KONVERSI
Homepage:
https://ppjp.ulm.ac.id/journal/index.php/konversi

Unveiling the role of cellulose solvent systems in direct and sustainable silica amination: A new pathway beyond aminopropyl agents

Hendrix Abdul Ajiz[1,*], Widiyastuti Widiyastuti[2], Heru Setyawan[2], Srie Muljani[1], Ade Sonya Suryandari[3], Nove Kartika Erliyanti[1]

[1]*Department of Chemical Engineering, Faculty of Engineering and Science, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya 60294, Indonesia*
[2]*Department of Chemical Engineering, Faculty of Industrial Technology and System Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo Surabaya 60111, Indonesia*
[3]*Department of Chemical Engineering, Politeknik Negeri Malang, Malang 65141, Indonesia*

ARTICLE INFO

Article history:

Received: 11 August 2025
Received in revised form: 10 August 2025
Accepted: 17 October 2025

Keywords:

Amine loading, biomass waste, carbon capture, chemical grafting, functional material

ABSTRACT

The functionalization of silica surfaces using sustainable amine sources is critical for advancing environmentally friendly materials in CO_2 capture technologies. In this study, bio-based organosilanes derived from coconut coir fiber cellulose were explored as a green alternative to conventional aminosilane. Two solvent systems DMSO/NH_4OH and NaOH/urea were utilized to dissolve and regenerate cellulose, enabling direct grafting onto silica surfaces. Comparative analysis revealed that while DMSO/NH_4OH-dissolved cellulose exhibited a modest amine loading of 23.43% wt, comparable to aminopropyl-based modification (22.41% wt), the NaOH/urea system significantly improved the grafting efficiency, reaching 40.52% wt. This enhancement is attributed to urea's amphiphilic properties, which facilitate both hydrophobic interactions and carbamate formation. The use of a sulfur-free NaOH/urea system not only improves performance but also aligns with green chemistry principles. These results demonstrate the potential of biomass-derived cellulose as a viable modifying agent for silica, paving the way for scalable, low-toxicity, and circular-economy-based material design strategies.

1. Introduction

In the modern era, the dynamics of society increasingly demand the integration of circular economy principles into daily life. This paradigm shift presents a challenge and opportunity for communities to contribute to sustainable technological innovation through the optimal utilization of natural resources. The acceleration of sustainable technologies aims to address pressing global issues, covering economic drivers and the preservation of ecological balance. Among the most critical challenges over the past decade is the reduction of greenhouse gas emissions, particularly carbon dioxide (CO_2), which is generated extensively across both domestic and industrial sectors [1]. Post-combustion CO_2 capture systems have long employed liquid-phase absorbents, such as amine-based solvents and potassium carbonate (K_2CO_3), a practice that dates back over six decades [2]. However, the high energy requirements for solvent regeneration, coupled with the corrosive nature of these liquids on absorber column components, have driven a shift towards solid amine-based adsorbents. Solid amine adsorbents typically consist of an inert host material with surface-functionalized amine ligands, introduced via controlled amination processes.

To date, carbon and silica have emerged as the two most prominent solid support candidates [3,4,5,6]. Although activated carbon exhibits a significantly higher surface area often exceeding that of silica by more than an order of magnitude its inherent brittleness restricts its application under certain operational conditions. In contrast, silica, with its comparatively lower surface area, offers excellent mechanical strength and thermal stability, making it a promising support for amine-based CO_2 capture. Morphological engineering of silica through structuring techniques has enabled the development of materials with enhanced physical properties, including increased surface area and porosity [7,8,9]. These advances allow silica-based materials to be precisely tailored to meet specific application requirements, positioning them as versatile platforms in the development of next-generation adsorbents for sustainable carbon capture technologies.

Despite the advantages of silica as a support for solid amine adsorbents, engineering its surface chemical structure presents a distinct challenge in the synthesis of silica-based solid amines [10,11]. Traditionally, amine functionalities are introduced via ligands such as γ-aminopropyltriethoxysilane (APTES), which are grafted onto the silica surface through random condensation reactions [12,13]. These reactions covalently bond the amine ligand to surface oxygen atoms of silica, with water (H_2O) produced as a by-product. Although conceptually straightforward, the amination of silica using aminopropyl ligands faces several limitations, primarily due to the non-uniform distribution of amine groups on the silica surface, which leads to a relatively low amine loading per gram of silica. This inefficiency arises from the possibility of forming three distinct bonding configurations between the aminopropyl ligand and the silica surface: monodentate,

* Corresponding author.
Email: hendrix_abdul.tk@upnjatim.ac.id
http://dx.doi.org/10.20527/k.v14i2.23610

This open access article is distributed under a Creative Commons Attribution (CC-BY-SA) 4.0 license

bidentate, and tridentate [10,12]. Ideally, a complete and stable grafting requires the presence of three hydroxyl (-OH) groups from surface silanols (Si-OH) to accommodate a single amine ligand [14]. Consequently, the aminopropylation process can significantly reduce the availability of surface silanol groups limiting hydroxyl accessibility to approximately one-third of the original value. Therefore, there is a growing need for alternative surface-modifying agents capable of substituting aminopropyl ligands without compromising their essential chemical characteristics as CO_2 acceptors. These alternatives should enable more efficient surface functionalization while preserving or enhancing CO_2 capture performance, particularly for applications in carbon capture and storage (CCS) systems.

