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Utilization of Wheat Husk Ash as Silica Source for the Synthesis of MCM-41 Type Mesoporous Silicates: A Sustainable Approach towards Valorization of the Agricultural Waste Stream

Isak Rajjak Shaikh[*1] and Alamgir Abdulla Shaikh[2]
[1]Department of Chemistry, Shri Jagdishprasad Jhabarmal Tibrewala University (JJTU), Vidyanagari, Jhunjhunu-Churu Road, Chudela – 333 001, Jhunjhunu district, Rajasthan State, INDIA
[2]Department of Chemistry, Poona College of Arts, Science & Commerce, Camp area, Pune – 411 001, Maharashtra, INDIA

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Abstract

After acid pre-treatment, the product extracted from the wheat husk ash is utilized as a silica source for the preparation of mesoporous siliceous material(s). The MCM-41 type samples using CTAB as template were synthesized using commercially available silica and wheat husk ash silica at room temperature. The materials were characterized by XRD, SEM, etc. to prove crystallinity, siliceous framework, overall material morphology, etc. A comparison is also made between the characteristics of (i) MCM-41 synthesized from the commercially available silica source; (ii). MCM-41 synthesized using wheat husk ash as silica source, and (iii). the MCM-41 reported earlier. This methodology opens up new methodology for the utilization of renewable sources and also for the concepts of 'valorization of agricultural waste stream' and the 'silicon elemental sustainability.' The crystalline siliceous mesoporous MCM type silica presents an interesting potential for their applications in adsorption, ion-exchange and shape-selective catalysis.

Keywords: Wheat husk ash, silica source, mesoporous silica, MCM-41, valorization of agricultural waste ashes, sustainability.

Introduction

Today sustainable development is recognized as emerging culture and multifaceted methodology comprising environmental, ecological, scientific, economic, social and political issues of global significance. In 1987, the United Nations Commission on Environment and Development (Brundtland Commission)[1] defined sustainable development as the development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Two of the key aspects of sustainable development from an energy and chemical perspective are to develop more renewable forms of energy and to reduce pollution. The International Union of Pure and Applied Chemistry - IUPAC (1996) defined Green Chemistry as "the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances".[2]

Agricultural produces and residues attract widespread attention for renewable energy generation and also for their large-scale combustion. Many agricultural products or by-products such as palm oil, sugarcane bagasse and also the end products or wastes like ashes produced from palm oil fuel, rice-husk ash or wheat-straw/husk ash are considered potential raw materials for preparing high-value products. Moreover, the irrigation methods and fertiliser usage in the growth of herbaceous plants leads to higher contents of inorganic species, compared to wood or coal, with ash contents of between 3–12 wt%[3,4]. This underscores the urgent need to extract or recover, recycle and reuse inorganic species or elements, not just carbon, in bio-refinery approach from biomass or their ashes[5,6]. The combustion of herbaceous biomass usually results in fly ash and the bottom ash. The fly ash is mainly composed of potassium, sodium, sulfates chlorides and phosphates whereas the bottom ash is rich in silica or silicates[4,7]. Recent investigations demonstrated that the bottom ashes from biomass (rice husk) ash[8] and biomass (miscanthus) power station waste[9] could be used for forming silicate solutions by alkaline extraction and with the use of these solutions a higher value end-product could be produced.

Wheat husk (WH) is one of the highest-volume bio-residues in agriculture based economy of (Republic of) India. Current applications of WH are limited and so discovering and recovering value added products or materials from WH are desirable. The organic matter within WH gets decomposed upon burning in air and leaves behind silica-rich wheat husk ash. Silica makes the ash valuable. S. H. Javed et al extracted amorphous silica from wheat husk[10]. Pinar Terzioglu et al. studied effects of parameters on structural and surface properties for magnesium silicate synthesized from wheat husk ash[11]. The authors report herein the utilization of wheat husk ash as an agricultural source of silica for the preparation mesoporous silica MCM-41.

The researchers conceived the concept of recovering silicon/silica from wheat husk ash for the preparation of mesoporous MCM-41. The as-synthesized mesoporous MCM-41 material were characterised. In short, the simplicity and potential scalability of the synthesis of WH-derived mesoporous silica sounds promising for new era of biomass derived material synthesis, particularly from the wheat husk based power station ashes.

