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Development of preparation method for Tc-99m labelled bamboo biomass radiotracer for its use in pyrolysis reactor

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Abstract

The objective of this study is preparation of Tc-99m labelled bamboo biomass or bamboo shreds as radiotracer for its eventual use in measurements of flow dynamics in pyrolysis reactors. The bamboo shreds were chemically modified and radiolabeled using short lived radioisotope Tc-99m. The labeled bamboo shreds were characterized for analysis of morphology, crystallinity/amorphous nature, surface functionality and quantitative analysis of transfer of adsorbate using SEM, XRD, FTIR and neutron activation analysis (NAA), respectively. The radiolabeling experiments were performed at different pH of solution, temperature, different concentration of precursors and effect of reducing agent. The experimental condition was optimized for maximum transfer of Tc-99m as pertechnetate onto the shreds. Perrhenate as a non-radioactive analogue of pertechnetate was used as surrogate to investigate the adsorption kinetics as well as to characterize the adsorbed shreds. Freundlich model showed best fit with experimental result for describing the adsorption phenomena. Based on experimentally-determined value of enthalpy, the adsorption was found to be physisorption in nature.

Keywords: Technetium-99m, radiotracer, bamboo biomass, pyrolysis reactor, adsorption isotherm, neutron activation analysis

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Introduction

Pyrolysis is a thermochemical decomposition and conversion of different biomass materials into drop-in chemicals, such as bio-fuels, bio-fertilizers, bio-oil and bio-char under influence of zero or lean oxygen [1, 2, 3]. Among this, biochar has garnered significant attention owing to its wide range of applications such as, remediation of hazardous substances, bio-fertiliser, energy resources [4, 5]. The widespread application of biomass material for adsorption of both cationic or anionic heavy ions, such as, AsO_3^-, PO_4^{3-}, ReO_4^-, Cs^+, Pb^{2+}, Cu^{2+}, Cr^{6+} etc. can be attributed to their enhanced structural and functional properties, high stability and considerable porosity [6, 7]. In India, bamboo (Bambusoideae family) is a fast-growing, most-abundant lignocellulosic biomass with significant ecological and industrial relevant [8]. Its rapid growth, high cellulose content, cost-effectiveness and structural properties make it an attractive feedstock for different thermally induced conversion processes such as pyrolysis and gasification [9]. Over last decades, progressive development of pyrolysis reactor has taken intensive discussions for enhancing productivity for practical purpose, such as,coal gasification, bio-oil, biochar production[10]. Consequently, evaluation of flow dynamics of pyrolysis reactor is important to understand mechanism and maintain performance and quality of biomass-derived products [11, 12]. Residence time distribution (RTD) analysis provides in-depth quantitative understanding of flow dynamics, mixing patterns, dead zones, and material residence times of chemical reactor [13]. To determine performance of pyrolysis reactor using radiotracer techniques, radiolabelling of solid phase (biomass) is key step to produce radiotracer [14]. For tracer preparation, three methods are mainly used, such as, neutron activation analysis of activable elements, artificial tracer method, radiolabelling. In the direct method, neutron activation analysis (NAA) is applied to identify activable elements in the process material, after which the material is subjected to neutron-flux in a reactor to produce the desired radioactivity. This method is extensively implemented in polymer industry, fluid catalyst cracking facilities [14], refineries and metal processing industries. In the artificial tracer approach, solid matrix mixed with trace amount of an activable element is meticulously formulated to possess physicochemical properties analogous to those of experimental system. Artificially engineered scandium or iridium doped glass particles have been previously utilised as solid-phase radiotracers in sediment transport investigations owing to their stability, detectability, and compatibility with complex flow environments [15]. Additionally, desired radioisotope is mechanically tagged to prepare solid-phase radiotracers in radioactive particle tracking studies which has become integral to different industry facilitating accurate

elucidation of flow and hydrodynamics parameters, particle transport behaviour [16]. Other than this, radiolabelling is a powerful technique which is applied in healthcare and bioscience, enabling the tracing of nutrient uptake, transport pathways, and metabolic processes with high precision [17]. Over last decade considerable effort has been carried out on different methods of radiolabelling of various substances. Radiolabelling methods can be broadly classified as external (adsorption-based) and internal (chemical incorporation) [17]. In internal labelling, radioisotopes, like C-14 or P-32, are directly incorporated into biomolecules, providing uniform, stable distribution suitable for metabolic or thermal transformation studies. This approach is mainly suitable for medical and healthcare science and has limited scope in industrial perspective. Conversely, external labelling involves adsorption of radioisotopes onto the surface of solid matrix or surrogates [17]. External labelling methods are fast, simple and suitable for short-term tracking of tracer for flow measurement studies in industrial scenarios [15]. Depending on requirement of experiment and nature of tracing medium, some of short-lived radioisotopes such as, Au-198, Br-82, I-131, Sc-46, Tc-99m, La-140 are widely used as radiotracers in industry. Technetium-99m (Tc-99m) is a gamma-emitting radioisotope with a short half-life of six hours, offering rapid detection, minimal environmental persistence, and suitability for real-time tracing applications [18]. Pertechnetate ($^{99m}TcO_4^-$) is easily eluted from generator loaded with fission or reactor-produced $^{99}Mo/^{99m}Tc$. Although, use of Tc-99m has been extensively publicised in medical diagnostics, its potential as radiotracer for studying biomass transformation in pyrolysis reactor remains underexplored [19]. This work is envisioned to provide a framework for radiolabelling of bamboo biomass with Tc-99m in the fields of radiotracer application to monitor material flow, measure process parameters, and residence times of feedstocks in pyrolysis reactor. By tracking the radioactive signature with the help of strategically mounted detector across pyrolysis reactor, it is possible to visualize flow behaviour and reactor performance with high accuracy.