Cellulose has emerged as a promising alternative to conventional aminopropyl ligands for surface functionalization of adsorbents [15,16,17]. As a naturally abundant polymer derived from plant biomass, cellulose offers significant potential as a sustainable functional material [18,19,20,21]. However, its widespread utilization remains constrained by challenges related to its dissolution process. Similar to silica, which can be structurally engineered to enhance its physical characteristics, cellulose being a linear polysaccharide composed of β-D-glucose units can also be regenerated to exhibit various functional properties depending on the solvent system employed during processing. Regenerated cellulose can exhibit distinct structural and crystalline phases, such as cellulose I, II, or amorphous forms, depending on the solvent environment used during dissolution and reformation [22,23,24,25]. One widely studied class of cellulose solvents involves ionic liquids (ILs), which facilitate cellulose dissolution through disruption of intra- and intermolecular hydrogen bonding networks. However, despite their efficiency, IL-based systems suffer from several drawbacks, including corrosiveness, toxicity, and high regeneration costs. These issues limit their applicability in the context of green chemistry and sustainable synthesis. Consequently, although cellulose is inherently a renewable and biodegradable resource and aligns well with circular economy principles, the sustainability of cellulose-based synthesis is highly dependent on the nature of the solvents employed [17,26]. There remains a critical need to develop environmentally benign, low-toxicity, and cost-effective solvent systems that can dissolve cellulose efficiently while supporting long-term application and minimizing ecological impact. Two types of solvent systems have shown potential as dual-function media for forming regenerated cellulose applicable in carbon capture processes, namely dimethyl sulfoxide (DMSO)/tetrabutylammonium acetate (TBAAc) and NaOH at low temperatures [15,22]. However, the reported results remain relatively limited and have not been extensively explored. Therefore, the development of cellulose solvent systems for carbon capture applications presents a promising opportunity, particularly by introducing amine sources to enhance the grafted amine content on cellulose, thereby improving its CO_2 adsorption capacity and functional performance.

The modification of silica using cellulose as an active modifying agent remains relatively limited compared to the extensive use of alkoxy-based ligands such as APTES as an amine source. Nevertheless, the incorporation of cellulose offers a promising pathway toward sustainable hybrid material development due to its renewability, abundant hydroxyl functionalities, and structural versatility. Several synthesis strategies have been reported, with the direct blending method followed by freeze-drying being among the most effective routes to produce three-dimensional (3D) cellulose-modified silica networks. The NaOH/urea solvent system has been predominantly employed over dimethyl sulfoxide (DMSO) due to its sulfur-free composition, environmental benignity, and superior cellulose dissolution capability through strong hydrogen bonding interactions between hydroxyl groups and solvent molecules. The modification process involves direct mixing of the silica precursor (e.g., tetraethyl orthosilicate, TEOS) with cellulose dissolved in the NaOH/urea system, followed by condensation initiated through pH reduction using an acid catalyst. The decrease in pH triggers the condensation of Si-OH groups to form Si-O-Si linkages, leading to the formation of a hybrid silica-cellulose gel network stabilized by both covalent and electrostatic interactions. Ethanol is subsequently introduced as an anti-solvent to promote cellulose regeneration and enhance the homogeneity of the silica matrix. The final freeze-drying step allows solvent removal without collapsing the internal network, yielding cellulose-modified silica aerogels with high porosity, large surface area, and excellent structural integrity [27]. The synergistic interaction between cellulose hydroxyl groups and silica silanol moieties plays a crucial role in strengthening interfacial bonding, improving thermal stability, and enabling further functionalization of the hybrid framework.

In this study, a non-ionic liquid-based cellulose solvent system was developed to overcome the sustainability limitations associated with conventional ionic liquids. The cellulose was extracted from coconut fiber, a lignocellulosic biomass waste, thereby aligning the material sourcing with circular economy principles. The cellulose purification process involved a two-step treatment alkaline digestion followed by peroxide bleaching to enhance the cellulose content by removing hemicellulose and lignin components. Two distinct solvent systems were evaluated for their ability to dissolve the purified cellulose: (i) dimethyl sulfoxide (DMSO)/ammonium hydroxide (NH_4OH) and (ii) sodium hydroxide (NaOH)/urea. The dissolved cellulose was subsequently grafted onto silica surfaces through direct modification techniques. The performance of cellulose-grafted silica was systematically compared to that of conventional aminopropyl-grafted silica under equivalent grafting ratios, with a focus on amine loading capacity. Comprehensive physicochemical characterizations were carried out to evaluate the grafting efficiency and investigate the influence of different solvent systems on the distribution and density of grafted amine groups. These insights are critical for understanding the interaction mechanisms between the cellulose derivatives and the silica surface, as well as their potential applicability in CO_2 capture systems.

2. Materials and Methods

2.1. Materials

Coconut coir fiber was used as the cellulose source and obtained from a coir waste treatment center in Tulungagung, Indonesia. Sodium hydroxide (NaOH, p.a.), sodium silicate (Na_2SiO_3, 27% SiO_2, SiO_2:Na_2O = 3.3, p.a.), absolute ethanol (C_2H_5OH, 100%, p.a.), glacial acetic acid (CH_3COOH, 99%, p.a.), ammonium hydroxide (NH_4OH, 25%, p.a.), and dimethyl sulfoxide (DMSO, C_2H_6OS, 100%, p.a.) were purchased from Merck. γ-Aminopropyltriethoxysilane (APTES, 99%, p.a.) was obtained from Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 50%, technical grade) and urea (CH_4N_2O, technical grade) were purchased from CV. Hekto Gemilang Meraki and PT. Petrokimia Gresik, respectively. Demineralized water (pH ≈ 5) was used throughout all procedures without further purification.

