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A new breakthrough in the P recovery from sewage sludge ash by thermochemical processes†‡

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For the first time, the thermochemical treatment of sewage sludge ash made by using microwaves, associated with a devoted patented chamber, was realised. It promotes the formation of bioavailable $CaNaPO_4$ compound, offering a new breakthrough in recovering phosphorus from sewage sludge ash and providing new possibilities in terms of sustainability.

Introduction

Reducing greenhouse gas emissions and limiting the use of fossil fuels are primary global objectives. In this context, biomass is considered to be a carbon-neutral renewable resource, sometimes derived from by-products that can be properly managed. In particular, the use of secondary biomass, that is the waste derived from primary biomass, has been identified as a strategic approach, which is able to reduce also the amount of generated waste.[1] However, potential disadvantages due for example to low energy density, the presence of contaminants, and high moisture content may also originate from this application. In particular, concerning sewage sludge, one of the most important phosphorus-bearing waste streams, the incineration approach is critical, mainly due to residual ash management. Indeed, although sewage sludge ash (SSA) is potentially considered a promising secondary raw material for the production of phosphorus(P)-based fertilizers, it generally does not contain bioavailable phosphate phases, and leachable heavy metals are often found.[2]

In the literature, there are several treatments able to increase the advantages of SSA reuse.[3] For instance, the thermochemical approach intends to increase the plant availability of P *via* the formation of soluble mineral phases:[2] the whitlockite type $Ca_{3-x}(Mg, Fe)_x(PO_4)_2$ phase is the main P-bearing mineral in SSA.[4] However, phosphorus in SSA is generally poorly available to plants, and then SSA cannot be directly reused in agriculture.[2] Whitlockite can be converted into buchwaldite ($NaCaPO_4$), when SSA is thermally annealed in the presence of certain sodium compounds.[5] Buchwaldite has the advantage of being bioavailable, which is generally demonstrated by evaluating its high solubility in ammonium citrate.[6] At the same time, thermal processes would be very efficient in reducing the heavy metals' load by their separation *via* the gas phase. For example, metals with higher vapor pressures in comparison to the respective oxides (Hg, Pb, and Cd) can partly evaporate or sublimate, with the possibility of their recovery in conventional gas cleaning systems. This depends on the reaction conditions and on the added raw materials.

Despite all these advantages, the literature associates thermochemical treatment processes with a high energy demand. As a result, the potentialities of P-resource recovery offered by suitable management of SSA are still considered not attractive.

For the first time, this paper presents the recent advances in thermochemical process integration with microwaves (MW), which can promise a reduction of energy consumption in comparison to classical thermal treatments and may represent a suitable alternative to the use of wet chemical processes for P extraction. The MW use has two main advantages: (a) the energy usually necessary to heat the chamber is saved (only the sample is heated), and (b) the heating process requires less time and less energy than traditional heating technologies.[7] Then MW heating represents a potential eco-friendly treatment with a major trend toward sustainable development.

Methods

This method and used chambers were patented under Italian legislation (nr. 102022000002351) and won the 2022 EIT RAW MATERIALS business idea competition on Critical Raw Materials (EIT).[8] It is based on a hybrid heating mechanism: a

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MW absorber is added to the samples to efficiently transfer the heat it absorbs from the MW radiation.[9] In addition, an external susceptor is used. It is a secondary microwave absorbent that absorbs microwaves and converts the energy into heat, allowing it to be transferred to the sample through conventional heat transfer modes. The susceptor is coupled with a MW transparent material (with low microwave absorption, allowing the MW penetration) to benefit thermal insulation for the heat generated in the sample and by the susceptor. The objective is not only to ensure homogeneous heating of the sample, but also to limit the thermal losses from its surface.[10] Then, the material reaches a higher temperature and uniform heating compared to simple direct microwave heating. The MW transparent material allows thermal insulation for the generated heat. For this activity, the great focus must be devoted to the selection of suitable MW transparent materials, because their transition to a MW absorbing material depends on the temperature that is reached in the chamber. Fig. 1 shows a schema of the proposed chamber.