In this perspective, an experimental process has been developed for radiolabelling Tc-99m onto bamboo shreds through batch adsorption experiments in the present study. For practical purpose, rapid transfer of Tc-99m onto biomass was also established using suitable reducing agent. One of the main difficulties encountered in the radiolabelling process was that of the rigid, recalcitrant lignocellulosic structural backbone of the bamboo shreds, which is three-dimensional aromatic biopolymeric network derived from three phenyl propanoid alcohol precursors. For labelling purpose, this hard lignocellulose was leached using acid or alkaline

medium [20, 21]. Hereafter, optimisation of various experimental parameters such as, pH, temperature, concentration of biomass and reducing agent has been investigated and standardised both in presence and absence of reducing agent. Due to their similar chemical and physical properties, including ionic radii and presence of same form of oxygen anion, perrhenate (ReO_4^-) served as non-radioactive surrogate for pertechnetate ($^{99m}TcO_4^-$) for kinetic study and characterization of the adsorbed biomass [22]. The chemically treated, untreated as well as adsorbed biomass was analyzed for morphology, crystallinity/amorphous nature, surface functionality and quantitative analysis of transfer of adsorbate are characterised using different modern analytical method such as SEM-EDX, XRD, ATR-FTIR, neutron activation analysis (NAA), respectively. This systematic and comprehensive study will be utilised in understanding of rapid, sensitive, and eco-friendly assessment of biomass conversion in pyrolysis reactor.

Experimental

Materials and Methods

All chemicals were of analytical grade and were used without additional purification. Deionized water was used to prepare all the solutions. Technetium-99m was sourced from TCM-1 coltech ^{99m}TcO generator (BRIT, India) and eluted with 0.9 % NaCl solution in the form of Na $^{99m}TcO_4$. The eluted activity was further diluted with deionized water and in each experiment approximately 1 MBq of $Na^{99m}TcO_4$ was used. The gamma activity was measured using a well type $2^{//}$ x $2^{//}$ NaI(Tl) spectrometer. The infrared *(*IR*)* spectra were captured using an attenuated total reflectance ATR FTIR spectrophotometer (Shimadzu IR affinity 1). *The* Scanning electron microscope (CamScan-4DV, *Cambridge,* UK) was used to investigate surface morphology. For SEM measurements, the samples were coated with a thin layer of gold and mounted on a copper grid using a double stick carbon tape. The chemical analysis for the trace level of adsorbate was quantified using neutron activation analysis (NAA). A high resolution γ-ray spectrometer consisting of HPGe detector coupled to a PC-based 4 K channel analyzer (MCA) obtained from Eurysis Measures, France and related software was employed in NAA measurements.

Preparation of bamboo shreds

The cylindrical blocks of bamboo were mechanically chopped into small shreds of irregular sizes as shown in Figure 1. The shreds were segregated to sizes 501-1000 µm, 51- 500 µm and < 50 µm using an automated sieving apparatus and weight of each size fraction was measured. The results showed that the fraction of shreds with sizes 501-1000 µm, 51- 500 µm and < 50 µm were 96.47 %, 2.45 % and 1.08 wt%, respectively. For each experiment the adsorbent was prepared by mixing each size fraction as per the actual composition.

Batch adsorption studies of bamboo shreds

Accurately measured bamboo shreds were first washed with distilled water to remove dust and other loose contaminants. Subsequently, 10 g (dry weight) bamboo shreds were subjected to continuous stirring for 1 hour in 50 ml aqueous $^{99m}TcO_4^-$ solution having activity 1 MBq. Activity in 1 ml of $^{99m}TcO_4^-$ solution before and after contact with the adsorbent was measured using a well-type NaI(Tl) gamma spectrometer. Prior to the measurement of activity of the solution after the completion of the adsorption process, about 5 ml of the suspension was centrifuged at 5000 rpm for 5 minutes. The activity content of 1 ml of the supernatant of centrifuged aliquot was taken for measurement in the gamma spectrometer. The efficiency of adsorption is given in Eq (1) and was estimated by calculating the difference between the activity of initial and final solution with respect to the initial solution. The efficiency of adsorption was found to be very low, i.e., ~10-11%.

$$\text{Adsorption efficiency (\%)} = \frac{A_i - A_t}{A_i} \text{ x } 100 \qquad \text{Eq (1)}$$

Where, A_i is the initial activity of the adsorbate (count rate), A_t is the activity of the adsorbate after equilibrium (count rate).

To increase the uptake of the adsorbate by the biomass, the adsorption method was modified. 10 g of bamboo shreds were first mixed with 500 ml of 1 x 10^{-2} mol dm^{-3} stannous chloride ($SnCl_2$) solution and stirred for 1 hour. Subsequently, the shreds were filtered and washed thoroughly with distilled water to remove residual $SnCl_2$. The $SnCl_2$ soaked bamboo shreds were then transferred to an aqueous solution containing $^{99m}TcO_4^-$ and similar procedure was followed as mentioned in the above paragraph for adsorption studies. The efficiency of adsorption was estimated to be 33-34 %.

To further increase the efficiency of adsorption, the washed bamboo shreds were treated with either acid or base separately. For acid treatment 10g of the shreds were mixed with 250 ml aqueous solution of 1 mol dm^{-3} HCl and stirred for 1 hour. Subsequently, the shreds were filtered and washed thoroughly with distilled water till the pH of the washed solution was 7, followed by soaking in $SnCl_2$ solution. Thereafter, the $SnCl_2$ soaked bamboo shreds were transferred to an aqueous solution containing $^{99m}TcO_4^-$ and similar procedure was followed as mentioned in above paragraph for adsorption studies. The percentage of adsorption was found to be 87 - 89 %.

For alkali treatment, the bamboo shreds (4 g) were mixed with 50 ml of 1 mol dm^{-3} NaOH and stirred for 1 hour, filtered and rinsed with distilled water till the washed solution had a neutral pH. The shreds were immersed in 50 ml of 1 x 10^{-2} mol dm^{-3} $SnCl_2$ solution for 1 hour, followed by washing with distilled water to remove residual $SnCl_2$. The treated bamboo was then soaked in a $^{99m}TcO_4^-$ solution for 1 hour and after the activity in the adsorbate was measured. The schematics of detailed procedure of radiolabelling is shown in Figure. 2. The radiolabelling efficiency of $^{99m}TcO_4^-$ onto bamboo shreds was optimized, achieving an adsorption efficiency of 98–99%.

To observe the spontaneous adsorption of $^{99m}TcO_4^-$ on bamboo shred the above experimental procedure was repeated without addition of the reducing agent ($SnCl_2$). Under this condition the adsorption efficiency of 95% was achieved. The radiolabelling protocol for bamboo shreds was successfully scaled up to 50 g for practical applications.