2.2. Methods

2.2.1. Aminopropyl-Modified Silica Particles Synthesis

The synthesis of aminopropyl-functionalized silica particles was carried out via a two-step process: (1) pre-condensation of the modifying agent in a co-solvent system, followed by (2) direct incorporation into the sodium silicate precursor. In the pre-condensation step APTES was mixed with absolute ethanol and deionized water in a 1:1:1 volumetric ratio and stirred for 10 min to initiate hydrolysis and control the condensation rate. Subsequently, the pre-hydrolyzed APTES mixture (1 mL per 30 mL of 0.1 M sodium silicate solution) was added dropwise into the silicate precursor under vigorous stirring. During the mixing process, 1 M HCl was added dropwise to adjust the pH to a range of approximately 10-11, facilitating the simultaneous condensation of silica and organosilane moieties. The resulting solution was subjected to 30 min of ultrasonication to further suppress agglomeration and ensure uniform dispersion. Spray drying was employed to convert the sol into solid particles. The aerosol-based synthesis was performed using a custom-built spray dryer equipped with a cylindrical glass chamber (150 mm diameter x 500 mm height). A two-fluid nozzle atomizer was used to generate fine droplets via compressed air. The nozzle featured concentric feed lines with internal diameters of 1.755 mm (precursor feed) and 10.22 mm (air), and terminated in sharp-tipped needles (ID: 0.5 mm for feed, 1.5 mm for air). The dried particles were collected using a cyclone separator, where centrifugal force separated the solid particles from the gas stream. The heavier particles settled at the cyclone base, while the air and fine vapor exited through the top outlet. The synthesized aminopropyl-functionalized silica was collected for further physicochemical characterization.

2.2.2. Cellulose-Modified Silica Particles Synthesis

Bio-based organo-silane-modified silica particles was synthesized using dissolved cellulose derived from coconut coir fiber, utilizing two solvent systems: DMSO/NH_4OH and a sulfur-free NaOH/urea system. Coconut coir fiber was first refined through a two-step purification process involving alkaline treatment followed by peroxide bleaching. The raw fiber was ground and sieved to 150 mesh, then subjected to alkaline digestion using 17.5% NaOH (20 mL/gram of fiber) under reflux at boiling temperature for 2 h. After cooling, the mixture was filtered to separate the Na-lignin-rich black liquor, and the remaining fibers were washed with demineralized water until the filtrate reached neutral pH. The cleaned fibers were oven-dried at 105°C for 2 h. The dried, digested fibers were then bleached using H_2O_2 (20 mL/gram of fiber), with the solution pH adjusted to 9 using 0.1 M NaOH. The mixture was stirred at 90°C for 1 h, then filtered and rinsed until a clear, neutral filtrate was obtained. This process yielded high-purity cellulose pulp with enhanced whiteness and reduced lignin content. To prepare the cellulose solution, 1 g of dry cellulose pulp (moisture content ~86.42%) was dissolved using either: (i) 5.4 mL DMSO + 7.7 mL NH_4OH, or (ii) a NaOH/urea system consisting of 1 g NaOH, 4 g urea, and 10 mL demineralized water. Dissolution was performed at low temperatures (-5 to -12°C) in an ice bath with vigorous stirring (~600 rpm) for 30 min. The resulting solutions were centrifuged to remove undissolved solids, and the supernatants were used as cellulose precursors. Silicate-cellulose precursors were prepared by mixing 0.1 M Na_2SiO_3 with the cellulose solution in a 10:1 volume ratio. To assist the formation of a regenerated cellulose network, absolute ethanol was added to the mixture at a 1:1 ratio relative to the cellulose volume. The pH was adjusted to the range of 10-11 by the dropwise addition of 0.1 M CH_3COOH to initiate silica nanoparticle formation. The final mixture was spray-dried using an aerosol-assisted system to produce cellulose-modified silica particles. The dried particles were collected and subjected to physicochemical characterization.

2.3. Characterization

The increase in cellulose content as a result of sequential treatment was evaluated using the Chesson-Datta method. The success of the silica surface modification was qualitatively confirmed by Fourier Transform Infrared (FTIR) spectroscopy (Agilent Technologies) within the spectral range of 650-4000 cm^{-1}. Quantitative determination of the grafted modifying agent was performed via thermogravimetric-differential thermal analysis (TG-DTA). The amount of organic modifier anchored to the silica surface was expressed as a mass fraction, calculated based on the mass loss during thermal decomposition. The thermal analysis was carried out in two stages. In the first stage, the moisture content was measured by drying the sample at 105°C until a constant mass was achieved. In the second stage, the dried sample was heated up to the decomposition temperature specific to each modifying system: approximately 700°C for aminopropyl-modified silica, 610°C for cellulose modified via the DMSO/NH_4OH system, and 660°C for cellulose modified via the NaOH/urea system. All thermal treatments were conducted under a nitrogen atmosphere with a heating rate of 10°C/min to avoid oxidative degradation. Upon completion of heating and subsequent cooling to ambient temperature, the residual sample mass was recorded. The mass loss, corresponding to the decomposition of the grafted organic components, was used to determine the loading of the modifying agent on the silica surface (expressed in grams of modifier/gram of total sample). To visually evaluate the morphological transformation mechanism of regenerated cellulose, scanning electron microscopy (SEM, Hitachi

FlexSEM 1000) was employed. This technique provides direct insight into the structural reorganization occurring during cellulose regeneration, allowing detailed observation of surface texture, fibril alignment, and the formation of three-dimensional network architectures.