Material and Methods

Experimental: Most of the chemicals were used as received, except the alcohol and water were double distilled.

Method: Silica extraction from the wheat husk ash raw material: Wheat husk ash was collected from grain polish power plant. The ash was first boiled in 1 M hydrocholoric acid (HCl) at 90^0C. It was then washed with double distilled water. The material was slowly subjected to thermogravimetric decomposition and calcined at 550^0C for 6 hours in muffle furnace. Then, thus extracted silica was utilized as a raw material for the preparation siliceous mesoporous MCM-41.

Different silica sources for different mesoporous materials: Hexadecyltrimethylammonium bromide (CTAB) – the template and two different sources of silica: i. the silica extracted from wheat husk ash, and ii. the commercially available silicon oxide (SiO_2), were used separately as reactants for the crystalline mesoporous *Mobile Composite Material* number 41 i.e. MCM-41 synthesis. The as-synthesized materials were named as (i) WH-MCM-41 and (ii) MCM-41 respectively. The parent WH-MCM-41 and MCM-41 were synthesized at room temperature under atmospheric condition by following a method from the previous literature with little modification[12].

A starting gel with a molar composition of $4SiO_2$.1NaOH:1CTAB:200H_2O was prepared and the gel pH was adjusted to 10 and stirred constantly for 48 hours at room temperature. The crystallization was done in a Teflon-lined autoclave at 100°C in static conditions for 48 hours. The solid was separated by centrifugation, washed with distilled water and rinsed with ethanol, dried and calcined at 550°C for 6 h to remove the CTAB template. The material was stored in the desiccators before actual characterization begins.

Characterization of WH-MCM-41: After calcinations, the as-synthesized solid materials were characterized by powder X-Ray Diffraction (Miniflex-2; CuKα radiation filtered by Ni) in scan range from 10 to 80^0 (2theta) with 15 mA and 30 kV; Scanning Electron Microscopy (SEM), and the data from Transition Electron Microscopy (TEM) and N_2 adsorption-desorption (BET method) is eagerly awaited.

Results and Discussion

X-Ray Diffraction: The powder XRD patterns of the MCM-41 synthesized from wheat husk ash and the commercially available silicon oxide was observed and compared for their respective crystallinity (figure 1 and 2). MCM-41 has a well-ordered lattice structure with hexagonal unit cell. The characteristic reflections of mesoporous MCM-41 are seen only in the low angle region and correspond to (100), (110), (200) and (210) planes. The reflections of SiO_2 crystals at 2θ (degrees) around 2.24, 3.8, 4.46, and 5.85 obtained in the low-angle region are known to be characteristic of the ordered hexagonal array of parallel silica tubes and are in-line with the earlier literature.[13]. The characteristic long range orders of the uniform cubic mesoporous structure were identified. Just for record and also to identify other reflections, the wide-angle XRD patterns of as-synthesized samples were recorded and are shown in figure 3.

While the low-angle XRD pattern is consistent with the existence of mesoporous silica MCM-41, the wide-angle XRD pattern exhibits quite strong reflections, which are not due to MCM-41[14]. Therefore, a second phase or material is present which needs to be identified. This leads to understand the importance of TEM and porosimetry data that are required before one can reasonably state the purity of the as-synthesized material.

Scanning Electron Microscopy: The Scanning Electron Micrograph (SEM) of both the types of mesoporous MCM-41 exhibited the agglomerated particles with the uniform size in a range 0.3-0.5 μm (figures 1 and 2). The SEM images show cubic and rhomboidal morphology indicating well-organized assembly of the silicate ions reacted with cationic template in crystallization forming siloxane network (Si-O-Si).

Infrared spectra of fresh CTAB and re-crystallized CTAB from the waste mother liquor are shown in Figure 4. The presence of -OH bands at 3375 and 1630 cm^{-1} in re-crystallized CTAB are due to the adsorption of moisture from environment. The absorption bands at around 2850-3000 cm^{-1} and 1500 cm^{-1} in the spectrum are assigned to C-H stretching and bending vibrations of the CTAB template.

