H-bonding between chitosan and HMT, which restricts the later samples to coordinate water molecules with functional groups of chitosan (Fig. 2). CB-0 exhibited the 1st decomposition stage from 175°C to 330°C with a maximum decomposition temperature at 240°C. This may be due to the degradation of functional groups and side chains, i.e. –NH₂, -OH, -CH₂OH and -NH(CO)CH₃. The decomposition for NCB-1 started around 190°C and ended at 410°C with a maximum decomposition temperature at 275°C. The initial shoulder at 220°C for NCB-1 observed in Fig. 4(b) may be due to the removal of functional groups and side chains of chitosan followed by the decomposition of HMT. The corresponding decomposition for NCB-3 started at 175°C and ended at 415°C with a maximum at 290°C as a single decomposition event,
which may be due to the simultaneous decomposition of functional groups, side chains of chitosan and HMT. The enhancement in the thermal decomposition temperatures for NCB-1 and NCB-3 as compared to CB-0 may be due to the existence of H-bonding interaction between chitosan and HMT, due to which a higher thermal energy is required to overcome the bonding interaction and to degrade the structure. The 2nd stage of decomposition for CB-0 started at 330°C and ended at 570°C with a maximum at 410°C, while the corresponding decomposition temperature for NCB-1 and NCB-3 was observed between 430 to 700°C with a maxima at 560°C, which may be attributed to the degradation of polymer backbone structure [25]. The slower degradation profile for NCB-1 and NCB-3 as compared to CB-0 indicates the polymer chains are held by HMT due to stronger physico-chemical interaction. NCB-3 showed the highest thermal stability as compared to CB-0 and NCB-1 both in terms of thermal degradation profile and char yield. Figure 5 (a) & (b) represented the TGA and DTG graphs of activated carbons respectively. The TGA and DTG plot reveals that the decomposition for activated carbon samples occurred around 500°C, which was caused by the elimination of labile functional groups –CO and –OH forming a stable carbon-carbon bond in the framework [26]. The thermal stability of N-doped carbon was found to be better than the undoped activated carbon. While considering the residues around 800°C NC-1, and NC-3 possessed about 61%, whereas C-0 had 57% of residues. A similar result was reported by Hai Long Peng et al. where the doping of activated carbon with pentaethylenhexamine (PEHA) resulted in an improved thermal stability of the carbon [27], which is attributed to the confining effect of nanopores.

**FT-IR Analysis**

Fig S2 (a) shows the FT-IR spectra of samples before carbonization. The bands obtained around 3600 – 3400 cm⁻¹ for the three samples correspond to the O-H stretching vibration. The band at 1593 cm⁻¹ for the samples corresponds to the primary amine N-H bending while the bands around 1050 cm-1 attributed to the C-N stretching of amine groups [28]. The sharp peak at 1380 cm⁻¹ could be assigned to the –CH₃ symmetrical deformation mode. Even though there arises a H-bonding due to the HMT addition in case of NCB-1 and NCB-3, it is not prominently observed due to the broadened FT-IR peaks. Fig. S2 (b) represents the FT-IR spectra of samples after carbonization. The bands around 3600 – 3400 cm⁻¹ correspond to the O-H stretching vibrations, which was similar in the case of samples before carbonization. The bands around 1740 cm-1 was attributed to the –C = O stretching vibrations. The appearance of a band at 1452 cm⁻¹ was attributed to the C-H stretching vibration [29].

**XRD Analysis**

The diffraction patterns of C-0, NC-1, and NC-3 are depicted in Fig S3. No significant difference in the diffraction patterns was observed among the three samples. All the samples possessed patterns of a non-ordered material i.e. an amorphous structure with a very low degree of graphitization [30]. The broad and weak peaks obtained at 2Θ = 25° was ascribed to the (002) plane of polycyclic aromatic C- sheets of amorphous carbon in irregular orientation and reflection of graphene, whereas 2Θ = 42° represented the (100) plane of 2D in-plane diffraction of graphene sheets. A similar result was observed by Limin et al. in the case of activated carbon prepared from urea modified coconut shell [31]. The percentage of crystallinity from the XRD peaks were calculated to be 52.3%, 34.7% and 31.1% respectively for C-0, NC-1
and NC-3 which indicated that the amorphous nature of the carbons increased with the incorporation of HMT. The decrease in the crystallinity can be attributed to the fact that during nitrogen doping, elemental nitrogen enters into the carbon ring by replacing carbon, thereby destroying its graphitic lamellar structure [32].