Result and Discussion

Characterization of bamboo shreds

Perrhenate (ReO_4^-) as a non-radioactive surrogate of pertechnetate ($^{99m}TcO_4^-$) was used to investigate adsorption isotherms as well as for characterization of the bamboo biomass after spontaneous adsorption without addition of the reducing agent. The unmodified bamboo biomass (UBM), alkali treated bamboo biomass (ABM) and perrhenate adsorbed bamboo biomass (RBM) were characterized for analysis of morphology, crystallinity/ amorphous nature, surface functionality and quantitative analysis of transfer of adsorbate on to the biomass, using SEM-EDX, XRD, ATR-FTIR and neutron activation analysis (NAA), respectively.

Infrared (IR) Spectroscopy

Comparative analysis of the infrared (ATR-FTIR) spectra of the untreated (UBM), alkali treated (ABM) and perrhenate adsorbed bamboo biomass (RBM) provides deep insights into the modifications of surface functional groups within the bamboo shreds (Figure 3). The bands at 1420, 1510, and 1622 cm^{-1} were attributed to the vibration of C=C bond stretching in the aromatic lignin skeleton, 1237 cm^{-1} was attributed to the C–O stretch, while the peak at 1458 cm^{-1} resulted from asymmetric bending in the CH_3 of lignin in UBM. Additionally, a notable peak in between 2849 to 2918 cm^{-1}, indicative of cellulosic O-H and C-H stretching vibrations in UBM. The intensity of bands at 1105, 1237, 1420, 1460, 1505 and 1622 cm^{-1} significantly decreased in ABM compared to UBM. This indicates the alkali treatment substantially removed the lignin from the biomass. Moreover, considerable decrease in intensity at 1027 cm^{-1} corresponding to C-O bond stretching of primary alcohol is accounted, corroborating leaching of lignocellulosic matrix under alkaline conditions. While comparing ABM with RBM, a slight shift in the band position accompanied by discernible decrease in intensity at 3365 cm^{-1} was observed. This corresponds to effect t of metal cation adsorption on the hydroxyl stretching frequency. This observation validates successful interaction of surface hydroxyl group with ReO_4^-.

Neutron Activation Analysis (NAA)

To rigorously evaluate the adsorption characteristics under consistent experimental conditions and to quantify the surface-bound rhenium on bamboo specimens, exploiting $^{187}Re(n,\gamma)^{188}Re$ nuclear transmutation, neutron activation analysis (NAA) of unmodified bamboo biomass (UBM) and perrhenate adsorbed bamboo biomass (RBM) were performed. Quantitative analysis of the samples clearly revealed that amount of Re adsorbed on bamboo was found to be 1630 ± 160 ppm (0.16 %) which is in lieu with experimental result.

XRD

The X-ray diffraction patterns of the biomass, UBM, ABM and RBM are shown in Figure 4, were characterized by a broad diffuse peak at 2θ angle of approximately 22° with a shoulder at 15°. Findings by Huiling et al. [23] and Lin et al. [24] suggest crystalline property of bamboo biomass. Lignin and hemicellulose are known to possess amorphous properties, whereas,

cellulose is semi-crystalline in nature. In the present work the diffused diffraction peaks support these findings.

SEM-EDX

The change in surface morphology during alkali leaching was investigated by performing scanning electron microscopy of the untreated (UBM) and alkali treated (ABM) bamboo shreds, and is shown in Figure 5. According to the micrograph depicted in Figure 5 (a,c), the texture of untreated bamboo surface (UBM) seems to be rough, wrinkled and non-porous. Post-leaching (ABM), the pore network of the bamboo substrate can be observed as a loosely associated, macroporous architecture as shown in Figure 5 (b,d). It should be emphasized that the elevated adsorption of Tc-99m is facilitated by development of porous network as corroborated by the SEM micrograph.

Comparison of Tc-99m radiolabelling efficiency under different conditions

A comparative analysis of different methods of radiolabelling under optimised conditions are shown in Figure. 6. The main hindrance for adsorption of Tc-99m (as TcO_4^-) on the bamboo biomass is its native highly-ordered structurally-rigid lignocellulosic matrix. To overcome this, the bamboo shreds were subjected to acid and alkali separately. After acid treatment, the relative percentage of adsorption is enhanced drastically to 87 to 89 %. Acid pretreatment initially promotes acid-catalyzed hydrolysis of hemicellulose which selectively removes hemicellulose while induces partial lignin solubilization through cleavage of acid-labile linkages. However, effect of acids is constrained by their inability to remove complex lignin. However, the highest labeling efficiency (~ 99%) was attained when the bamboo was leached with an alkali solution as evident from Figure 6. The chemical structures of hemicellulose and lignin are shown in Figure 7 adapted from [25]. NaOH is popularly well known for disrupting and removing lignin from bamboo biomass by dissolving polysaccharides and inducing chemical swelling of aromatic phenolic network as well. This, in turn, leads to an increased surface area and increased porosity of the biomass for enhanced adsorption of Tc-99m [26].

Effect of different parameters on radiolabelling of alkali leached bamboo shreds

Effcet of NaOH concentration

One of the key steps in the labelling process was the leaching of the lignocellulosic components, which significantly modulated radiolabelling efficiency by developing expanded porous network. Hence, systematic investigation into the influence of NaOH concentration in the leaching medium is valuable for practical applications. Figure 8 delineates the effect of NaOH concentration in the leaching medium on the sorption kinetics. As the concentration of NaOH varied from 3.0 x 10^{-3} mol dm^{-3} a significant increase in the percentage of Tc-99m adsorption was accounted (Table 1). The treatment of bamboo-derived bio-adsorbents with NaOH basically removes lignin and hemicellulose, widens existing pores, increases specific surface area, and exposes active functional groups that bind the metal ion. With increase in the alkali concentration these effects are enhanced. When the NaOH concentration was increased from 2 mol dm^{-3} to 3 mol dm^{-3}, no significant change in the adsorption capacity was observed. This may be due to the saturation of the delignification process.