Biomass and the ashes: Biomass ashes have been widely used in the past for soap production and glass making[15]. Research on rice hulls has demonstrated the potential for producing silicate solutions by alkaline extraction of the hulls, pyrolysed, combusted or gasified below 800°C.[16-17] Rice husks (RHs) burn in air to form rice husk ash; in this process, the organic matter decomposes and silica is the major remnant. RHs are therefore rich in silica. Moreover, the silica within the RHs naturally exists in the form of nanoparticles[18]. It is reported that recovery of over 90% of the silica contained in rice husk ash is possible by simple digestion with aqueous sodium hydroxide and precipitation of silica by acidification of the sodium silicate solution so obtained[11,16-18]. The silica obtained is generally amorphous. Silica materials including the amorphous ones have many uses[19-20]. It was reported that the Indian Space Research Organization (ISRO) has successfully developed a technology for producing high purity silica from RH ash that can be used in silicon chip manufacture[21-24].

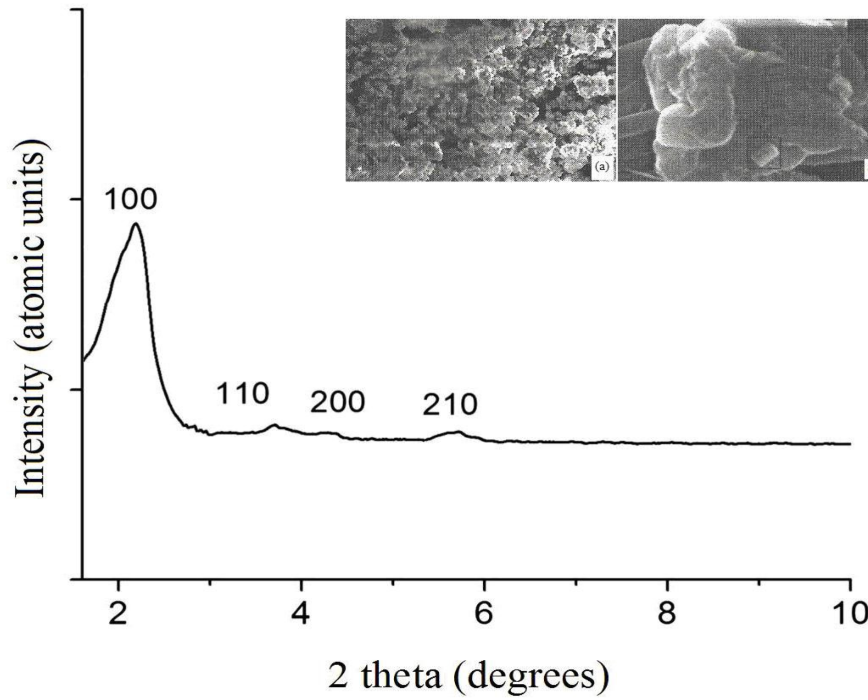


Figure-1
Low-angle X-Ray Diffraction pattern and Scanning Electron Micrograph (as inset) of MCM-41 (synthesized by using commercially available silica source) [(a) Pre-calcined, and (b) Calcined sample]

