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Biomass Mediated Conversion of Acidic Phosphogypsum into Alkaline Material through Thermal Treatments

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The application of phosphogypsum waste is limited to alkaline soil primarily due to its highly acidic pH. Its application can be widen for the acidic soil by converting phosphogypsum into alkaline material. In this context, conversion of acidic phosphogypsum into alkaline material by mixing banana peduncle biomass in powder form in different proportions followed by thermal pyrolysis treatments (300–700°C) were investigated. Acidic phosphogypsum pH (3.2) increased without biomass mixing to 6.3, 6.6 and 7.4 at 300, 500 and 700°C, whereas phosphogypusm-biomass-mixtures elevated pH to relatively higher values 6.7–7.2, 8.2–9.6 and 10.1–10.4 respectively. Alkaline pyrolysed material also contained carbon (25.8%), potassium (10%), and sulfur (12%) and their toxic flouride concentration was lesser (0.39%) than raw phosphogypsum (0.44%). The XRD analysis revealed formation of water soluble anhydrite, arcanite, potassium calcium sulfate and calcite mineral phases. These results established and highlights about process of conversion of phosphatic fertiliser industry acidic phosphogypsum waste to nutrient rich alkaline material by utilising banana peduncle biomass through thermal treatment. The reseach findings has implication towards phosphogypsum industrial waste management, value addition and potential for its alternative use in acidic soils.

Keywords: Banana peduncle, Fertilizer industry, Nutrients, Pyrolysis, Solid waste

Introduction

Phosphogypsum (mainly composed of $CaSO_4.2H_2O$) is a major waste of phosphate fertilizer industries. It is generated during the sulfuric acid treatment of rock phosphate for production of phosphoric acid.[1] Global phosphogypsum production was estimated to be approx. 100–250 million tonnes[2–4] including 11 million tonnes per annum in India (assuming per ton of phosphoric acid production generates 5 tonnes phosphogypsum).[5] Due to the acidic pH and presence of toxic impurities (fluoride and heavy metals), effective utilization of phosphogypsum has been a major challenge. About 85% of phosphogypsum are mainly stockpiled inside industrial premises, and only about 15% utilized for different applications such as calcium-sulfur fertilizers or soil amendments in alkali/sodic soils, substitute for mineral gypsum in cement and plasterboard manufacturing, etc.[4] The acidic pH of untreated stacked phosphogypsum increases the mobility and leachability of toxic fluoride and heavy metals, which causes environmental hazards like water pollution and consequently health risk to humans and other living organisms.[6–8] Several methods are documented to solve above said limitations by neutralizing or converting acidic phosphogypsum into alkaline material for different applications. Methods for purification and treatment of phosphogypsum comprised of washing with water, sieving (100-micron sieve), neutralizing with calcium hydroxide, and calcination.[9] Thermal treatment of phosphogypsum are also reported to increase pH and reduce/stabilize its toxic contaminants concentrations.[10–12]

The major limitations of the above-mentioned treatment processes for phosphogypsum are an excessive requirement of water, lime, or other alkaline chemical additives etc. Furthermore, the involvement of several steps makes these processes complex and expensive. Phosphogypsum waste utilization can be broadened by solving its limitations like acidic pH and reducing concentration of toxic contaminants (e.g., fluoride).

The novelty of current research work is value addition of phosphogypsum by using waste biomass and process without chemicals. Potassium-rich

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banana peduncle (abundantly available waste biomass) was utilized for conversion of acidic phosphogypsum into alkaline material for its potential application in acidic soil. The present work was part of process innovation, which is filed for Indian patent (Application No. 201711022958)[13] and follow up of earlier published studies on waste biomass and phosphogypsum.[14–19] The prime objective of current work was to study the effect of different ratios (Wt./Wt.) of phosphogypsum and biomass on pH of produced alkaline value added material produced by thermal treatments (300, 500 and 700°C).