3. Results and Discussion

The effectiveness of sequential chemical treatment in enhancing cellulose purity from coconut coir fiber was quantitatively assessed using the Chesson-Datta method, with results summarized in Figure 1. A notable increase in cellulose content was observed across the treatment stages. Untreated coconut coir exhibited an initial cellulose content of 39.28%, which increased to 52.22% following alkaline treatment using 17.5% NaOH. A further increase to 59.40% was achieved after subsequent bleaching with 3% H_2O_2, indicating the progressive removal of non-cellulosic components. This improvement in cellulose content was accompanied by a concurrent reduction in hemicellulose and lignin fractions. The decline in hemicellulose content can be attributed to the selective degradation of β- and γ-cellulose, which possess lower degrees of polymerization and are more susceptible to alkaline hydrolysis than the more crystalline α-cellulose. The alkaline treatment efficiently disrupts hemicellulosic chains, promoting solubilization and removal during filtration and washing steps. In contrast, the lignin content remained relatively stable after alkaline treatment, suggesting that the 17.5% NaOH under atmospheric conditions was insufficient to effectively break down the lignin matrix. Lignin is known to exhibit greater chemical resistance, requiring oxidative or more aggressive conditions for depolymerization. The subsequent bleaching step using hydrogen peroxide addressed this limitation. The oxidative action of H_2O_2, particularly at pH 9 and elevated temperatures (90°C), facilitates partial lignin degradation, as evidenced by both chemical analysis and the visibly lighter color of the treated fiber. This visual indicator further supports the removal of chromophoric lignin structures. Overall, the two-step refining process comprising alkaline delignification followed by peroxide bleaching not only significantly enriches the cellulose fraction but also effectively reduces the presence of interfering lignin and hemicellulose. The resulting high-purity cellulose pulp is thus better suited for downstream functionalization and incorporation into silica matrices for material synthesis.

Coconut coir, with its notably high cellulose content of up to 59%, presents a promising biomass-derived feedstock for sustainable silica amination. To evaluate the effectiveness of amine functional group grafting from regenerated cellulose onto the silica surface, a comparative analysis was conducted against conventional amination using γ-aminopropyltriethoxysilane (APTES) as the modifying agent. Unlike direct functionalization with aminopropyl ligands, cellulose-based modification requires a prior structural transformation into regenerated cellulose, which necessitates dissolution in specific solvent systems that can disrupt the hydrogen bonding network and facilitate molecular dispersion. In this study, two distinct cellulose solvent systems: DMSO/NH_4OH and NaOH/urea were employed, both serving dual roles: as cellulose-dissolving media and as intrinsic nitrogen sources for amine functionality. While both solvent systems are capable of dissolving cellulose and supporting regeneration, they differ in their solubilization mechanisms and the chemical pathways through which amine grafting occurs. These differences significantly influence the efficiency of amine group loading onto the silica surface and result in distinct chemical and structural characteristics of the final modified particles. To comprehensively assess and compare the performance of the different modifying systems, both qualitative and quantitative analyses were carried out. Functional group incorporation and bonding interactions were evaluated using Fourier Transform Infrared Spectroscopy (FTIR), revealing characteristic peaks associated with Si-O-Si, N-H, O-H, and organic residues. Meanwhile, the actual amount of amine groups grafted onto the silica surface was determined quantitatively through thermogravimetric analysis (TGA) based on mass loss profiles. This two-pronged analytical approach allowed for a detailed comparison of functionalization effectiveness between the aminopropyl route and the cellulose-based systems, offering insight into the role of solvent-mediated cellulose regeneration in silica surface amination.

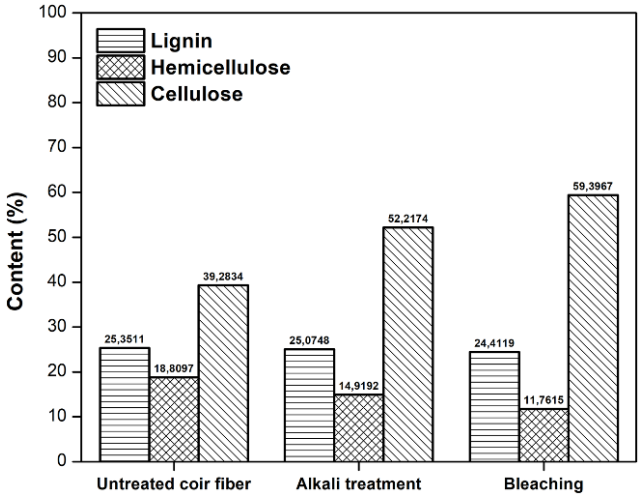

Fig. 1. Physicochemical transformation of coconut coir fiber before and after sequential chemical treatments

The chemical interactions between the silica surface and various modifying agents were thoroughly investigated using Fourier Transform Infrared (FTIR) spectroscopy, as shown in Figure 2. The FTIR spectra revealed significant differences in both the position and intensity of key absorption bands, reflecting the nature and extent of surface functionalization induced by aminopropyl and cellulose-based modifiers. A broad absorption band centered at 3368 cm^{-1}, corresponding to hydroxyl group (O-H) stretching from adsorbed water, appeared in all samples [7]. However, its intensity varied depending on the modifying agent and solvent system. Unmodified silica exhibited a relatively weak signal, while cellulose-modified silica especially those synthesized using the NaOH/urea solvent system displayed markedly stronger intensity. This enhancement can be attributed to the increased hygroscopicity resulting from the presence of hydroxyl and amine-rich functionalities introduced by cellulose and the alkaline solvent system. Modifications also influenced the siloxane bonding region. In unmodified silica, the asymmetric siloxane group (Si-O-Si) stretching vibration appeared at 1056 cm^{-1} [7,8]. This peak shifted to lower wavenumbers upon modification: to 1042 cm^{-1} in cellulose-modified silica and to 1029 cm^{-1} in aminopropyl-modified silica. These downward shifts suggest successful formation of Si-O-C or Si-O-Si