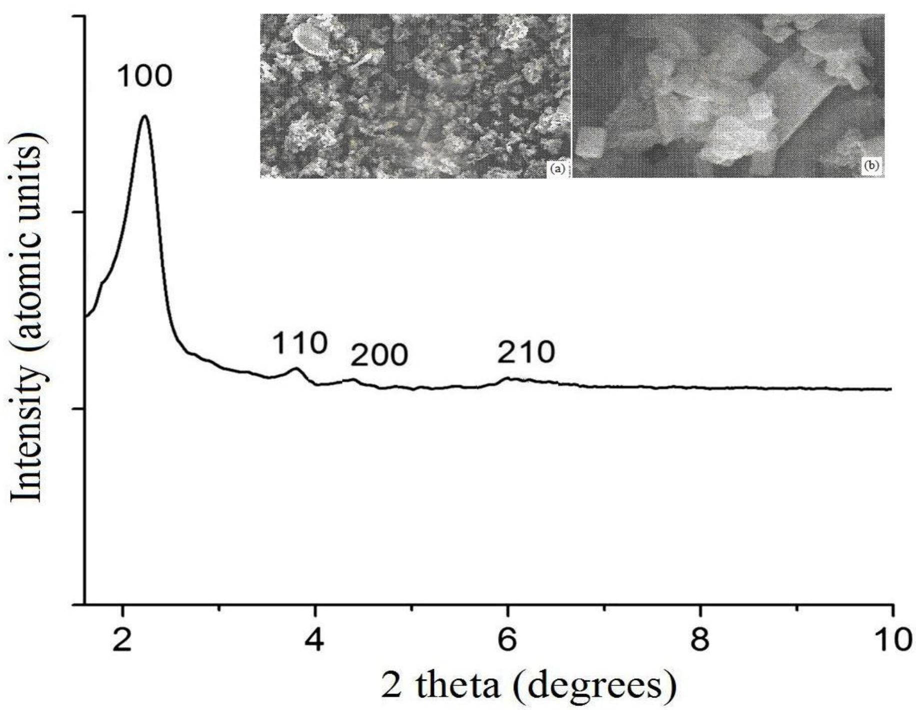
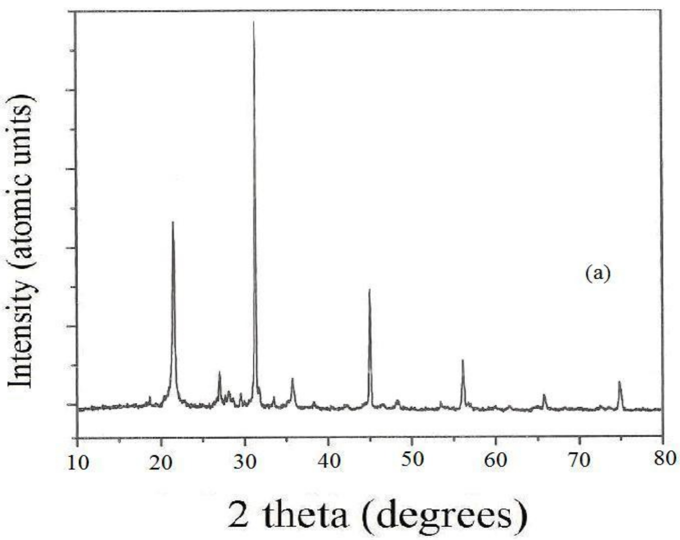


Figure-2
Low-angle X-Ray Diffraction pattern and Scanning Electron Micrograph (as inset) of WH-MCM-41 (synthesized by wheat husk ash as a source of silica) [(a). Pre-calcined, and (b). Calcined sample]



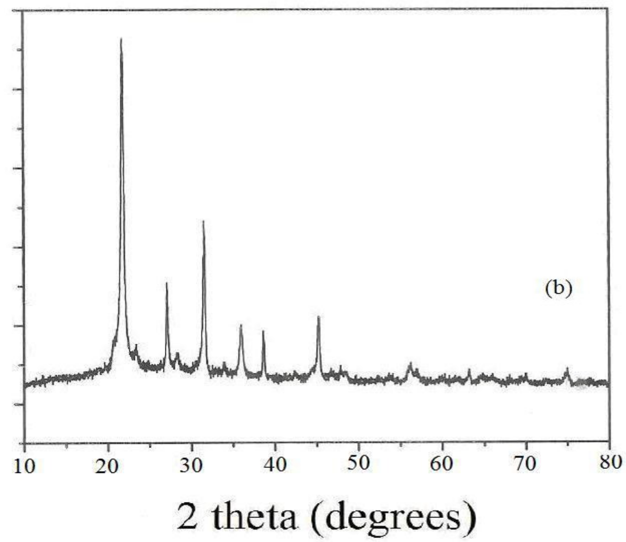


Figure-3
Wide-angle X-Ray Diffraction pattern of MCM-41 synthesized from the commercially available silica source and Wheat Husk (WH) ash silica source [(a). MCM-41 synthesized using using commercially available SiO_2, and (b). WH-MCM-41 type material synthesized from Wheat Husk (WH) ash as the silica source. Both the samples were properly calcined]

Table-1
All the peak reflections with their corresponding 2θ (degrees), Flex Width, d-Value, Intensity and Relative Intensity (I/I_0) on the powder XRD patterns of the WH-MCM type mesoporous silica