Effect of pH

The pH of the adsorption medium containing TcO_4^- constitutes a critical experimental variable in radiolabelling studies, because the chemical property of the surface functional groups on the bamboo biomass is dependent on prevailing pH conditions. The radiolabelling of bamboo shreds was executed at different pH, such as 3, 5 and 7 of TcO_4^- solution and the corresponding sorption kinetics is shown in Figure 9 and the estimated adsorption efficiency are given in Table 1. It is evident that the adsorption of Tc-99m is more efficient at lower pH. This is possible due to the cellulose matrix of the bamboo shreds attains a net positive charge caused by partial protonation of the functional groups of cellulose. Thus, a strong electrostatic interaction exists between the positively charged cellulose matrix with the anionic pertechnetate (TcO_4^-), which leads to enhanced adsorption at lower pH. Nevertheless, the biomass surface is modified through continuous deprotonation as the solution pH increase which in turn results in reduction in electrostatic force of attraction between the similar-charged sorbent and sorbate, thereby exhibiting poor sorption capacity at higher pH. This concept supports the findings by other researcher [26]. Based on investigation by Wang et al. [26], sorption of $^{99m}TcO_4^-$ is primarily due to replacement of OH^- groups with pertechnetate ions through ionic mechanism shown below:

$$R\text{-}C\text{-}OH + {}^{99m}TcO_4^- \longrightarrow R\text{-}C\text{-}O^- + {}^{99m}TcO_3 + OH^- \quad \text{Eq (2)}$$

Effect of temperature

An optimal thermal condition enhances the reaction kinetics, facilitates reactant adsorption–desorption dynamics, thereby maximizing the overall radiolabelling efficiency of the system. The influence of solution temperature on the adsorption of Tc-99m on the bamboo shreds is shown in Figure 10 and Table 1. The inverse relationship between adsorption efficiency with temperature suggests that ions/molecules adsorbed initially on the bamboo surface tend to de-adsorb from the surface at elevated temperatures. A decrease in the adsorption efficiency at elevated temperature is an indicative of exothermic physisorption mechanism between bamboo surface and Tc-99m. Different thermodynamic parameters, such as, the Gibb's free energy ($\Delta G°$, kJ mol^{-1}), enthalpy ($\Delta H°$, kJ mol^{-1}), and entropy ($\Delta S°$, J mol^{-1} K^{-1}) change associated with Tc-99m adsorption were calculated using the Gibb's free energy change ($\Delta G°$) equation (Eq. (3)), and Van't Hoff equation (Eq. (4)).

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \qquad \text{Eq (3)}$$

$$\ln K_c = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \qquad \text{Eq (4)}$$

Where, K_C is the distribution coefficient of adsorption, T is temperature (in K), and R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

The equilibrium constant (K_c) values corresponding to the adsorption of Tc-99m ions onto bamboo shreds were delineated over a range of temperatures, after attaining adsorption equilibrium within 40 minutes. The variation of $\ln K_c$ as a factor of the reciprocal of temperature is portrayed in Figure 11. A systematic and monotonic decrease in $\ln K_c$ with progressive elevation in temperature was observed, thereby implying subdued adsorbate–adsorbent interactions at higher thermal conditions. From the slope and intercept of $\ln K_c$ vs 1/T plot, the value of ΔH and ΔS was estimated to be -24.48 KJ/mol and -62.55 J/mol, respectively. The values of the free energy of adsorption for the present system ($\Delta G°$) at temperatures 25, 40, 55 and 60°C were estimated to be -5.78, -5.02, -4.03, and -3.08 kJ mol^{-1}, respectively. The negative values of ΔG^{o} suggests spontaneous nature of adsorption process. However, the ΔG^{o} value become less negative at elevated temperature, thus suggesting the driving force for adsorption decreases with increase in the temperature. These results confirmed that, the adsorption of Tc-99m on bamboo shreds is a spontaneously driven exothermic-physisorption

process that exhibits maximum efficiency at lower temperatures, because elevated thermal conditions weaken the adsorbate-adsorbent interactions.

Adsorption isotherms

In order to evaluate the sorption capacity and adsorption isotherms on bamboo shreds, perrhenate, a non-radioactive surrogate of pertechnetate was selected as the adsorbate. An aqueous NH_4ReO_4 solution across an initial concentration spanning 4 x 10^{-3} mol dm^{-3} to 1 x 10^{-2} mol dm^{-3} were spiked with $^{99m}TcO_4^-$ radiotracer for the adsorption studies. The sorption behaviour of perrhenate anions onto the bamboo matrices was systematically evaluated at constant temperature of 25 ^{0}C and pH 3 and subsequently quantified via gamma spectrometric analysis after reaching adsorption–desorption equilibrium. The resultant adsorption equilibrium data, was fitted and compared with both Freundlich and Langmuir isotherms (Table 2). It exhibited pronounced conformity with the Freundlich isotherm based on R^2 and residual sum of squares (Figure 12), therefore substantiating the intrinsic heterogeneity of bamboo and distribution of energetically non-equivalent sorption sites. The distribution coefficient (K_d), sorption capacity (Γ) and equilibrium concentration of perrhenate (C_{eq} in mol dm^{-3}) were evaluated with the help of following equations:

$$K_d = \frac{A_i \quad A_t}{A_i} x \frac{V}{m} \qquad \text{Eq (5)}$$

$$\Gamma = K_d \ x \ C_{eq} \qquad \text{Eq (6)}$$

$$C_{eq} = C_i \ x \ \frac{A_t}{A_i} \qquad \text{Eq (7)}$$

Where, C_i is initial concentration of perrhenate, V is volume of adsorbate (ml) and m is amount of the adsorbent (g).

The expression of Freundlich isotherm is is given in Eq. (8).

$$\Gamma = C^{1/n} K_F \qquad \text{Eq (8)}$$

Where, K_F and n are Freundlich constants, n serves as an index of surface heterogeneity and adsorption intensity. The Freundlich constant n and K_F of bamboo shreds were found to be 0.83 and 9.36. Moreover, applicability of the Freundlich isotherm for $^{99m}TcO_4^-$ uptake on bamboo shreds was well documented in literature, thereby reinforcing its mechanistic relevance [26, 27].