**Raman Spectral Analysis**

Figure 6 represents the Raman spectra of C-0, NC-1 and NC-3. All the samples showed two peaks at 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\) corresponding to the D and G bands of graphitic carbon respectively. D band corresponds to the A\(_{1g}\) mode similar to the in-plane breathing vibration, which is Raman inactive in large crystals that becomes active due to the presence of disorder parts like grain edges. The G band is attributed to the E\(_{2g}\) in-plane vibrational mode of sp\(^2\) carbon framework in the planar hexagonal crystal lattice [33]. The degree of disorder in the graphitic structure is determined by the intensity ratio, I\(_D\)/I\(_G\). In the case of C-0, NC-1 and NC-3 the I\(_D\)/I\(_G\) values were calculated from the peak heights and found to be 1.21, 1.23 and 1.25 respectively. The increase in the values of I\(_D\)/I\(_G\) indicated the increase of disorder in the graphitic structure, which may be caused by the doping of nitrogen. As the defect in the N-doped activated carbons increases due to the incorporation of nitrogen into the graphitic framework, the intensity of D band increased and as a result the I\(_D\)/I\(_G\) value also increased. A similar result was reported by Shuai Zhang et al., where the undoped activated carbon possessed an I\(_D\)/I\(_G\) of 1.15 and the doping of activated carbon using polyethylenimine (PEI) in different ratios resulted in the increase in I\(_D\)/I\(_G\) to 1.32, 1.35 and 1.45 due to the irregularity in carbon atom configuration by the incorporation of nitrogen [34]. The increase in the I\(_D\)/I\(_G\) value was consistent with the XRD data and this reveals doping of nitrogen in case of NC-1 and NC-3.

**N\(_2\) adsorption desorption isotherm**

The N\(_2\) adsorption desorption isotherms represented in Fig. 7 (a) showed characteristics of mesoporous materials having a typical Type 4 isotherm with a hysteresis loop caused by the capillary condensation [35]. The N\(_2\) adsorption decreased as the ratio of HMT impregnation was increased. Subsequently, the surface areas for NC-1 and NC-3 were lesser than that of C-0 as shown in Table S2. Hai Long Peng et al. reported a comparable results with PEHA loadings on the activated carbon [27]. Considering the BJH pore size distribution in Fig. 7 (b), the distribution around 2 nm showed the presence of micropores and the distribution around 2–50 nm showed presence of mesopores. The mean pore diameters 2.211 nm, 2.105 nm and 2.125 nm for C-0, NC-1, and NC-3 respectively calculated from the BJH pore size distribution indicates that all the three samples possessed mesoporous characteristics [36].

The iodine values for the three samples obtained using ASTM D4607-94 [37] were 1262 mg/g, 1196 mg/g and 1080 mg/g respectively, which also indicated that HMT doping results in the decrease of porosity. The total pore volume of C-0, NC-1 and NC-3 were 0.138 cc/g, 0.095 cc/g and 0.075 cc/g respectively. Among the three samples C-0 possessed the maximum surface area and pore volume. Therefore, it was observed that by the doping of activated carbon with HMT, there occurred a deterioration
in the structural characteristics, which corroborate with XRD analysis. The surface characteristics, nitrogen content as well as the CO\textsubscript{2} adsorption capacity of these samples were compared with other activated carbons recorded in the literatures and is listed in Table 1. On comparison, it was observed that the activated carbon adsorbents in this study exhibited better adsorption capacity but using simple synthesis method than that of many other activated carbons. In the case of carbon sorbents, which showed higher surface area as well as adsorption capacity in the previous literatures, the method of preparations were complex and further, the raw materials used in the processes were costlier.

| Sample | Carbon precursor, nitrogen dopant | N content (%) | BET surface area (m\textsuperscript{2}/g) | CO\textsubscript{2} adsorption capacity (mg/g) at 25\textdegree C (method) | Ref |
|--------|----------------------------------|--------------|------------------------------------------|----------------------------------------------------------------|-----|
| C-0    | Chitosan                         | 7.563        | 391.502                                  | 97.98 (U-Tube method)                                              | This work |
| NC-1   | Chitosan, HMT                    | 9.458        | 259.017                                  | 72.95 (U-Tube method)                                              | This work |
| NC-3   | Chitosan, HMT                    | 13.06        | 111.717                                  | 55.11 (U-Tube method)                                              | This work |
| Biochar| Cotton stalk, NH\textsubscript{3} | 0.71         | 435                                      | 79.20 (Thermogravimetric analysis)                                 | [38] |
| AC-NH-400| Eucalyptus wood, NH\textsubscript{3} | 3.14        | 1637                                     | 48.40 (Volumetric method)                                          | [39] |
| ANF-0.5T | PAN, TEPA                        | 9.51         | 59.66                                    | 18.48 (Monosorb)                                                   | [15] |
| SU-25-1-650 | Sucrose, urea                   | 7.7          | 1745                                     | 189.20 (Thermogravimetric analysis)                                | [40] |
| PTSA-β-CD-2.5 | β-cyclodextrin                 | Not reported | 620                                      | 112.64 (Thermogravimetric analysis)                                | [41] |
| CSc-2-700 | Carboxymethyl cellulose         | Not reported | 1705                                     | 182.00 (ASAP 2020)                                                 | [42] |
| KQA-1/1-500 | Furfural, urea                  | 7.5          | 1013                                     | 202.4 (ASAP 2020)                                                  | [14] |
| Carbon cryogel | Phenol-Urea-Formaldehyde resin | 2.08         | 1710                                     | 242.44 (ASAP 2020)                                                 | [43] |
**CO₂ adsorption studies**