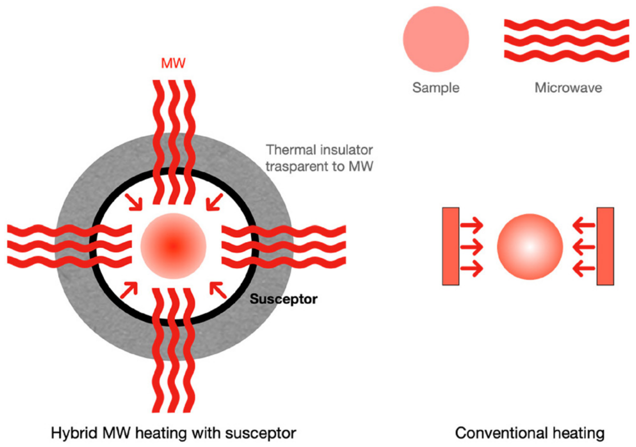

Fig. 1 Hybrid heating mechanism compared with conventional heat transfer: a susceptor allows the material to be heated from the surface, while the microwaves heat from the center.[10]

Seven samples of SSA were provided by a waste-to-energy plant located in Corteolona (Lombardy-Italy) with different sampling spots inside the plant. SSA samples are derived from mono-combustion and co-combustion experiments of sewage sludge treated by A2A company using the fluidized bed combustion system. Table 1 reports the sample description with the main elemental composition evaluated by X-Ray Fluorescence analysis (XRF). They contain different amounts of P. The core process used in this work is based on already established thermochemical reactions occurring in a devoted kiln, where the SSA is mixed with a sodium source and a reducing agent (for example dry sewage sludge, anthracite, graphite) and treated at a temperature operating around 1000 °C for more than 15 min.[11] Usually, fuel is also added to take advantage of the temperature rise. The reaction is based on the calcium ions partial replacement by sodium ions in the phosphates. The expected result is the formation of a bio-soluble $CaNaPO_4$ compound.

In the present work, to demonstrate the process feasibility, sodium bicarbonate is used as a sodium ion source, due to its relatively low cost and high availability. Anthracite is used as the absorber. In particular, the SSA corresponds to 60% of the sample mass, and 25% $NaHCO_3$ and 15% carbon are added. All the as-received samples were treated in the same way: after the $NaHCO_3$ and anthracite addition, they were placed in the dedicated chamber and inserted into the oven (a 2.4 GHz Panasonic commercial MW oven was used for food treatment). The treatment was made on 0.4 g of the sample, by setting the MW power at 1000 W for 15 minutes.

The susceptor-assisted microwave heating is referred to as hybrid microwave heating. In the present case, the use of the chamber enhances the microwave heating efficiency.

The combined effect of a susceptor and a chamber has several advantages: increased heating efficiency and temperature (better energy transfer), reduced heat loss, enhanced process reproducibility, rapid heating, non-contact heating, quick start-up and stopping, better resource use, reduced costs, the possibility to optimize the susceptor and chamber

Table 1 Sample description and the corresponding elemental analysis evaluated by XRF

		Element (%)						
	Description	Na	Mg	Al	Si	P	S	Fe
Sample 1	Cyclone ash from the mono-combustion of sewage sludge	0.7 ± 0.2	1.4 ± 0.4	8.5 ± 2.5	15.2 ± 4.6	4.4 ± 1.3	0.26 ± 0.08	4.7 ± 1.4
Sample 2	Boiler post combustion ash from the mono-combustion of sewage sludge	0.9 ± 0.3	1.1 ± 0.3	6.5 ± 1.9	14.4 ± 4.3	3.2 ± 1.0	0.8 ± 0.2	4.0 ± 1.2
Sample 3	Bottom ash from the mono-combustion of sewage sludge	0.7 ± 0.2	1.3 ± 0.4	6.7 ± 2.0	15.2 ± 4.6	3.8 ± 1.1	0.4 ± 0.1	4.0 ± 1.2
Sample 4	Boiler post combustion ash from the co-combustion of sewage sludge and municipal solid waste	0.5 ± 0.2	0.9 ± 0.3	5.0 ± 1.5	9.5 ± 2.9	3.6 ± 1.1	0.26 ± 0.08	5.3 ± 1.6
Sample 5	Cyclone ash from the co-combustion of sewage sludge and municipal solid waste	0.8 ± 0.2	1.1 ± 0.3	3.8 ± 1.1	6.3 ± 1.9	1.8 ± 0.5	0.9 ± 0.3	2.8 ± 0.8
Sample 6	Bag filter ash from the co-combustion of sewage sludge and municipal solid waste	10.6 ± 3.2	1.1 ± 0.3	2.4 ± 0.7	3.0 ± 0.9	1.2 ± 0.4	3.3 ± 1.0	1.8 ± 0.5
Sample 7	Bottom ash from the co-combustion of sewage sludge and municipal solid waste	3.1 ± 0.9	1.1 ± 0.3	5.6 ± 1.7	24.4 ± 7.3	0.7 ± 0.2	0.27 ± 0.08	1.9 ± 0.6