linkages between the silanol groups of silica and the functional groups of the modifiers, altering the structural environment of the silica network. The symmetric Si-O-Si bending vibration was consistently observed at 768 cm^{-1}, further confirming the siloxane framework. Evidence for primary amine incorporation is indicated by characteristic peaks around 1558 cm^{-1} (aminopropyl) and 1577 cm^{-1} (cellulose-NH_4OH or Cellulose-urea), representing N-H bending vibrations [28,29]. The appearance of additional peaks at 1476 cm^{-1} (alkoxy ligands from aminopropyl), 1414 cm^{-1} (cellulose backbone), and 2930 cm^{-1} (C-H stretching) further support the grafting of organic modifiers onto the silica surface [10]. Notably, cellulose-based modification led to higher overall transmittance intensity than aminopropyl, reflecting a higher density of grafted functional groups. This can be ascribed to the multiple hydroxyl groups in cellulose, which serve as active sites for bonding, as well as the formation of cellulose-urea carbamate intermediates that facilitate silica interaction. Interestingly, the cellulose-modified samples also exhibited minor peaks associated with residual biomass-derived components. A peak at 1346 cm^{-1}, corresponding to C-O stretching in aryl-alkyl ether bonds, indicates the presence of trace lignin. Another peak at 922 cm^{-1}, attributed to C-O-C asymmetric stretching, suggests residual hemicellulose [29,30]. These observations are more prominent in the NaOH-urea system, which is known to partially dissolve lignocellulosic components. Nevertheless, the presence of these impurities does not appear to interfere significantly with the cellulose regeneration or its subsequent interaction with the silica matrix. Overall, the FTIR analysis confirms that both the nature of the modifying agent and the solvent system play crucial roles in determining the structural and chemical properties of the functionalized silica. The NaOH/urea-cellulose system demonstrated the most extensive surface modification, as reflected by greater peak shifts and intensities, supporting its potential as a sustainable and effective alternative to conventional aminopropyl-based modification routes.

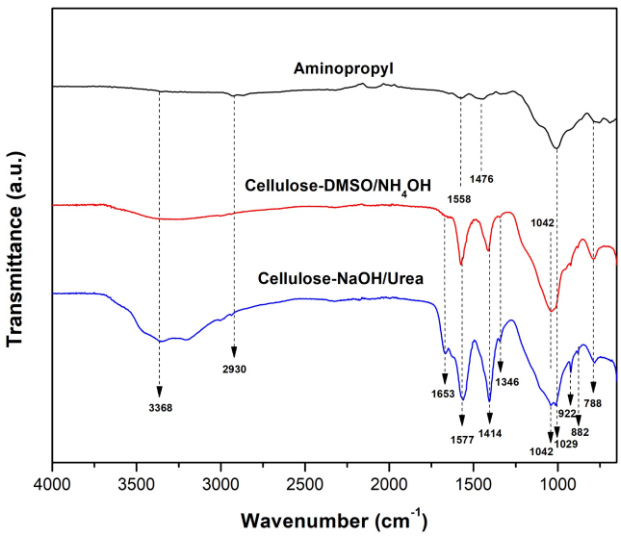

Fig. 2. FTIR comparison of amine-functionalized silica prepared with conventional (aminopropyl) and biobased (cellulose) modifiers

The grafting process of amine functional groups onto the silica surface via regenerated cellulose as a substituent for the alkoxy ligand in APTES exhibits a comparable mechanism to conventional silane coupling. Regenerated cellulose is formed through the disruption of intra- and intermolecular hydrogen bonds along the hydrophilic regions of cellulose. This disruption causes cellulose chains to dissociate into smaller fragments, which subsequently reorganize into long polymeric chains through interactions with solvent macromolecules. Amine-containing dopant species (-NH_2), derived from ammonia and urea, tend to associate with the exposed hydrophilic domains of the cellulose-solvent system, forming ionic linkages depending on their respective affinities. Due to its amphiphilic nature, urea can simultaneously establish dual interactions-hydrogen bonding and hydrophobic associations-between cellulose chains, thereby promoting a stabilized structural arrangement. During the condensation reaction, the amine-containing species polymerize between the cellulose chains, forming extended cross-linked networks that restore a long-chain configuration within the regenerated structure. This transformation can be visually observed in the SEM images (Figure 3), which clearly illustrate the morphological evolution of cellulose before and after regeneration. Initially appearing as short, rod-like fragments with sharp ends, the regenerated cellulose transforms into a denser, elongated three-dimensional network, reflecting enhanced structural compactness and interchain connectivity.

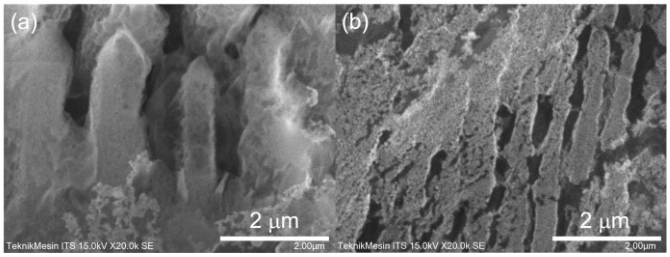

Fig. 3. SEM micrographs of cellulose (a) prior to and (b) following regeneration in the NaOH/urea solvent system

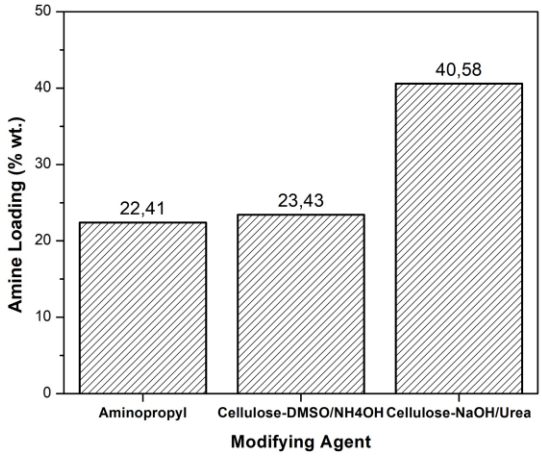

Fig. 4. TGA comparison of silica particles modified with different surface functionalizing agents: aminopropylsilane, cellulose dissolved in DMSO/NH_4OH, and cellulose dissolved in NaOH/urea

The grafting efficiency of amine functional groups onto the surface of silica particles was quantitatively assessed via thermogravimetric analysis (TGA), as illustrated in Figure 4. The proportion of modifying agent grafted onto the silica surface was expressed as the percentage mass loss attributed to the thermal decomposition of organic moieties. This value is directly proportional to the peak intensity observed in FTIR spectra, confirming the consistency between qualitative and

quantitative characterization methods. The results reveal that the type of modifying agent and its corresponding grafting mechanism play pivotal roles in determining the final amine loading. Among the three systems studied, silica modified with APTES exhibited the lowest grafting efficiency, with a loading of only 22.41% wt. This limited performance is likely due to the structural nature of APTES, where each amine group requires at least three hydroxyl groups on the silica surface for effective anchoring. This stoichiometric limitation restricts the extent of surface coverage achievable by aminopropyl-based agents.