Optimization of $SnCl_2$ on labelling of Tc-99m

Optimization of $SnCl_2$ concentration

In order to establish impact of variation of reducing agent ($SnCl_2$) on the radiolabelling of Tc-99m, the labelling experiments were carried out across $SnCl_2$ concentrations, 0.5-1.5 x 10^{-2} mol dm^{-3} at pH 3. The reaction was observed to be slowed down at lower concentration of the reducing agent, while, higher concentrations of $SnCl_2$ accelerated the rate of reaction as it can be evident from Figure 13 and Table 1. The reaction of TcO_4^- with $SnCl_2$ is given by following stoichiometric equation.

$$2\ TcO_4^- + 3\ Sn^{2+} + 8\ H^+ \longrightarrow 2\ TcO_2 + 3\ Sn^{4+} + 4\ H_2O \qquad \text{Eq (9)}$$

Under low pH combined with reducing conditions, soluble pertechnetate (Tc-VII) is readily reduced to insoluble lower oxidation states like Tc-IV ($TcO_2\ nH_2O$ or $TcO(OH)^+$), which precipitate or bind much more tightly onto the solid cellulosic backbone. Therefore, it can be inferred that the concentration of the reducing agent has a substantial impact on radiolabelling performance by modulating reaction kinetics.

Optimization of pH for radiolabelling of Tc-99m

Due to the pronounced pH sensitivity of the Sn^{4+}/Sn^{2+} redox pair and modification of formal potential of $^{99m}TcO_4^-/TcO_2$, drastic enhancement on reduction of $^{99m}TcO_4^-$ become significant under acidic conditions as evidenced from relevant Nernst equation (Eq, (10)). To maintain pH of tracer medium, a fixed amount of alkali leached bamboo was subjected to radiolabelling at fixed temperature 25 ^{0}C. The pH was changed by adding aqueous HCl dropwise in presence of 1 x 10^{-2} mol dm^{-3} $SnCl_2$. As evident from Figure 14 and Table 1, the rate of radiolabelling is accelerated in the pH range 1-5, whereas, it decreases at pH 7. This is beacause, $SnCl_2$ acts as a powerful reducing agent that converts highly mobile Tc(VII) into less mobile Tc(IV) species.

The redox potential for this reduction process is highly pH-dependent and is significantly more thermodynamically favourable in acidic conditions. In additions to this, the pertechnetate exists as a stable, negatively charged oxoanion (TcO_4^-), which is strongly attracted to the positive sites of biomass adsorbent via electrostatic interactions above pH 7. Hence, the acidic medium is most suitable for radiolabelling of bamboo with Tc-99m with enhanced adsorption efficiency for practical purpose.

$$E_{Tco_{4/Tc}} = E^0_{Tco_{4/Tc}} - \frac{2.303RT}{nF}\log\frac{[H+]^8\ [Sn^{2+}]^3}{[TcO4-]\ [Sn^{2+}]^3} \qquad \text{Eq (10)}$$

Or, $E_{TcO4-/Tc}=E^0{}_{TcO4-/Tc}+0.0197\log[TcO_4^-]+0.0788\ \log[H^+]+0.02955\log[Sn^{2+}]-\ 0.02955\ \log[Sn^{4+}]$ Eq (11)

Conclusion

In the present study, a radiotracer method was successfully implemented to investigate adsorption characteristics of $^{99m}TcO_4^-$ on bamboo shreds at various conditions and eventually optimum conditions for maximum radiolabelling efficiency were standardised. Under optimized condition of adsorption, about 99.2 % of $^{99m}TcO_4^-$ could be transferred onto the bamboo biomass. The study helps to choose optimum amount of activity required for tracing solid biomass in different scale pyrolysis reactors. Therefore, unnecessary radiation exposures during the preparation and handling of the radiotracer can be avoided without compromising the accuracy of the measurements. From the experimental findings, following conclusions can be inferred, there is substantial increase in the radiolabelling efficiency when the bamboo shreds are conditioned under alkali in comparison to acid treatment. The adsorption of $^{99m}TcO_4^-$ on to bamboo shreds was found to be physisorption in nature as per observed exothermicity of the reaction. Under constant adsorbate concentration, adsorbent amount, temperature and time of contact, the adsorption capacity of Tc-99m on biomass was found to decrease with increasing pH and reached a maximum value under acidic condition both in presence and absence of reducing agent. At constant pH of tracer solution, adsorbent amount, temperature and contact time the rate of adsorption of $^{99m}TcO_4^-$ ions was significantly enhanced with increase in concentration of the reducing agent, $SnCl_2$. Freundlich adsorption isotherm was established to provide the best correlation for adsorption of $^{99m}TcO_4^-$ onto the bamboo

biomass. These experimental findings will be utilised for fast and efficient radiolabelling of bamboo biomass to trace solid phase in pyrolysis reactors.

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Tables

Table 1: Adsorption efficiency of TcO_4^- adsorption on alkali leached bamboo shreds estimated under different conditions

Experimental Parameter	Adsorption efficiency of TcO_4^- adsorption on bamboo shreds without using $SnCl_2$ (%)	Adsorption efficiency of TcO_4^- adsorption on bamboo shreds treated with $SnCl_2$ (%)
25 ^{0}C	80	99.9
35 ^{0}C	54.9	99.8

Temperature	55 ^{0}C	35.2	99.6
	65 ^{0}C	24.3	99.9
pH of adsorbate medium	3	92.1	99.6
	5	48.3	99.6
	7	65.2	94.8
Concentration of NaOH used for leaching	0.5 x 10^{-3} mol dm^{-3}	68.2	
	1.0 x 10^{-3} mol dm^{-3}	99.2	
	2.0 x 10^{-3} mol dm^{-3}	98.8	
	3.0 x 10^{-3} mol dm^{-3}	98.1	
Concentration of reducing agent, $SnCl_2$	0.5 x 10^{-2} mol dm^{-3}		78.3
	1.0 x 10^{-2} mol dm^{-3}		82.9
	1.5 x 10^{-2} mol dm^{-3}		99.4

Table 2: Best-fit parameters for isotherm models of 99m-Tc sorption onto bamboo shreds at 25 °C

Isotherms	**R^2**	**Residual sum of squares**
Freundlich Isotherm	0.9947	2.8555 E-4
Langmuir Isotherm	0.9271	1.1549 E-5