design, lower manipulation of dangerous substances (for example heavy metals), the ability to treat waste *in situ*, and the portability of equipment and processes. An increase in carbon content can allow the reduction of the time and/or the power for MW carbothermal reduction reactions. It should also be pointed out that MW heating does not require the use of fuel, often necessary to support conventional processes.[12]

Results

Preliminary experiments were performed to demonstrate the efficacy of the proposed technology in the realization of thermochemical reactions with MW support. The literature shows that the $Ca_3(PO_4)_2$ conversion to $CaNaPO_4$ occurs at temperatures ranging from 900 to 1000 °C.[11] The results (not reported here, see supporting S1‡) show that the use of the chamber is mandatory to obtain a suitable temperature, even if it was demonstrated that MW can decrease the reaction's activation energy, making it less energy-intensive. To verify the sustainability of the treatment, energy consumption and associated carbon dioxide emission are evaluated in comparison to the ASHDEC thermochemical process[12] (see Table 2 and S2‡), which is realised at the industrial level. This was done by considering that the MW energy requirement per mass, from grams to kilograms, decreases exponentially with the increase of treated mass.[13] The data reported in Table 2 demonstrate that the MW technology is greener, even if it is evaluated on a laboratory scale, in terms of the involved energy and emission. When a mass of several kilograms of samples is used, pilot-scale studies show a further increase in MW energy efficiency, which is not considered in Table 2, because it must be experimentally evaluated.[13,14]

After the technology proof of concept (see S1‡), the work was devoted to investigating the process feasibility on seven SSA samples (described in Table 1).

Leaching tests (see a study by Benassi *et al.*[15]) were conducted on the as-received samples (RAW samples) and on the corresponding samples (with $NaHCO_3$ and anthracite addition), treated by MW (NC-MW samples) to evaluate the change in the phosphorus bioavailability due to the treatment (see Table 3). All the results reporting the concentration of elements found in the leaching solutions are available in the ESI (S3‡), where also mineralogical analysis is shown (S4‡). It is clear that a change in the P solubility in water occurs (see Table 3): the availability of P in NC-MW samples is higher than that of the corresponding RAW samples, thanks to the thermochemical treatment, strongly supporting the possibility of direct reuse of the obtained products as fertilizers. Indeed, XRD analysis (S4‡) highlights the formation of $NaCaPO_4$ in several samples due to MW treatment. Other crystalline phases containing P were also found (for example $AlPO_4$). In order to propose the possible direct use of MW-treated SSA as a fertiliser, the leachable metals must also be evaluated. Table S3‡ shows that the water solubility of Pb, Zn, and Cr is decreased after the treatment. This is another clear advantage of the thermochemical method: the incineration removes pathogens and organic matter from the sewage sludge, but the fate of the remaining heavy metals can represent a problem. Indeed, the literature shows that the main metal components of the sewage sludge are generally not transferred into the gaseous phases except for potassium.[16] Instead, thermochemical treatment has the advantage that heavy metals, in SSA, can be transferred into the gaseous phase and eventually separated in the off-gas treating system.[16] As a consequence, potassium chloride and heavy metal chlorides are the main expected phases that are generally found in the off-gas. It is also interesting to highlight that heavy metal removal is normally improved by adjusting the temperature, generally resulting in a low concentration of leachable heavy metals after thermochemical treatment at 1000 °C.[16,17] However, it is clear that a process optimization, for example for different SSA, could be highly onerous and time-consuming, making the thermochemical conventional treatments not always feasible also in terms of process investigation and optimization. In contrast, the new MW proposed technology is feasible with the need for low treatment energies and a short time (15 minutes in the present work), making the technology optimization very promising and less onerous in comparison to conventional treatments.

