SILICA OF THE OIL PALM EMPTY FRUIT BUNCHES – AN INFINITE AMAZEMENT

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The abundance of silica in plants is to fit many purposes. In the oil palm empty fruit bunches that was initially intended for extraction of paper making fibers, silica bodies were found to range between 10-20 μm and these were effectively removed by mechanical impacts. Removal of silica was also aided by the subsequent chelation with DTPA and this provides evidence of the adjacent localisation of the mineral to the silica bodies. Despite removing 86% of the microbodies, the treated biomass revealed the presence of 0.3% (Wt/Wt residual silica. Scanning electron microscopy of the ash of the EFB cellulose mass unveiled the presence of siliceous thread amidst the common microbodies. SEM examination of the alpha-cellulose and the EFB pulp ash presents evidence of siliceous fluid transport structures believed to be part of the skeletal silica in the palm fruit bunch structure. The smorgasbord shapes and sizes of the found siliceous structures reflect nature's amazing craftsmanship of living things for serving such specific functions as mechanical, aesthetical, defence and infinite other purposes.

Keywords: EFB; pulp; paper; oil palm biomass; silica, SEM.

INTRODUCTION

Elaise guineensis, the cash crop that avails Malaysia as world's second largest palm oil producer [1], generates 17 million tonnes of empty fruit bunch (EFB) residue [2]. With product LCA clinging to the knowledge of waste management system, ideas of products' end-of-life are aligned to recycling and reusing possibility. With the aforesaid phenomenon, EFB, the once accumulating waste, has become today's commodity. This is especially enlivened with the blooming of pulping, papermaking and bioenergy sectors where cellulosic biomass is in great demand [3]. Apart from being the precursor in pulping, papermaking [3-5], biofuel production [3, 6], panel product fabrication and cleansing of water bodies [7], the high mineral contents of EFB has given it strong credit for use as glazing materials [8].

Although the EFB industrial application has by now been proven feasible, minerals residing the biomass may become a major source of problem in applications where organic mass is favoured in solo. The transition metals, for instance, are known to cause colour reversion of certain high-brightness products like paper. Apparently, this is the typical tribute of copper, iron and manganese [9], also commonly reported to cause uncontrolled peroxide consumption [10].

One other member in the controversial family of mineral is the opal of plants, known scientifically as silica. 0.3% of these abrasive materials could hamper process efficiency [11] due to wearing and thus, the need for periodic replacement of cutting tool. The propensity of silica to dissolve in alkaline reaction system, in addition, results in thickening of black liquor (when pulping in concerned), which in turn, poses a problem in the chemical recovery process [12, 13]. Furthermore, when present in paper-base endproducts, silica could cause abrasion of such gadgetry as knives, dies, punch, typewriter [14] or printer head and causes micro-scratch on sensitive surfaces. Meanwhile, silica occupying its craters in intact biomass could prevent penetration of chemical [5] exactly the way pathogenic invasion is prevented [6].

In biological systems such as plant, silica bears specialized functions and never existed in elemental form [7]. The smorgasbord nature of the studied siliceous structures of EFB is hereby mapped to the rationale of their existence. This was achieved by zooming into the native and the treated microstructures using SEM as a tool for marveling at nature.

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METHODOLOGY

EFB Preparation

EFB, supplied by Sabutek (M) Sdn Bhd in the form of vascular bundles, were washed and dried away from direct sunlight. The dried strands were then cut to 2 cm, homogenised before storage and before each withdrawal.

Mechanical Treatment of EFB

EFB was packed in a HDPE zip-seal plastic to produce a single layer EFB mat. This was ensured deaerated upon sealing. The packed material was hammered systematically with a fast and elastic staccato impact, causing EFB strands to stick onto the HDPE surface.

Chelation of Minerals in EFB

EFB was soaked in 1% (gram per gram EFB) diethylenetriaminepentaacetic acid (DTPA) with a liquor-to-EFB ratio of 10:1 and this was performed at 70°C. DTPA was selected for its known suitability to effectively perform chelation process in the alkaline pulping system [15, 16].

The treated strands were washed thoroughly till the pH of the liquor shows neutrality. These were then ground and fractionated to different particle sizes in Retsch sieve shaker and then, packed in airtight container for analyses.