In contrast, cellulose-based modifying agents demonstrated higher grafting efficiencies due to the abundance of hydroxyl groups along the cellulose polymer, which facilitate multiple anchoring sites for amine functionalities. Interestingly, cellulose dissolved in the DMSO/NH_4OH system yielded a slightly higher amine loading of 23.43% wt, suggesting that despite the presence of external nitrogen donors (NH_4OH), the dissolution and subsequent grafting interactions remain limited by the solvent's ability to fully disrupt the crystalline structure of cellulose and expose hydroxyl sites. The most significant improvement was observed in the NaOH/urea solvent system, which achieved an amine loading of 40.52% wt. This considerable enhancement is attributed to the dual functionality of urea within the solvent system. Urea not only assists in cellulose dissolution and regeneration but also acts as an amphiphilic amine donor, enabling chemical interactions in both hydrophilic and hydrophobic domains of the cellulose matrix [17,23,31]. In the hydrophilic region, urea contributes to the formation of carbamate cellulose through chemical bonding, while in the hydrophobic region, physically adsorbed urea provides additional NH_2 groups for silica functionalization. This dual mechanism substantially increases the availability of amine groups for surface grafting. Collectively, these findings underscore the critical influence of the solvent system on the effectiveness of cellulose-derived surface modification. While both cellulose-based systems outperform conventional APTES modification, the NaOH/urea pathway stands out as a superior route for achieving high-density amine functionalization, demonstrating its potential as a sustainable and efficient alternative in the development of bio-based organosilane materials.

Beyond its influence on the grafting efficiency of cellulose-amine functional groups on silica surfaces, the type of cellulose solvent system also plays a crucial role in determining the functional characteristics of the resulting silica, particularly its thermal stability. The NaOH/urea solvent system, characterized by its strong alkalinity, acts as an effective catalytic medium that accelerates the hydrolysis and subsequent condensation of silica precursors. The presence of Na^+ ions enhances the condensation kinetics of silanol monomers, promoting the rapid formation of a compact three-dimensional siloxane (Si-O-Si) network. In contrast, the DMSO/NH_4OH system, which exhibits a weaker basic environment, leads to a slower rate of condensation [32]. This slower polymerization allows silanol monomers to undergo incomplete crosslinking, resulting in a more amorphous gel network with a higher fraction of unreacted silanol groups and open pore structures. Consequently, silica synthesized under NaOH/urea conditions exhibits greater thermal stability due to its denser siloxane framework and reduced concentration of residual silanol defects, which otherwise act as thermally labile sites during decomposition. Such behavior is consistent with earlier findings, where strong alkaline catalysts were reported to facilitate the formation of highly crosslinked silica structures with enhanced heat resistance. Therefore, the NaOH/urea solvent system not only improves the grafting efficiency of cellulose-based modifiers but also strengthens the intrinsic thermal robustness of the silica host, making it more suitable for high-temperature and sustainable material applications.

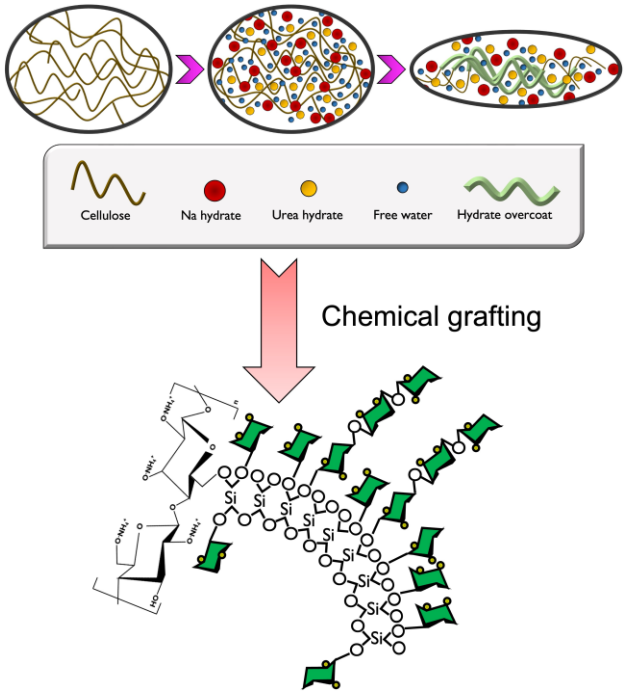

Fig. 5. Schematic representation of cellulose–silica hybrid formation in NaOH/urea system via in-situ grafting mechanism