Peak No.	2 theta (2θ) degrees	Flex Width	d-value	Intensity	I/I_0
1	20.700	0.353	4.2874	104	3
2	21.800	0.353	4.0735	5021	100
3	23.380	0.282	3.8017	147	3
4	27.060	0.282	3.2924	1247	25
5	28.300	0.235	3.1509	159	4
6	31.520	0.282	2.8360	2272	46
7	33.900	0.212	2.6421	118	3
8	35.960	0.306	2.4954	686	14
9	38.640	0.259	2.3282	682	14
10	45.220	0.282	2.0036	941	19
11	47.820	0.212	1.9005	116	3
12	56.160	0.282	1.6364	126	3
13	63.140	0.282	1.4713	147	3
14	59.920	0.235	1.3443	104	3

Wheat husk ash as silica source: Wheat husk is a byproduct from wheat mill. When burnt, the wheat husk has a calorific value of about 3500 kcal/kg. Thus, burning wheat husk as a fuel in boilers could be one the suitable ways to reuse the husk in an efficient and controlled manner. Burning wheat husk generates silica rich wheat husk ash as the residue which can be used as renewable silica source.[24] This not only reduces the amount of the ash waste but also adds value to the ash. A recent research paper in *RSC Advances* reported the potential for the direct formation of potassium silicate solutions from wheat straw ashes using their inherent alkalinity[25]. However, these studies were carried out on ashes produced at the laboratory scale and was combusted at lower temperatures than typically used in commercial power plants. More recently, research, published in the reputed *Green Chemistry* journal, has demonstrated the results of successful silicate extraction from Miscanthus bottom ash for the synthesis of a high value mesoporous silica sieve from the low value biomass waste ashes using simple environmentally benign techniques and minimal synthetic reagents[9]. This confirmed that the bottom biomass ashes could be used for forming silicate solutions by alkaline extraction to produce a higher value end-product i.e. bio-MCMs, including the MCM-41[9].