Analysis

Determination of ash was performed by TAPPI test method T211. Ash produced from a larger quantity of EFB was dissolved in acid, in accordance with TAPPI test method T244 and the filtrate was collected and analysed for metal contents using Atomic Absorption Spectroscopy (AAS). Some of the ash prepared via TAPPI test method T211 and T244 were further examined with Leo Supra 55VP scanning electron microscope interfaced with energy dispersive analysis of x-ray (SEM/EDAX). Special practice of using adhesive tape for picking up the freshly prepared cool ash was also performed for observing ash in its intact form under the scanning electron microscope.

For counts of silica, light microscope with image analyzer was used to view the surface of EFB before chelation. Scanning electron microscopic analysis of the treated EFB surface was run to investigate the chelation effect and the silica counts were obtained at the same magnification by spotting on 15 different areas. From the counts of silica on these areas, percentage desilication was calculated.

RESULTS AND DISCUSSION

Examination of EFB surface reveals fine bodies of 15-20 μm dimension (Fig. 1), understood as materials lending structure and support to the plant [8]. SEM for defining adequate area and EDAX for elemental analysis shows atomic percentage ratio for Si-to-O being 1-to-2, suggesting that the structure is in the form of SiO_2, as previously reported [8, 11, 17, 18], also found fused with other minerals.

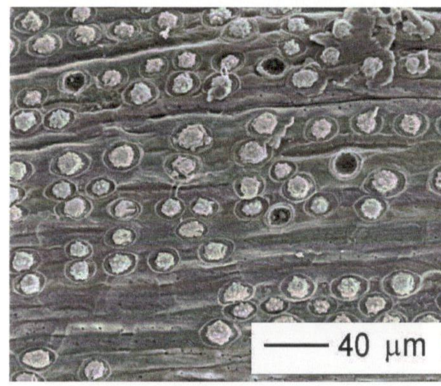

Fig. 1. Silica bodies in EFB (a) SEM of EFB surface showing high silica-to-craters ratio in intact EFB.

Owing to the relatively low inorganic contents, silica is hardly detected in the intact EFB biomass. The organic component, therefore, was decomposed by way of combustion at 550°C and the obtained ash revealed a co-existence of such metals as calcium, sodium and potassium in 5.2%, 9.9% and 6.3%, respectively when silica is 21.4% and oxygen is 57.1% in atomic weight, as given by EDAX for the bottom 'mineral layer' in Fig. 2

The mechanism of fusion of silica with these elements has yet been explained in literature. However, when mapped to the role of silica in plants, the co-existence could most plausibly be attributable to silica attracting the excess calcium, sodium and potassium absorbed by the plant [19]. The specific stoichiometry of silica bodies, which enables detoxification role may demonstrate the reason for nature to exist in certain predetermined portions, revealing the hidden meaning behind *"..inexhaustible treasures formed in due and ascertainable measures"* foretold in indigenous knowledge (15:21) [20].

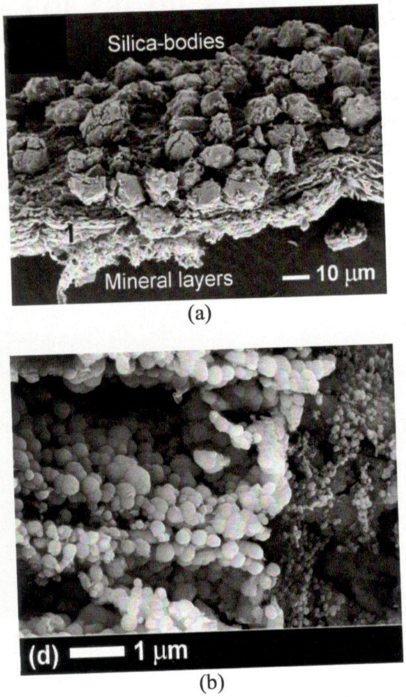

Fig. 2. Minerals in EFB ash depicting a) silica laying the top layer of minerals b) close-up look at the bottom mineral layer.

The said measure for controlling mineral levels by detoxification mechanism is a vivid demonstration of nature's purposeful creation. By having silica attracting the minerals, excess minerals are relocalised and prevented from spreading to the fruit. By the said nature of behaviour, palm fruits become a safe source of food. The specificity of function analogous to that served by silica (and other creations) is also proclaimed in the indigenous knowledge. Besides the general indication of submission in 51:56[20], the specific role of being an edible herbage assigned to certain plants is rendered clear reflections in 32:27, which states *"..do they not see that We do drive rain to parched soil, bare of herbage, and produce therewith crops providing food for their cattle and themselves"* [20].

From the view of EFB as a non-edible plant material, although embedded with micro-particles that are problematic to certain industrial processes, the usefulness of the two forms of silica (body or skeletal) in detoxification of plants [21] or specifically, the palm, has rendered the vascular bundles mechanical strength. This, in turn, allows the structure to robustly hold the fruit in inherent posture, rendering also aesthetical values to the oil palm tree as a component of nature.

As far as removing silica bodies is concerned, it was found that mineral-to-silica coordination could possibly be exchanged to minerals-to-DTPA upon chelation, as reported by Ghazali and team [8, 22]. As a result of re-coordination, silica was no longer attached to the minerals after chelation with DTPA. This has apparently freed silica from the craters, resulting in successful desilication exemplified in Fig. 3. The re-coordination mechanism is proposed as such, due to the known lability of silica to DTPA. Being an indirect effect of surrounding minerals, the successful 86% desilication clearly demonstrates the adjacent position of minerals (Ca, Na, K, Mn, Cu) to the silica bodies [8], in correlation also to the role of attracting and localising excess minerals.

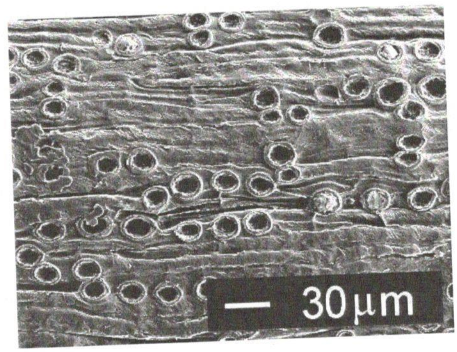

Fig. 3. SEM of EFB surface showing high craters-to silica ratio, suggesting desilication.

Acid dissolution of the aforementioned desilicated EFB for analysis with Atomic Absorption Spectroscopy (AAS) revealed 44% removal of calcium, 100% removal of copper, 93% removal of manganese and 87% reduction in sodium. The high percentage of riddance of copper, manganese and sodium was as high as expected. Similar relative ease of metal removal was also reported in the study of litter decomposition [23], suggesting also an aspect of nature's behaviour.

Besides its existence and function in EFB, silica is recognised as part of the building block of nutrients for rice, pasture grasses, sugarcane, barley, sorghum, oats, sunflower, tomatoes, cucurbits and several root crops. This was evidently highlighted from an improved growth and crop yield upon silica supplementation. In plant life cycle, silica is formed by absorption of silicic acid by the plant root, into some specialized tissue. Upon maturity, the bodies puncture through the plant structure [11]. The schematic visual (Fig. 4) of this phenomenon suggests the possibility of silica being deposited along the transpiration stream, causing molded siliceous structure. Based on the theory of silica affinity to excessive minerals, the possibility of siliceous structures co-existing with other minerals is also expected. Thus, besides giving phytolith as EFB remains, the skeletal silica, possibly envisaged as the schematic in Fig. 2b, form the pathway of fluid and nutrients absorbed by the root of the palm tree.

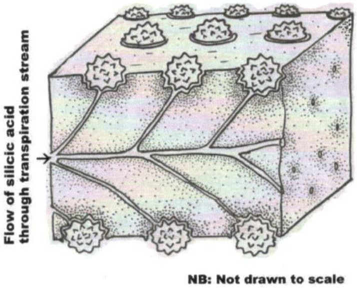

Fig. 4. Deposition of sillicic acid resulting in formation of silica bodies.

To visualise the distribution of minerals in the biomass, the paper produced from EFB pulp was combusted at 550°C as a way of destroying the organic matrix. SEM analysis of the obtained ash sample (Fig. 5a) reveals that although minute in weight percentage, minerals, being lightweight materials, are abundant enough to sculpture the organic fluid transport system, in relation to the illustration in Fig. 4.

Apparently, the obtained ash patterns portrayed in Fig. 5a are in partial resemblance of the dissected EFB strand presented in Fig. 5b, and this is a huge aid in rationalising the performance limit of non-woody fibre sources, with specific reference to EFB paper strength.

An issue pertinent to the ash-rich paper fiber apparent in Fig. 5a is poor network strength due to the presence of a non-cellulosic material. This is accounted for the interrupted inter-fiber bonding or less flexibility of fiber structure due to the relatively higher siliceous/ash content typical of non-wood pulp.

The close resemblance to the actual EFB strand in Fig. 5b in some ways implies retention of lignin, the essential building block of plant biomass. For also being non-cellulosic, this could aggravate the issue of paper network strength, defining also the limit of strength for papers made from EFB [24].

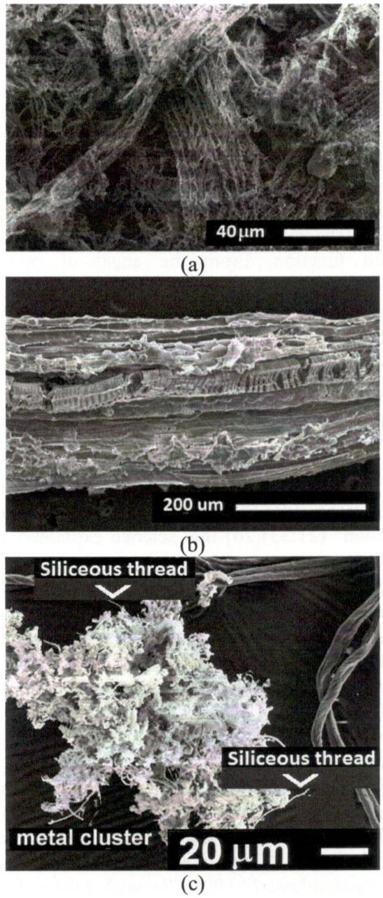

Fig. 5. SEM of EFB (a) ash of handsheet (b) area resembling the siliceous structure shown in a (c) siliceous thread amidst α-cellulose.

EDAX of the area corresponding to Figure 5a indicates the predominance of calcium (21.9%), suggesting the presence of cellular calcium possibly in the form of calcium pectate, if not calcium oxalate. Apart from that, magnesium and silica were 3.5% and 3.2%, respectively. These are mostly oxides, reflected by the high oxygen signal of 55.4% atomic percentage. Together with the siliceous thread (Fig. 5c) and other skeletal siliceous structures (Fig. 2b) found in the ash of α-cellulose and in the acid-insoluble ash of EFB, these account for the 0.3% recalcitrant silica not inclusive in the 86% of the eliminated silica structures. The overall desilication could better facilitate industrial processing of the biomass, despite the presence of the residual silica bodies and the less abrasive silica skeletons.

The studied sequential mechanical and chemical treatments of EFB (as well as the underlying science), also allow better understanding of the concept of creation versus the assigned function. This is even relevant to such fine materials as the micro-elements in the universe. The nature of atomic stoichiometry and affinity for other minerals is the deliberately designed nature to serve the defined function. From the angel of creations' behaviour, all these are indications of loyal submission to the Creator or Commander, in line with an indigenous saying: *not for naught have We created you..* (23:115) and that "*I have only created Jinns and men, that they may serve Me.* (51:56) [20].

Silica and the laid evidence of its functions are the less apparent signs when comparing to the huge and apparent natural behavior like alternation of night and day (2:190)[20], the sailing of ships on the water (2:164, 14:32)[20], the orbiting of the sun and the moon (21:33)[20] that science explained as the effect of gyration and inertia, the standing firm of mountain (21:31, 16:15) [20] and the sky as a station that exist without pillars (31:10) [20]. The witnessed amazing creation and amazing submission or obedience are reflections of the perfect craftsmanship of the All-knowing, the Governor, the Creator who is simultaneously the Commander who has complete knowledge of all living things(6:101-103)[20]. These are the natural phenomena that are visible and unveiled through contemplation as also guided by the indigenous saying: *..in the creation of the heavens and the earth and the alternation of night and day there is indeed Signs for men of understanding (man who contemplate)* (3:190). For such micro-elements as silica, the path to marvel at the science behind nature is particularly made feasible by scanning electron microscopy as tool for analysis.

CONCLUSION

Silica, forming EFB micro-component serves amazing functions visualised with the aid of SEM imaging of EFB and EFB-derivative ashes following bizarre desilication outcome achieved by treatment of EFB with DTPA. The smorgasbord shapes of the siliceous structures, whether spiky granular bodies or sculptured into the biomass structure, are evidently the match between design and function laid in the concept of purposeful creation. The undertaken functions that are regarded as true submission to the divine commands, reflects the an amazing craftsmanship of nature that is hardly realised without such superb imaging technique as SEM. The many correlations between the results of analysis and contents of indigenous knowledge forge an infinitely amazing connection between components of nature and the specificity of their functions.

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