The development of amine-functionalized cellulose was strategically approached using two distinct solvent systems DMSO/NH_4OH and NaOH/urea each offering unique physicochemical pathways to facilitate cellulose dissolution, molecular disruption, and subsequent functionalization as shown in Figure 5. These systems not only enable the breakdown of native hydrogen bonding in cellulose but also introduce reactive nitrogen-containing moieties critical for amine modification. In the DMSO/NH_4OH system, DMSO acts as a strong aprotic solvent that effectively disrupts intra- and intermolecular hydrogen bonds within cellulose chains, enhancing the solubility and accessibility of hydroxyl groups [22]. Concurrently, NH_4OH provides hydroxide ions (OH^-) that deprotonate surface hydroxyl groups of cellulose, generating nucleophilic oxygen sites capable of interacting with ammonium (NH_4^+) ions [18,19,25,28]. This electrostatic interaction fosters the incorporation of amine functionalities onto the regenerated cellulose during ethanol-induced precipitation. The amphiphilic nature of the solvent system aids in the homogeneous dispersion of amine species, promoting a uniform surface functionalization. Conversely, in the NaOH/urea system, cellulose dissolution is achieved under cryogenic conditions (-12°C to -5°C), wherein urea forms strong hydrogen bonds with the hydroxyl groups of cellulose, while NaOH disrupts crystalline domains by swelling the polymer matrix [15,29]. This synergistic action leads to the formation of a partially carbamated cellulose structure in solution. Upon the introduction of ethanol as an antisolvent, rapid coagulation occurs, resulting in a regenerated cellulose network with denser three-dimensional connectivity. Urea plays a dual functional role serving as both a hydrogen bond

disruptor and a nitrogen donor facilitating the formation of cellulose carbamate linkages through nucleophilic substitution reactions. The regenerated product displays a pronounced increase in nitrogen content, attributed to covalent bonding between urea-derived amine groups and the cellulose backbone. The dual-solvent strategy effectively produces amine-rich cellulose frameworks through a combination of physical interaction and chemical grafting mechanisms [17,24,31]. Nevertheless, the results indicate that the highest grafting efficiency of amine-functionalized regenerated cellulose is achieved when using the NaOH/urea solvent system. In addition to providing superior grafting performance, this sulfur-free solvent system offers greater environmental compatibility, making it more suitable for large-scale applications. Its green chemistry profile and scalability highlight its potential for integration into sustainable industrial processes. Compared to conventional aminosilane-based modifiers, the regenerated cellulose derived from these solvent systems offers a significantly higher surface density of amine functionalities. This is particularly advantageous for applications in surface modification of inorganic oxides such as silica, where enhanced interfacial bonding, improved dispersion, and greater chemical stability are essential. Overall, this integrated approach not only advances the functionalization of cellulose under green chemistry conditions but also broadens its applicability in sustainable materials design and hybrid nanocomposites.

4. Conclusion

A novel strategy for the functionalization of silica particles was developed by utilizing bio-based organosilanes derived from coconut fiber cellulose dissolved in non-ionic solvent systems. Two distinct solvent systems DMSO/NH_4OH and NaOH/urea were employed to regenerate cellulose and facilitate its role as an alternative surface-modifying agent to aminosilane. The experimental results revealed that while cellulose dissolved in DMSO/NH_4OH exhibited a comparable amine grafting efficiency (23.43% wt) to conventional aminopropyl silane (22.41% wt), the NaOH/urea system remarkably improved the grafting performance, achieving a significantly higher amine loading of 40.52% wt. This enhancement is attributed to the amphiphilic nature of urea, which not only promotes hydrophobic interactions but also chemically facilitates the formation of cellulose carbamates via aminolysis in the hydrophilic regions of the cellulose polymer. The findings underscore the critical influence of solvent-polymer interactions on the molecular accessibility and reactivity of cellulose during surface modification processes. Furthermore, the sulfur-free nature of the NaOH/urea solvent system offers environmental advantages over DMSO-based systems, strengthening its applicability in green chemistry approaches. Overall, this study presents a sustainable pathway for synthesizing amine-functionalized silica using renewable biomass resources and environmentally benign solvents. The successful replacement of fossil-derived aminopropyl silane with cellulose-based modifiers highlights the potential of integrating waste biomass valorization into the development of functional materials for CO_2 capture and other adsorption-based applications. These findings contribute to the growing body of research on circular economy technologies and support the advancement of green and scalable material engineering solutions.

References

[1] T. Nasiman and H. Kanoh, CO_2 capture by a K_2CO_3–carbon composite under moist conditions, *Ind. Eng. Chem. Res.* 59 (2020) 3405–3412.

[2] T. N. G. Borhani, A. Azarpour, V. Akbari, S. R. Wan Alwi and Z. A. Manan, CO_2 capture with potassium carbonate solutions: A state-of-the-art review, *Int. J. Greenh. Gas Control* 41 (2015) 142–162.

[3] Z. Hu, D. Zhang and J. Wang, Direct synthesis of amine-functionalized mesoporous silica for CO_2 adsorption, *Chin. J. Chem. Eng.* 19 (2011) 386–390.

[4] N. Bouazizi, J. Vieillard, B. Samir and F. Le Derf, Advances in amine-surface functionalization of inorganic adsorbents for water treatment and antimicrobial activities: A review, *Polymers* 14 (2022) 378.

[5] N. Hao, K. W. Jayawardana, X. Chen and M. Yan, One-step synthesis of amine-functionalized hollow mesoporous silica nanoparticles as efficient antibacterial and anticancer materials, *ACS Appl. Mater. Interfaces* 7 (2015) 1040–1045.

[6] X. Jiang, Y. Kong, Z. Zhao and X. Shen, Spherical amine-grafted silica aerogels for CO_2 capture, *RSC Adv.* 10 (2020) 25911–25917.

[7] H. A. Ajiz, A. A. Albar, W. Widiyastuti, T. Nurtono, H. Setyawan and I. M. Joni, High surface area silica particles using an anionic surfactant template prepared by one-step spray drying system for dye removal application, *Period. Polytech. Chem. Eng.* 66 (2022) 585–595.

[8] H. A. Ajiz, W. Widiyastuti, H. Setyawan and T. Nurtono, Spray-dried porous silica using an anionic surfactant template for advanced photoluminescence support via ultrasound-assisted deposition, *J. Mater. Sci.* (2024).