Table 2 Energy requirement and associated emissions for the ASHDEC[12] and MW technology. For the ASHDEC natural gas is considered as fuel (considering a different fuel the energy and emission are higher). In this table, the further increase in MW energy efficiency, when a mass of several kilograms of samples is used in a pilot plant, is not considered (see S2†).[13]

	ASHDEC process[12]	MW technology
Energy (MJ kg^{-1})	2.30	0.5–1.1
Emission ($kgCO_{2\text{-eq}}$ kg^{-1})	0.13	0.07–0.14

Table 3 Phosphorus (determined by inductively coupled plasma optical emission spectroscopy – ICP-OES) and phosphates (determined by ion chromatography – IC) concentrations in the aqueous leached of all samples. RAW = as received samples; NC-MW = samples (with sodium bicarbonate and anthracite) after microwave treatment. nd = not determined concentration, < LOQ = lower than the instrumental limit of quantification

Water leaching (solid/liquid = 1/10) (Benassi *et al.*[15])	Phosphate ions (ppm)		Phosphorus (ppm)	
Sample	RAW	NC-MW	RAW	NC-MW
1	nd	38.9 ± 6.8	0.05 ± 0.01	18.8 ± 4.4
2	nd	40.4 ± 7.0	< LOQ	18.9 ± 4.4
3	nd	26.0 ± 4.5	0.12 ± 0.03	14.9 ± 3.5
4	nd	32.8 ± 5.7	0.10 ± 0.02	15.0 ± 3.5
5	nd	0.8 ± 0.1	< LOQ	1.1 ± 0.3
6	nd	nd	< LOQ	< LOQ
7	nd	0.5 ± 0.1	< LOQ	1.2 ± 0.3

Throughout this work, we aimed to demonstrate for the first time the effectiveness of MW treatment in thermochemical processes for SSA. However, additional studies are necessary to verify the dependence of the results on the SSA chemical properties and the treatment parameters. In addition, in the present work, process optimization was not realized. For example, it is reported that the reaction to produce $NaCaPO_4$ can be competitive with Na consumption by the silicon oxides in the SSA. This may proceed at low Na mass fractions and may be followed by a conversion from whitlockite to buchwaldite, but at higher Na mass fractions.[4] It is also evident that a change in MW power and treatment time and a different selection of the raw material typologies and quantities used for mixing with SSA allow obtaining different (and possibly several) experimental setups, and other works are mandatory for investigating more suitable reactants in order to optimize not only the characteristics of the final products, but also the process sustainability.

Conclusions

Due to the energy involved and the raw materials required to recover phosphorus from SSA, the application of thermochemical processes is still very limited.

In this work, a new technology is presented. It is based on a patented chamber that allows the samples to rapidly absorb MW energy and maintain internal thermal insulation to optimize the thermochemical treatment. This results in faster heating, with limited reaction times, and lower associated energy consumption and emission compared with conventional heating processes. The results concerning the phosphorus bioavailability in the treated ashes are very promising, showing an increased water solubility, by about two orders of magnitude. The leachability of heavy metals is also reduced because of the treatment. The new proposed technology provides the possibility of different scenarios, connected with new strategies concerning sewage sludge management. Indeed, although end-of-life P recycling remains very limited, in some countries SSA is available from the recovery of thermal energy. In this frame, the proposed thermochemical treatment presents several advantages related not only to the quality of the final product, but also to the possibility of energy saving.

Finally, the opportunity to also investigate the MW behaviour of alternative P sources, like ash derived from the combustion of animal by-products, can allow opening new challenging research areas in the next future.

Author contributions

Conceptualization: E. B. Data curation: L. F. and A. F. Formal analysis: A. C. and S. F. Funding acquisition: E. B. and L. E. D. Investigation: L. F. and A. F. Methodology: E. B. and L. F. Project administration: E. B and S. F. Resources: E. B. and S. F. Software: A. C. Supervision: E. B and L. E. D. Validation: L. F. and A. F. Writing – original draft: E. B., L. F., and A. F. Writing – review & editing: E. B. and A. C.

Conflicts of interest

There are no conflicts to declare.

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