Figures



Fig. 1. Bamboo blocks mechanically chopped to shreds for radiolabelling

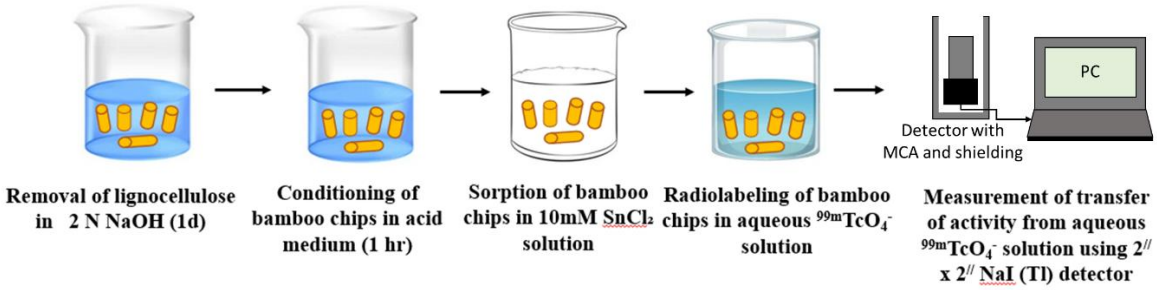


Fig. 2. Schematic representation of radiolabelling process of bamboo shreds

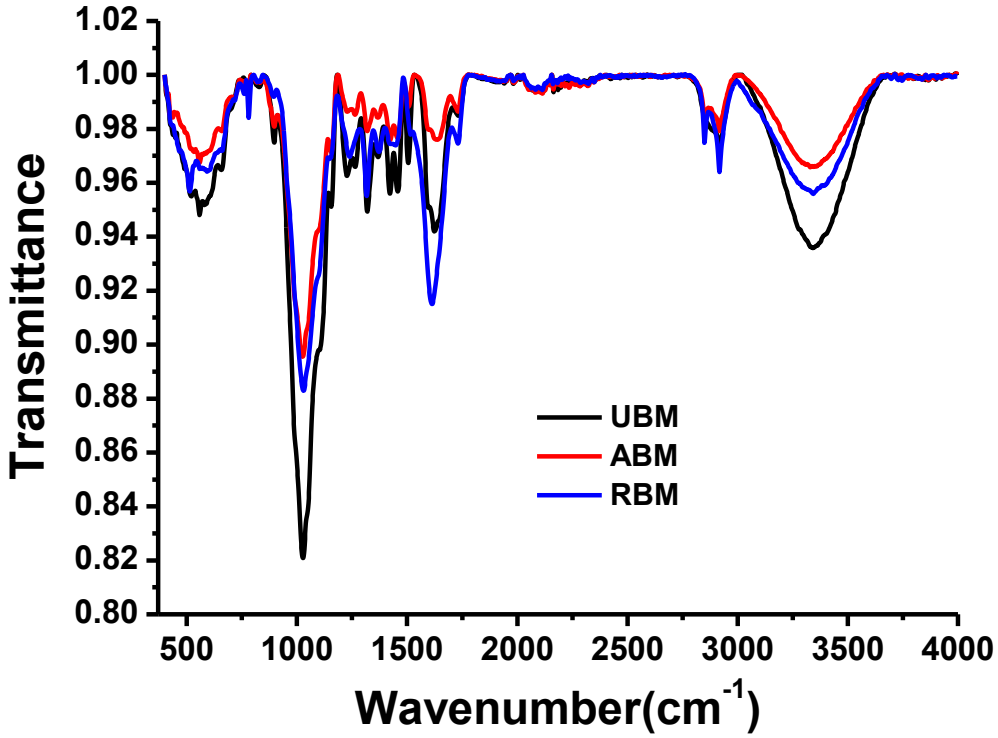


Fig. 3. FTIR spectra of untreated bamboo (UBM), alkali treated bamboo (ABM) and perrhenate adsorbed bamboo (RBM)

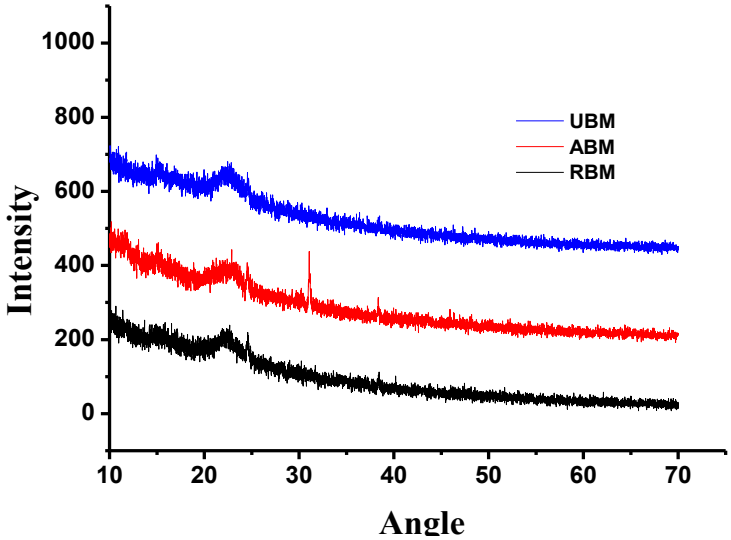


Fig. 4. XRD spectra of unmodified bamboo biomass (UBM), alkali treated bamboo biomass (ABM) and perrhenate adsorbed bamboo biomass (RBM)