The CO₂ adsorption uptake of C-0 was calculated to be 97.98 mg/g, whereas for NC-1 and NC-3 were 72.95 and 55.11 mg/g respectively (Fig. 8) with an average uncertainty of 2%. TGA and DTG studies were performed on the CO₂ adsorbed carbon samples (Fig. S4) to evaluate the optimal regeneration temperature. The initial weight loss started at 30°C and ended at 150°C with a maximum weight loss at about 60°C indicated the removal of CO₂ from the carbon samples [Fig. S4 (b)]. The amounts of residue after the initial weight loss was found to be 78%, 81% and 86% for C-0, NC-1 and NC-3 respectively [Fig. S4 (a)], which also confirms that the maximum CO₂ adsorption capacity is for C-0. The TGA plot also revealed that the complete desorption of CO₂ from samples occurred around 150°C. Therefore regeneration studies were performed on the samples at 150°C (Fig. S5). There observed an excellent regeneration capacity for C-0, NC-1 and NC-3. Among the three samples C-0 showed that maximum adsorption capacity with adsorption values of 97.98, 97.55, 96.34, 97.45, 95.34 mg/g respectively. It was expected an increase in the CO₂ adsorption for N-doped activated carbons as reported in previous studies [44, 45]. The basic nitrogen functionalities react with the Lewis acidic CO₂ to increase the chemisorption to a greater extent. However, in the present study, the decline in the adsorption capacity of activated carbon due to the N-doping with HMT was due to deterioration of structural characteristics (i.e. surface area and pore volume). The plausible reason may be due to (i) the hydrogen bonding interaction between HMT and chitosan polymer chain, which reduces the free volume between the polymer networks as discussed in previous paragraph (Fig. 2) and (ii) increase in pH of chitosan precursor solution with the addition of HMT. The addition of HMT to chitosan solution marked a significant increase in the pH. The pH of chitosan solution was measured to be 2.56, while that of chitosan solution mixed with 1:1 HMT and 1:3 HMT were 3.28 and 4.19 respectively. According to the course grind (CG) model reported by Hongcheng Xu et al. the chitosan polymer chains self-aggregate with gradual increase in pH of solution [46]. As depicted in Fig. 9, the self-assembly of chitosan polymer chains starts to form a physically cross-linked network as the pH of the solution is increased from 2.56 to 3.28 and then to 4.19 with respect to the increase in HMT concentration. The resulting physical cross-linking of polymer chains resulted in the deterioration in the surface characteristics such as surface area and pore volume. As a result, the adsorption capacity of N-doped activated carbon prepared from chitosan/HMT precursor system reduced as compared to that of the undoped activated carbon obtained from chitosan alone.

**Conclusion**

N-doped porous activated carbon was prepared by using chitosan as the carbon precursor and HMT as additional nitrogen source. A comparative study on the structural as well as the CO₂ adsorption properties were performed on the undoped and N-doped activated carbons. The nitrogen content for chitosan/HMT derived activated carbons were higher than that of the undoped carbon as observed from CHN as well as EDS analysis. The incorporation of HMT with chitosan solution for the preparation of N-doped activated...
carbon resulted in the deterioration in properties such as surface area, porosity and pore volume of the activated carbon. The N-doped activated carbon exhibited a reduced CO$_2$ adsorption capacity as compared to the undoped carbon and the extent of reduction increased as the ratio of HMT to the chitosan was increased. The decline in the surface characteristics as well as the adsorption capacity were attributed to (i) the H-bonding interaction between chitosan and HMT resulting in the reduction in the free volume of the polymer network and (ii) the physical cross-linking of chitosan polymer network effected by the increase of pH due to incorporation of HMT.

**Declarations**

**Author Contributions**

**Malini K**: Conceptualization, Formal analysis, Visualization, Investigation, Methodology and Writing-original draft. **D. Selvakumar**: Conceptualization and Methodology. **N. S. Kumar**: Project administration.

**Data availability**

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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**Competing interest**

The authors have no competing interests to declare that are relevant to the content of this article.

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**Figures**
Figure 1

SEM images of CB-0 (a), NCB-1 (b), NCB-3 (c); corresponding cross sectional images of CB-0 (d), NCB-1 (e), NCB-3 (f); SEM images of C-0 (g), NC-1 (h), NC-3 (i); corresponding higher magnification (10 kx) images of C-0 (j), NC-1 (k), and NC-3 (l)
Figure 2

H-bonding interaction between HMT and chitosan

Figure 3

EDS Mapping of C-0 (a), NC-1 (b) and NC-3 (c) and spot analysis of C-0 (d), NC-1 (e) and NC-3 (f)
Figure 4
(a) TGA and (b) DTG graphs of CB-0, NCB-1 and NCB-3

Figure 5
(a) TGA and (b) DTG graphs of C-0, NC-1 and NC-3

Figure 6
Raman spectra of C-0, NC-1 and NC-3
Figure 7

(a) $N_2$ adsorption desorption isotherm, (b) Pore size distributions of C-0, NC-1, and NC-3

Figure 8

$CO_2$ adsorption studies of C-0, NC-1, and NC-3

Figure 9

Reorganization of chitosan molecule with increase in pH

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