Physicochemical characterization and possible applications of the waste biomass ash from oleoresin industries of India

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HIGHLIGHTS

- Characterization and possible applications of waste biomass ash from oleoresin industries.
- Acid treatment yields high surface area material suitable as adsorbent.
- Magnetic separation affords iron rich fraction with excellent surface area.
- Ash suitable as fertilizer and cement substitute after pretreatment.
- Rich in carbon which could be recovered and used as adsorbent for pollutants and as additive in rubber composites.

ARTICLE INFO

ABSTRACT

The oleoresin industries in India make use of the spice residue as boiler fuel and the combustion of this waste biomass generates tons of ash everyday. Herein the study we have carried out the characterization of this industrial waste ash in order to have a broad awareness of its properties in terms of toxicity, composition and possible utility. Techniques like XRF, ICP-AES, SEM–EDS, surface area, pore volume analysis, powder XRD, TG–DTA, FTIR and elemental analyses were used for the purpose. Ash collected from the grate fired furnace (bottom ash) as well the flyash deposited on the boiler walls and pipes were analyzed. Elemental analysis of the ashes indicates its potential as a crude fertilizer or cement replacement material. PXRD indicates the presence of several crystalline phases such as harrisonite $(Ca(Fe^{3+},Mg)_6(PO_4)_2(SiO_4)_2)$, aphthitalite $((K,Na)_3Na(SO_4)_2)$, cryptomelane $(KMn^{4+}_6Mn^{2+}_2O_{16})$, varulite $(NaCaMn^{2+}_{2.25}Fe^{2+}_{0.5}Fe^{3+}_{0.25}(PO_4)_3)$, marokite $(CaMn_2O_4)$, fersilicite (FeSi) in the flyash fraction and the phases magnetite $(Fe^{3+}_2Fe^{2+}O_4)$, kalsilite $(KAlSiO_4)$, cryptomelane $(KMn^{4+}_6Mn^{2+}_2O_{16})$, fukuchilite $(Cu_3Fe^{2+}S_8)$, walthierite $(Ba_{0.5}Al_3(SO_4)_2(OH)_6)$, and magnesite $(Mg(CO_3))$ in furnace ash. The amorphous nature of silica in the ashes is evident from the characteristic broad hump around $2\theta = 30$. The iron rich fraction of the ash consists primarily of magnetite which leads to a greenish blue color on heating the ash above 650 °C. This magnetite fraction if separated could find use as catalysts in organic reactions. SEM images indicate the ashes to be highly agglomerated and EDX data shows the surface of the ash particles covered with potassium oxide and carbon. The percentage of K seems to be higher in the flyash due to the volatility of the potassium compounds which is carried up by the air current. Even though the surface area of the as received ashes is negligible an acid treatment removes the surface adsorbed species and increases the surface area to 368 m^2/g making it an effective adsorbent.

1. Introduction

Oleoresins and colors from spices like chilli, pepper, turmeric, clove, and nutmeg constitute an important export commodity in India. The residue left over after the extraction of these compounds is used as boiler fuel by the same industries. Though combustion of spice residue for energy generation in oleoresin industries is noteworthy as an ecofriendly and cost effective initiative, huge quantities of ash generated each day requires proper disposal. Much research work has been done in the case of ash obtained from combustion of coal [1–16] and that from biomass like rice husk [17–24], bagasse [25,26] olive husk, pine seed shells [27] cashew nut shell, arecanut shell and groundnut shell [28]. Yet, this waste ash obtained from combustion of spice residue remains unknown in terms of composition and chemical behavior. Due to this reason

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the potential uses of the ash remains unexplored. It has been established that the elemental composition, mineralogy and crystallinity of biomass ashes usually varies due to the extremely high variations of moisture, ash yield of the biomass used and different genetic types of inorganic matter in the biomass [29]. As the oleoresin industries process mostly herbaceous and agricultural biomass the ash is anticipated to be enriched in fixed carbon, K, O and volatile matter.

The present investigation is therefore focused on a preliminary characterization of the solid waste to analyze how it could be transformed into ecofriendly value added products. Analytical techniques including XRF, ICP AES, gravimetric and volumetric techniques have been made use of for determining the constituents of the ash while simultaneous thermal analysis, X-ray powder diffraction, FTIR, adsorption, and SEM-EDS studies were used respectively for obtaining information on the thermal behavior, the mineral phases present, plausible functional groups, adsorption capacity, morphology and surface composition of the samples.

2. Materials and methods

Ash samples were collected from Akay Flavours and Aromatics Ltd., an oleoresin industry at Kochi in the state of Kerala, India. Ash deposited as flyash on boiler walls and pipes (FL) and that from the grate fired furnaces were taken separately (FR). Due to the severe non-homogenity of the samples, these were homogenized using a ball mill prior to analyses.