[9] A. B. D. Nandiyanto and K. Okuyama, Progress in developing spray-drying methods for the production of controlled morphology particles: From the nanometer to submicrometer size ranges, *Adv. Powder Technol.* 22 (2011) 1–19.

[10] H. A. Ajiz, W. Widiyastuti, H. Setyawan and T. Nurtono, Amine-functionalized porous silica production via ex- and in-situ method using silicate precursors as a selective adsorbent for CO_2 capture applications, *Heliyon* (2024) e26691.

[11] H. Y. Huang, R. T. Yang, D. Chinn and C. L. Munson, Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas, *Ind. Eng. Chem. Res.* 42 (2003) 2427–2433.

[12] B. Qiao, T. J. Wang, H. Gao and Y. Jin, High density silanization of nano-silica particles using γ-aminopropyltriethoxysilane (APTES), *Appl. Surf. Sci.* 351 (2015) 646–654.

[13] S. Cui, S. Yu, B. Lin, X. Shen, X. Zhang and D. Gu, Preparation of amine-modified SiO_2 aerogel from rice husk ash for CO_2 adsorption, *J. Porous Mater.* 24 (2017) 455–461.

[14] J. T. Anyanwu, Y. Wang and R. T. Yang, Amine-grafted silica gels for CO_2 capture including direct air capture, *Ind. Eng. Chem. Res.* 59 (2020) 7072–7079.

[15] M. Gunnarsson, H. Theliander and M. Hasani, Chemisorption of air CO_2 on cellulose: An overlooked feature of the cellulose/NaOH(aq) dissolution system, *Cellulose* 24 (2017) 2427–2436.

[16] R. S. Dassanayake, C. Gunathilake, A. C. Dassanayake, N. Abidi and M. Jaroniec, Amidoxime-functionalized nanocrystalline cellulose–mesoporous silica composites for carbon dioxide sorption at ambient and elevated temperatures, *J. Mater. Chem. A* 5 (2017) 7462–7473.

[17] M. Fauziyah, W. Widiyastuti, R. Balgis and H. Setyawan, Production of cellulose aerogels from coir fibers via an alkali–urea method for sorption applications, *Cellulose* 26 (2019) 9583–9598.

[18] A. S. Suryandari, T. Nurtono, W. Widiyastuti and H. Setyawan, Hydrophobic modification of sulfonated carbon aerogels from coir fibers to enhance their catalytic performance for esterification, *ACS Omega* 8 (2023) 27139–27145.

[19] S. Susanto, T. Nurtono, W. Widiyastuti, M. H. Yeh and H. Setyawan, Controlling N-doping nature at carbon aerogels from biomass for enhanced oxygen reduction in seawater batteries, *ACS Omega* 9 (2024) 13994–14004.

[20] A. R. Amalia, R. F. Kumara and N. P. Putri, Manufacturing of bioplastics from cellulose empty fruit bunches waste with addition of glycerol as plasticizer, *Konversi* 8 (2019).

[21] I. F. Nata, H. Niawati and C. Muizliana, Pemanfaatan serat selulosa eceng gondok (*Eichhornia crassipes*) sebagai bahan baku pembuatan kertas: Isolasi dan karakterisasi, *Konversi* 2 (2013).

[22] M. Gunnarsson, D. Bernin, M. Hasani, M. Lund and E. Bialik, Direct evidence for reaction between cellulose and CO_2 from nuclear magnetic resonance, *ACS Sustain. Chem. Eng.* 9 (2021) 14006–14011.

[23] J. Juliananda, N. M. I. P. Suari, W. Widiyastuti and H. Setyawan, Electro-assisted alignment of coir fiber cellulose aerogel with low tortuosity channels for solar steam generation, *Cellulose* (2024).

[24] M. Fauziyah, W. Widiyastuti and H. Setyawan, Sulfonated carbon aerogel derived from coir fiber as high performance solid acid catalyst for esterification, *Adv. Powder Technol.* 31 (2020) 1412–1419.
[25] M. Fauziyah, W. Widiyastuti and H. Setyawan, Nitrogen-doped carbon aerogels prepared by direct pyrolysis of cellulose aerogels derived from coir fibers using an ammonia–urea system and their electrocatalytic performance toward the oxygen reduction reaction, *Ind. Eng. Chem. Res.* 59 (2020) 21371–21382.
[26] H. Setyawan, M. Fauziyah, H. S. S. Tomo, W. Widiyastuti and T. Nurtono, Fabrication of hydrophobic cellulose aerogels from renewable biomass coir fibers for oil spillage clean-up, *J. Polym. Environ.* 30 (2022) 5228–5238.
[27] Y. Miao et al., A facile method for in situ fabrication of silica/cellulose aerogels and their application in CO_2 capture, *Carbohydr. Polym.* 236 (2020) 116079.
[28] H. A. Ajiz et al., Silica surface modification using cellulose as a renewable organosilane derived from coconut coir fiber for carbon capture, *Results Eng.* (2024) 103060.
[29] H. A. Ajiz et al., Direct surface modification of a silica-based adsorbent for CO_2 capture from coir fibers dissolved in a sulfur-free alkali–urea system, *Adv. Powder Technol.* 36 (2025).
[30] W. Widiyastuti, H. A. Ajiz, H. Setyawan and T. Nurtono, Electrostatic charge pathway matching interactions between surfactant templates and silica: Effects on silica particle morphology and carbon capture performance, *Colloids Surf. A* 721 (2025) 137203.
[31] B. Xiong, P. Zhao, K. Hu, L. Zhang and G. Cheng, Dissolution of cellulose in aqueous NaOH/urea solution: Role of urea, *Cellulose* 21 (2014) 1183–1192.
[32] T. Gosiamemang, R. V. Law and J. Y. Y. Heng, Effects of base catalyst on the physicochemical properties and surface reactivity of silica nanoparticles, *Colloids Surf. A* 707 (2025).