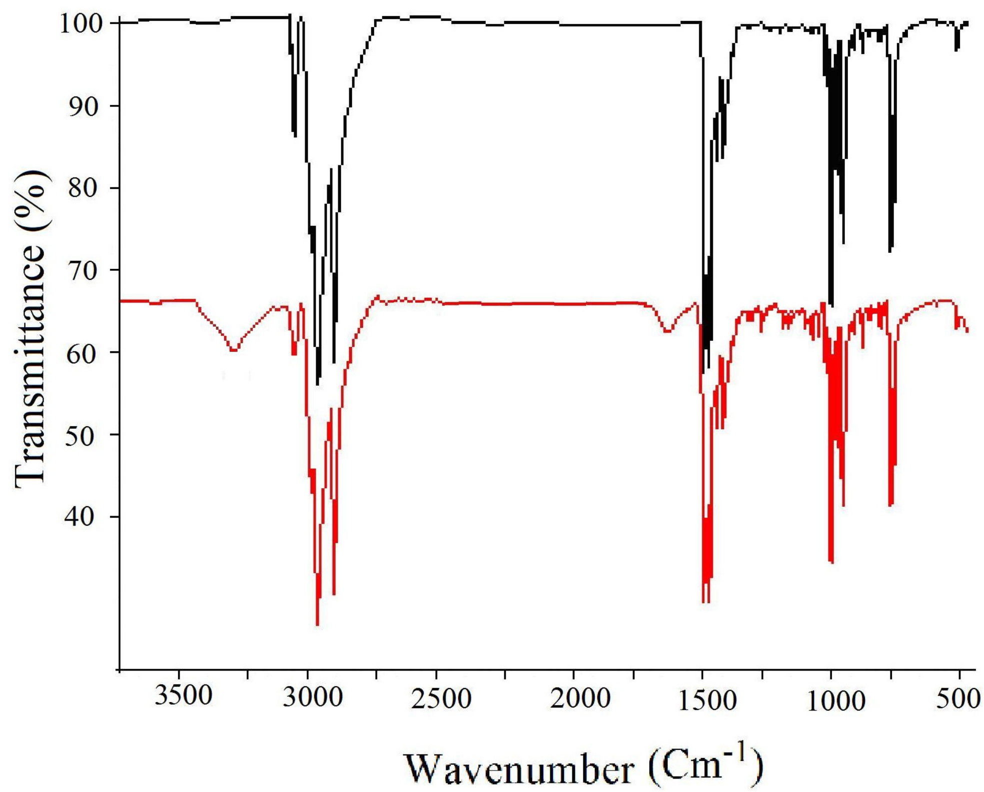


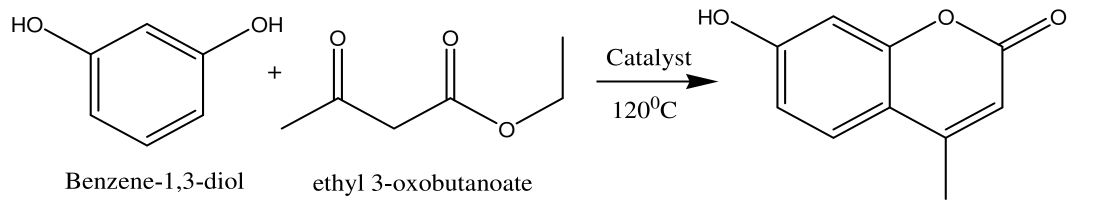
Figure-4
Infrared spectra of fresh CTAB (black) and CTAB re-crystallized from waste mother liquor (red)

Since antiquity, the energy needs of mankind had been fulfilled by the process of burning biomass. There are methods developed for the extraction of silica from biomass. Even the amorphous silica structure from wheat husk ash could also be a reactive form for silylation reaction. The authors report herein wheat husk (WH) ash as a sustainable source of mesoporous silica. By this methodology, the impact of the ash formed, due to combustion of wheat husk, is recognized by the utilization of WH ash as the source of silica for preparing crystalline mesoporous silica MCM-41.

Mesoporous MCM-41: Since the discovery of nanostructured/porous materials by Mobil Corporation such M4 IS in the late 1980s, the porous solids have become popular and useful material for chemical and environmental applications such as adsorbent, catalyst support, ion-exchanged material and nanofiter. Mesoporous Materials are crystalline sodium silicate or aluminate with framework based on extensive three dimensional tetrahedral network and attracted widespread attention for their varied industrial applications in catalysis, adsorption, semi-conduction, ion-exchange, etc[23]. MCM-41 was firstly synthesized in 1992[26-27]. MCM-41 is one of the members from the M4 IS family. This is a well defined short range ordered hexagonal pore structure with high surface area and hydrothermal stability[28-30]. Silica sources like coal fly ash[30-31] and gasified rice husk ash[33-34] MCM-41 were previously used for synthesizing MCM-41. There were lacks of studies looking at biomass ashes from commercial power stations. This research demonstrates the use of low value wheat husk ash from the power station to synthesize high value mesoporous MCM-41. The bio-derived mesoporous MCM-41 material could be applied in shape selective catalysis, adsorption, and separation. This methodology opens up new methodology for the ‘silicon elemental sustainability.’

We developed the use of MCM-41 type silica, prepared from wheat husk in Pechmann reaction. When resorcinol is reacted with the ethyl acetoacetate in the presence of this catalyst, three reactions, hydroxyalkylation, transesterification, and dehydration occur concomitantly condensing together the two reactants at two sites to form the coumarin derivative. This is an example of acid catalysis.

Catalytic Test: 10 mmol of ethyl acetoacetate was added dropwise with stirring to 10 mmol of resorcinol in a reaction flask. 300 mg of WH-MCM-41 type catalyst was added with a trace of $ZnCl_2$. The reaction was carried out at 120^0C and monitored by thin layer chromatography. After 20 minutes, the product is crystallized by adding ice cold water to the reaction flask. The product was filtered off and the yield (90%) was recorded.



Scheme-1
Synthesis of a coumarin (2*H*-chromen-2-one) derivative

In our future works, we also aim to develop the use of this siliceous material as an environmentally benign catalyst for the synthesis of benzimidazole derivatives from o-phenylenediamine and benzoyl chlorides.

Conclusion

This research is interesting and relevant as it addresses the valorisation of a significant waste stream i.e. the wheat husk ash from power stations. Mesoporous silica MCM-41 was prepared successfully using wheat husk ash as the silica source. This is a sustainable methodology for the extraction of silicon from wheat husk. Having said that, though the authors know that the 'silicon elemental sustainability' is really not a major issue (as "elemental sustainability" is often associated with "rare" elements), there is certainly an opportunity to develop this research further. The researchers focus to make sincere attempts to bring forth development of chemical technologies benefiting sustainability or ecological and environmental health on the planet by identifying and implementing scientific trends in utilization of biomass and valorization of ashes.

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