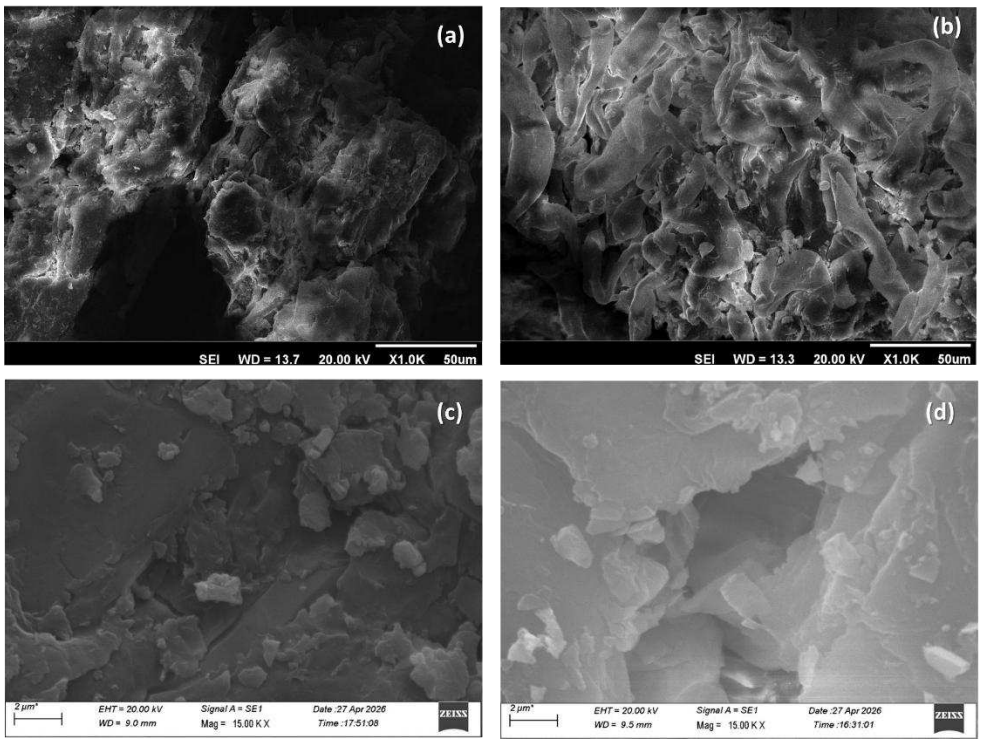


Fig. 5. SEM micrographs captured at 1 kX for **(a)** untreated bamboo shreds, **(b)** alkali treated bamboo shreds; and SEM micrographs captured at 15 kX for **(c)** untreated bamboo shreds, **(d)** alkali treated bamboo shreds

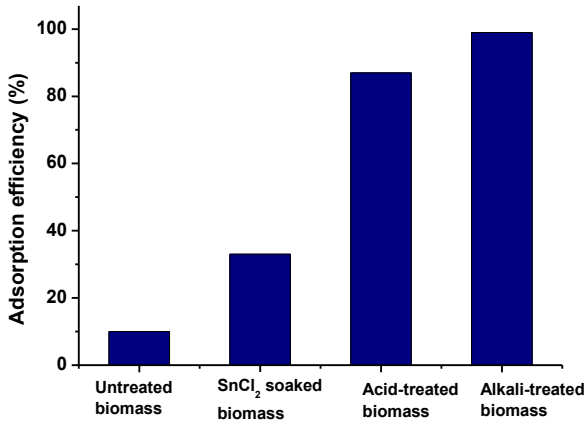


Fig. 6. Comparative analysis of radiolabelling efficiency under different conditions

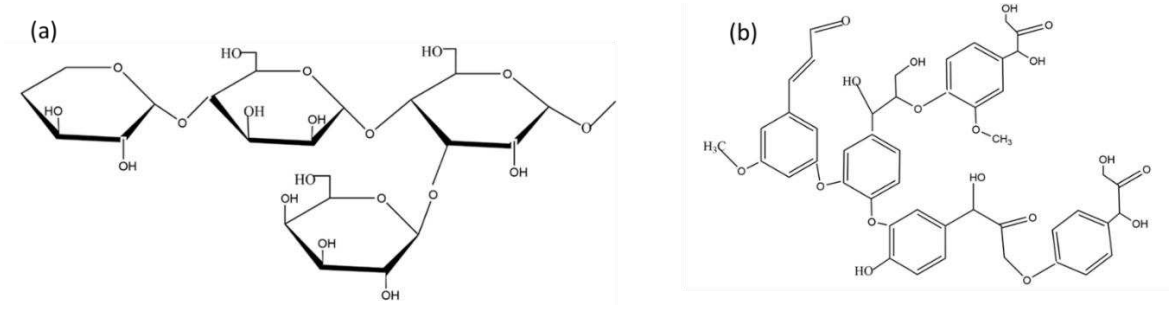
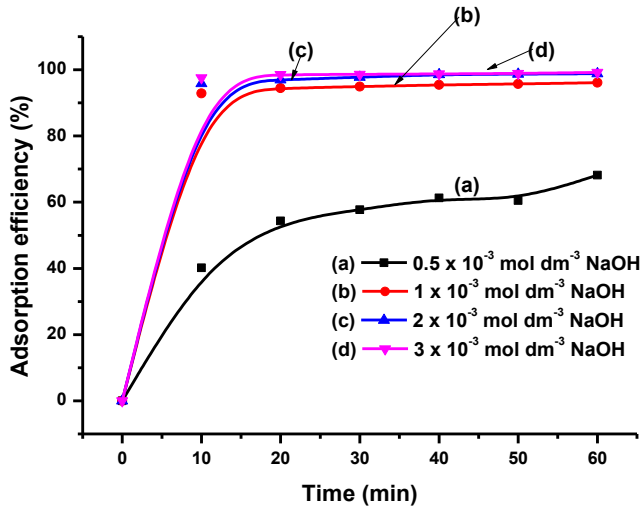


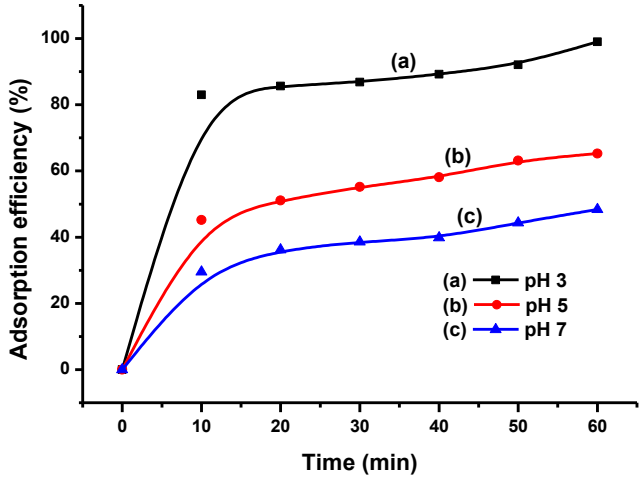
Fig. 7. Chemical structures of hemicellulose and (b) lignin [25]