Materials and Methods

Banana peduncles [henceforth Biomass (B)] were collected from Unit-1 fruit market, Bhubaneswar, India. Phosphogypsum (PG) was collected from Paradeep Phosphates Limited (PPL), Odisha, India. Peduncles were thoroughly washed with water to remove surface impurities, chopped into small pieces, oven-dried at 60°C for 48 hrs followed by grinding. Mixtures of powdered dried biomass and phosphogypsum were prepared in 1:1, 1:2, 1:4, 2:1, and 4:1 wt/wt ratios. These mixtures were put in a quartz sample container and thermally treated (pyrolysis) in a lab-scale tube furnace (Ants Ceramics Pvt. Ltd.) at three different temperatures i.e., 300, 500, and 700°C with 10°C/min heating rate for one hour residence time. The thermally treated materials were taken out from tube furnace in an air tight container. The aluminium locking flanges helped in controlling the air flow and maintaining oxygen limited condition. Experiments were conducted in triplicate.

Yield (%) of alkaline output material was determined by dividing its weight to dried phosphogypsum and biomass mixture. The pH of materials were measured through digital pH meter (Oakton, 310 series). Total carbon(C), hydrogen (H), and nitrogen (N) content of biomass and alkaline output material were estimated by CHN analyzer. Total sulfur (S) content of phosphogypsum and alkaline output material was measured by a carbon-sulfur analyzer (Leco, CS844). For crystalline minerals identification, samples were analyzed by X-ray diffractometer (Panalytical, Xpert Pro) with Cu target (Kalpha-1.5406 Å) and 2 theta values (angle of diffraction) scanning range 10 to 80 degrees. Surface morphology and elemental analysis (semi-quantitative) of alkaline output material were analysed through SEM-EDX analyser (EVO 18 SEM, Carl Zeiss, Germany). For total calcium and potassium analysis, samples were acid digested using HNO_3 mixed with H_2O_2 in a high performance microwave digester (Ethos One) at 180°C. Digested samples were filtered through Whatman filter paper-42 before analysis by flame photometer (Systronic 302). Total fluoride concentration in phosphogypsum and alkaline output material were determined by direct potentiometric method (EPA method-9214)[20] using a fluoride ion-selective electrode (ORION).

Results and Discussion

Thermal treatments of phosphogypsum (PG) without biomass (B) mixing resulted into 92, 88, and 76% yield at 300, 500, and 700°C respectively. Relatively higher yield of 84, 77, and 72% were estimated for thermally treated PG : B mixture of 4:1 ratio, whereas PG: B of 1:4 ratio produced lower yield 71, 53, and 43% at 300, 500, and 700°C respectively. It highlighted about effect of lower temperature and relatively higher PG content in PG-B mixture towards increase in alkaline output material yield, due to relatively lower loss of biomass and volatilization of PG constituents. As PG primarily composed of stable gypsum (Calcium Sulfate), very high temperature is required for its demineralization and subsequent volatilization. In contrast, higher temperature and higher biomass ratio in PG-B mixture decreased alkaline output material yield due to higher mass loss caused by an increased depolymerization and volatilization of biomass constituents.[14–17]

The PG was very acidic (pH 3.2) and its value increased due to thermal treatments 6.3–7.4 (Fig. 1).

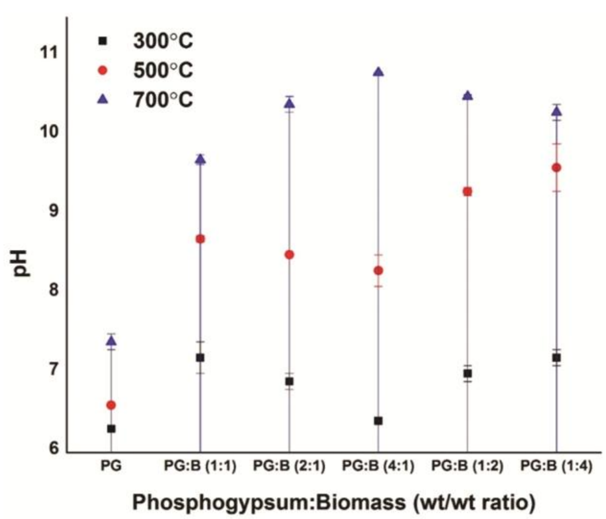

Fig. 1 — Effect of phosphogypsum and biomass weight ratio and thermal treatment temperature on pH of alkaline material

Increase in pH values of PG showed direct positive influence of higher temperature treatments. Mixing of PG with different proportion of biomass (wt/wt ratio) also influenced change in pH of output materials. Thermal treatments of different PG:B ratios lead to an increased pH of output materials i.e., 6.4–7.2, 8.3–9.6 and 10.3–10.8 at 300, 500, and 700°C respectively. At 300°C, in comparison to 4:1 PG:B mixture ratios (pH 6.4), increasing proportion of biomass resulted into relatively higher pH (maximum 7.2 for 1:1 PG:B ratio), whereas at 500°C, maximum pH value (9.6) was recorded for 1:4 PG:B ratio. In contrast, at 700°C, lesser influence of biomass towards increasing pH of output materials was observed. Irrespective of the PG: B ratio, an increase in temperature also contributed towards increase in the pH of output materials towards neutrality (at 300°C) and alkalinity (at 500 and 700°C). The increase in pH due to thermal treatment could be probably due to two reasons. First, due to removal of acidic impurities like phosphoric acid, hydrofluoric acid, and sulfuric acid from phosphogypsum, and second the addition of alkaline minerals/metals from biomass.[10]

The above described results highlights the role of mixing selected banana peduncle biomass with PG for increase in output material pH due to thermal treatments. Although, thermal treatment of PG at 700°C resulted into increased pH 7.4, comparable (7.2) or higher (9.6) value were achieved at relatively lower temperatures 300°C and 500°C by mixing with biomass. The results and findings bring to the fore that the addition of biomass with PG will increase the pH effectively and decreases requirement of high temperature and associated energy consumption to produce neutral or alkaline output material.

As one of the indicative example, major elemental analysis results of PG, biomass and their thermally treated (at 700°C) PG: B in 1:2 ratio output material are presented in Table 1. PG contained relatively higher calcium (16.7%) and sulfur (12.5%) due to calcium sulfate as main mineral constituent. In contrast to PG, output alkaline material constituted higher carbon (25.8%) and potassium (9.3%) along with calcium (18.1%) and sulfur (10.8%). Moreover, alkaline output material also contained 1.04% hydrogen and 0.37% nitrogen. The utilization of biomass which contained 37.23% carbon, 4.56% hydrogen, 1.46% nitrogen and 6.60% potassium[16] was the major reason for getting higher concentrations of these elements in alkaline output material. The fluoride content of alkaline output material (0.39%) also got considerably reduced than PG (0.44%), and it may be due to volatilization of residual fluoride at high temperature.

The SEM-EDX analysis based semi-quantitative elemental composition of alkaline output material is

Table 1 — Elemental analysis of PG, Biomass and alkaline output material [treatment of PG:B mixture (1:2 wt/wt ratio) at 700°C]

Parameters	Phosphogypsum	Banana Peduncle	Alkaline output material
Total Carbon (%)	0.05 ± 0.0	37.23 ± 0.85	25.8 ± 0.5
Total Hydrogen (%)	NA	4.56 ± 0.11	1.04 ± 0.1
Total Nitrogen (%)	NA	1.46 ± 0.02	0.37 ± 0.03
Total Sulfur (%)	12.5 ± 0.45	0.02 ± 0.0	10.8 ± 1.2
Calcium (%)	16.7 ± 0.02	0.66 ± 0.11	18.1 ± 0.24
Potassium (%)	0.02 ± 0.0	6.60 ± 0.20	9.8 ± 0.5
Flouride (mg/kg)	4420 ± 10.0	NA	3341.5 ± 103.0

Note: The values of biomass and phosphogypsum were taken from earlier published paper[16]

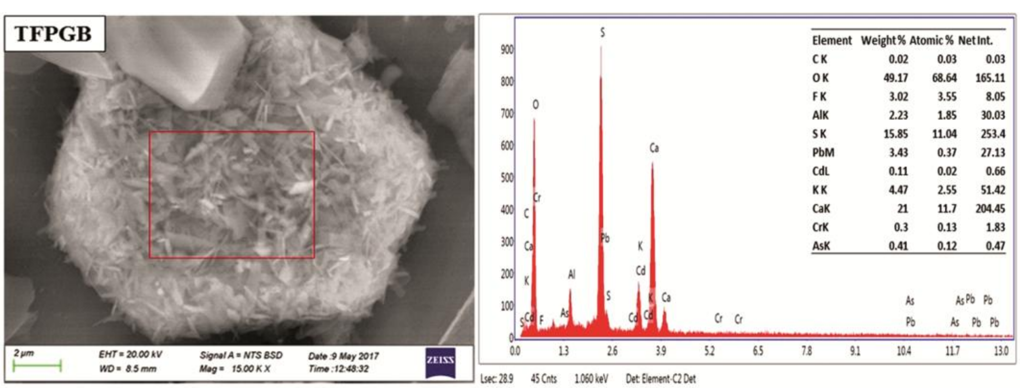

Fig. 2 — SEM-EDX analysis of alkaline output material [thermal treatment PG:B mixture (1:2 wt/wt ratio) at 700°C]

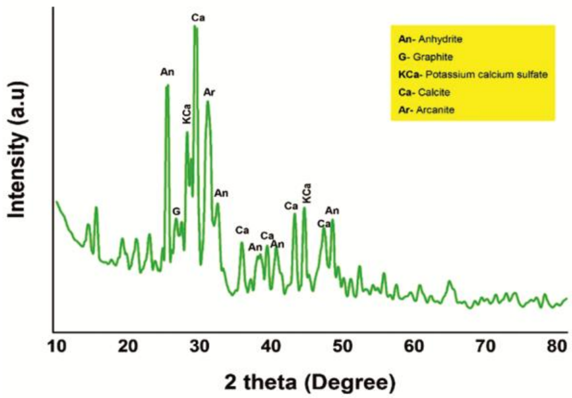

Fig. 3 — XRD analysis of alkaline material [treatment PG:B mixture (1:2 wt/wt ratio) at 700°C]

presented in Fig. 2. Calcium, sulfur, oxygen and potassium were dominant elements in alkaline output material. The presence of these elements were due to dominant calcium sulfate mineral of PG and potassium content in banana peduncle biomass (6.6%). In addition, toxic elements mainly flouride, arsenic, chromium, cadmium and lead were also detected in alkaline output material, which were derived from PG. These toxic elements presence in PG were earlier reported by several researchers.[21–22]

The XRD diffraction pattern (Fig. 3) showed the formation of Anhydrite (ICDD: 01-072-0916, Graphite (ICDD: 00-001-0640), Calcite ($CaCO_3$, ICDD: 00-005-0586), Arcanite (K_2SO_4, ICDD: 00-024-0703), and potassium calcium sulfate ($K_2Ca_2(SO_4)_3$; ICDD: 00-020-0867) minerals due to themal treatment of PG:B mixture. Anhydrite ($CaSO_4$) formation in alkaline material was due to dehydration of gypsum ($CaSO_4{\cdot}2H_2O$) mineral of PG during thermal treatment, which is in agreement with previous studies.[21–25] As the minerals formed in alkaline output material are mostly water soluble, it possess potentiality for potassium, calcium, and sulfate nutrients replenishment in acidic soils.

Conclusions

Phosphogypsum is an important waste generated from phosphatic fertiliser industry and are being conventionally used for alkaline and sodic soils. Several research studies has highlighted different methods to improve quality of PG through value addition. The major treatment methods reported are washing, high temperature processing, use of lime for pH neutralization etc. The present experimental work explored the opportunity of thermal treatment of acidic phosphogypsum by mixing with selected banana peduncle waste biomass. The salient findings elaborates about prospects of alkaline output material production from phosphogypsum at different temperature range (300–700°C). Also, the produced alkaline material contains high amount of potassium derived from selected biomass source. Overall, the research outcome establishes a method of value addition to industrially important PG waste without use of chemicals. In view of potential prospect of alkaline material to be used as liming agent and source of potassium, field related experiments for plant growth and development must be undertaken in future.

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