A semi quantitative XRF (PW2404 XRF spectrometer) scan was done for the identification of the elements present in the sample. The elements, except for silica, were quantified by ICP-AES (Thermo Electron IRIS Intrepid II XSP Duo). The samples were dissolved completely by a modification of the procedure by Fermo et al. [30]. 2 ml of 40% (w/v) HF and 5 ml of conc. Nitric acid were added to about 1 g of sample in a Teflon flask. The suspension was digested on a Milestone model MLS 1200 digestion/drying module for 30 min. HF was completely eliminated from this with addition of 70% (w/v) perchloric acid and heating. The solution was then made up to 100 ml with Milli-Q water and the elements analyzed by ICP AES.

Si in the samples was estimated by XRF. It was also determined by the wet analysis method in which the dried sample was accurately weighed ('x' g) and transferred to a beaker, digested with sufficient quantity (10–15 ml) of conc. HCl and evaporated to almost dryness. This process was repeated with another 10–15 ml HCl and the solution cooled and filtered. The residue obtained was dried to 1000 °C in a Pt crucible, cooled and weighed ('a' g). Hydrofluoric acid (10 ml) was then added and evaporated carefully and finally ignited to 1000 °C, cooled and weighed ('b' g). The percentage of silica was then calculated as %SiO_2 = $100 \times (a - b)/x$.

The degree of amorphousness of silica was estimated by the silica activity index which was determined by calculating the percentage of available silica that is dissolved in an excess of boiling NaOH in a 3 min extraction period.

The mineralogical constituents present in the flyash were analyzed using powder XRD with Cu Kα radiation of 1.5406 Å from a Bruker AXS D8 Advance Model X-ray diffractometer and the crystalline phases present were identified with the JCPDS database software.

Morphology and surface composition of the ashes were probed by SEM (JEOL JSM-6390LV) coupled with EDS (JEOL JED-2300). Small quantities the ash samples were sprinkled onto double-sided carbon tape mounted on a SEM stub. Each sample was characterized by randomly selecting 4–5 fields of view and examining the particles within the selected domain.

Simultaneous TG–DTG–DTA was done on a Perkin Elmer Diamond TGA at a heating rate of 10°/min from 30 °C to 1000 °C. The heating was carried out in air and nitrogen.

Fourier Transform Infrared spectra of the ash samples were recorded with KBr pellets of ash samples in the 4000–400 cm^{-1} range on a Thermo Nicolet Avatar 370 FTIR spectrophotometer.

Surface area of the ash samples were measured using a Micromeritics Tristar 3000 V6.07 analyzer.

3. Results and discussion

3.1. Chemical composition of ash

Table 1 provides information on the total elemental composition of the ash samples. The major elements ($\geqslant$10,000 μg/g) happen to be K, Si, P, S, Cl, Ca, and Mg. Si content was found out to be 90,700 μg/g and 103700 μg/g respectively in FL and FR. Minor constituents (1000–10,000 μg/g) include Al, Fe and Na. Other elements present in concentrations less than 1000 μg/g are also given in the table. The biomass ash used in this study is derived mainly from the combustion of chilli (capsacin or pepper) residue. Ash generated from the burning of pepper plant biomass is reported to contain Ca as the most abundant element [31]. However, in this case it is potassium that is present in largest concentration. This may be because it is only the residue of the fruit (seeds, pericarp and stalk) that is burned. The fruit contains more of K which volatilizes during firing. This volatilization of K during firing justifies its higher percentage in the flyash in comparison with the furnace ash. A high leachate pH (>11.5) observed for both the ashes indicate that they are highly basic in their raw form, possibly due to the presence of the soluble alkaline and alkaline earth oxides like K_2O, CaO, Na_2O, and MgO. In the case of biomass ashes studied so far it is seen that 90% of the potassium and sodium exist as water soluble salts while Ca and Mg may exist in a more complex form. More than 80% of the total sulfur, phosphorus and chlorine also exist in the form of sulfates, phosphates and chlorides. Since sulfur is present in large proportions in the ash existence of alkali and alkaline earth metals in the form of sulfates is

Table 1
Bulk composition of the waste biomass ash.

Ash composition (determined by ICP AES) % of oxide	FL	FR
CaO	4.04	4.44
MgO	2.04	3.45
K_2O	35	27
Na_2O	0.7	0.9
Fe_2O_3	0.5	1.26
Al_2O_3	0.5	0.96
SiO_2[a]	19.5	23
P_2O_5	4.5	7.77
SO_3	8.9	3.2
Minor elements (wt% of element)		
B	0.036	0.036
Ba	0.02	0.009
Cd	0.0004	BDL[b]
Bi	0.0013	BDL
Co	0.0007	.0011
Cr	0.0014	0.003
Cu	0.0207	0.012
Mn	0.02	0.037
Ni	0.001	0.002
Pb	0.001	0.0006
Sr	0.023	0.031
Zn	0.041	0.023
Ti	0.018	0.057
Loss-on-ignition analysis	15	5

[a] Determined by XRF and gravimetry.
[b] Below detectable limit.