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570 **Fig. 8.** Effect of NaOH concentration in the leaching medium on the sorption kinetics Tc-99m

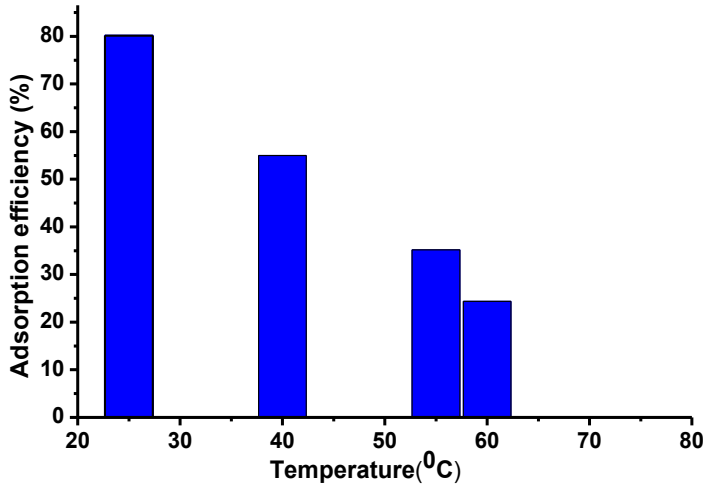
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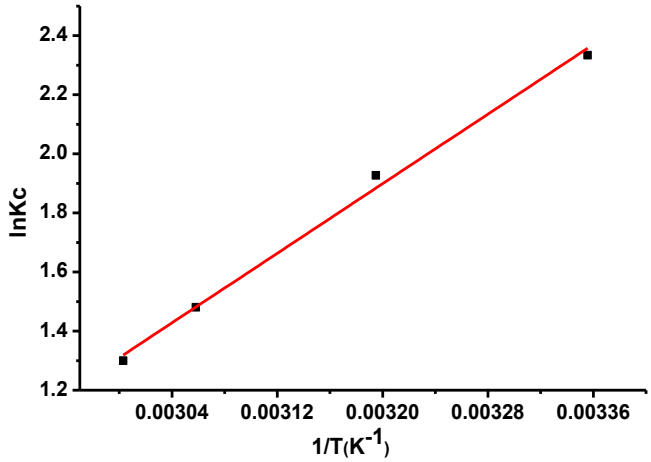
573 **Fig. 9.** Effect of pH of the adsorption medium on the sorption kinetics of Tc-99m

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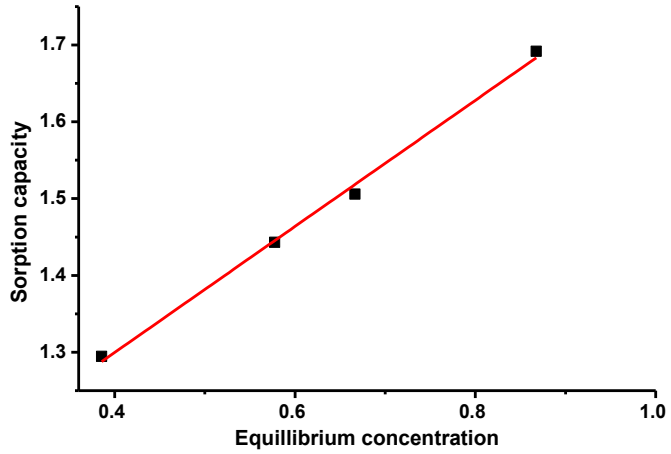


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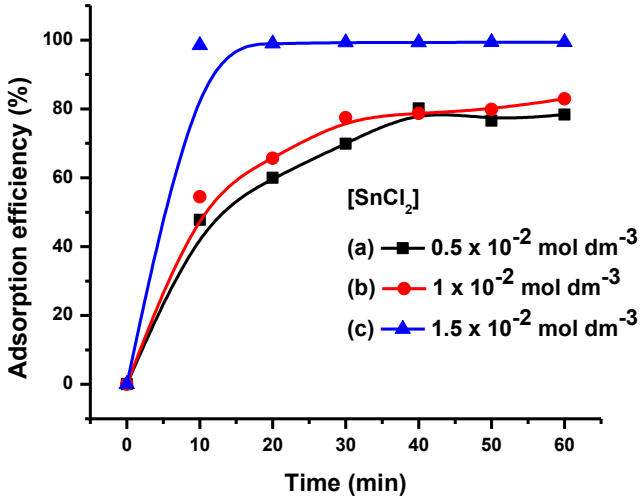
576 **Fig. 10.** Effect of temperature on radiolabelling



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578 **Fig. 11.** Plot of $\ln K_c$ versus 1/T
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582 **Fig. 12.** Plot of Freundlich isotherm fits for Tc-99m adsorption onto bamboo biomass
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585 **Fig. 13.** Effect of variation of reducing agent ($SnCl_2$) concentration on adsorption of 99m-Tc

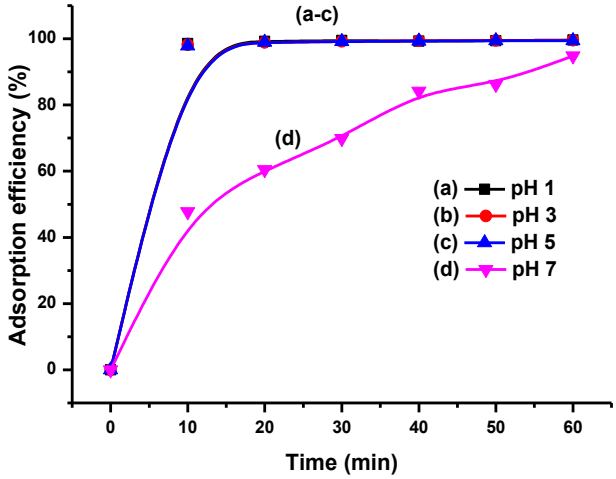


Fig. 14. Effect of pH of Tc-99m labelling solution in presence of reducing agent

Graphical Abstract of the study:

