GEOPOLYMERS FOR MUNICIPAL WASTEWATER TREATMENT PRODUCED BY USING NATURAL AND WASTE-DERIVING PRECURSORS

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Materiali innovativi per uno sviluppo sostenibile: dal laboratorio alle applicazioni

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Introduction

In recent years, geopolymer materials have captured attention in wastewater treatment as efficient, environmentally-friendly and low-cost adsorbents for elimination, decontamination, and purification of inorganic and organic hazardous pollutants from aqueous environments.

The main goal of this work is to evaluate the physical, chemical and mineralogical properties of geopolymers designed for the wastewater treatment. In addition to a commercial kaolin, geopolymerization reaction was tested on wastewater treatment sludge (WWTS), resulting from the tertiary treatment and subsequent dehydrated in phyto-depuration bed at the wastewater treatment plant of Lago Forcatella (Fasano, Italy). Both precursors were heat-treated at 700°C to promote the kaolinite dehydroxylation in the former case, and the organic matter removal in the latter, then activated by using a solution of NaOH and sodium silicate.

Aquasoil s.r.l.

The company Aquasoil S.r.l. projected and implemented a pilot experimental plant for wastewater potabilization in the Forcatella Lake site of Fasano (Br). The plant intercepts water from the municipal purification system and, after refining it for agricultural reuse, distributes water to 50 farms. It consists of three experimentation lines sharing the advanced oxidation process (O_3/H_2O_2) and lamellar pack sedimentation.

Aquasoil

METAKAOLIN GEOPOYMER

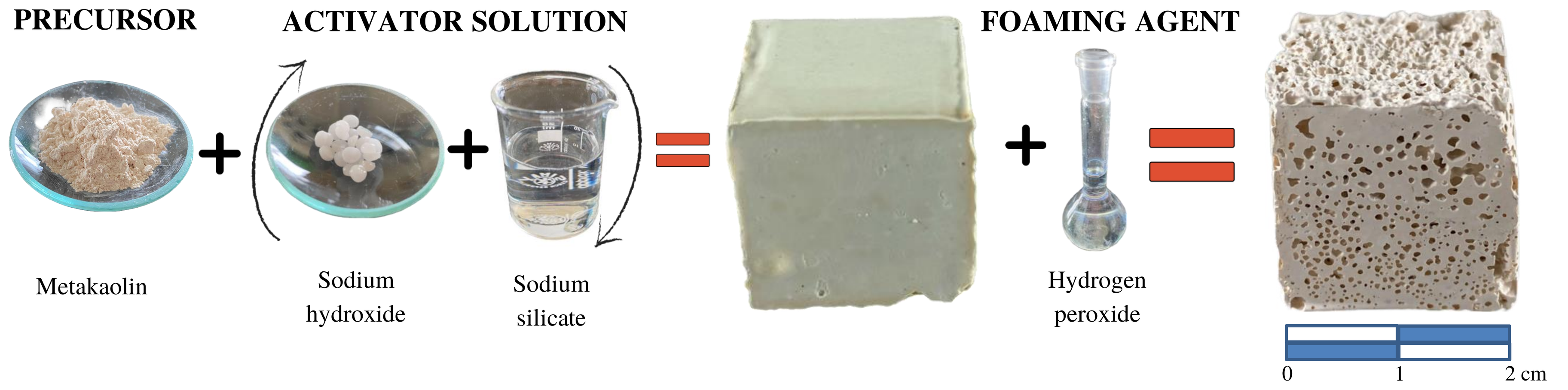
WASTEWATER SLUDGE GEOPOYMER

Materials and methods

A commercial kaolinitic clay, thermally treated up to 700°C to increase its reactivity, was used as precursor. Kaolin and metakaolin were characterized by X-ray powder diffraction (XRPD) and X-ray Fluorescence (XRF). Geopolymer samples were prepared by mixing metakaolin with the alkaline activator and cured in different conditions (85°C for 5 hours and 40°C for 24 hours) in order to evaluate as curing influences the geopolymers features. Hydrogen peroxide (H_2O_2) diluted to 3wt%, was used to produce porosity.

Geopolymers were studied through XRPD and at a macroscopic and microscopic scale by stereomicroscope and SEM-EDS, respectively. Test of integrity of samples in water (by immersing samples in distilled water for 5 days) and pH measurements on leached water, were also performed on all samples.

The characterization of the sludge produced in tertiary wastewater treatment plant at Forcatella Lake was performed in order to evaluate its feasibility as new waste-deriving precursor for geopolymers. For this purpose, the naturally dehydrated sludge (FDN) contained in the phytodepuration tanks, was characterized by XRPD, XRF and SEM-EDS. Sludge was pre-treated by heating to 700°C and grinded in a rotary jar mill (< 0,149 mm in size). Geopolymers were made by combining sludge, silica fume and the alkaline solution in order to theoretically balancing the SiO_2/Al_2O_3 and SiO_2/Na_2O ratios of geopolymer. The same curing parameters used for MK-based geopolymers were selected for these samples.



Results

Table 1

Sample	LOI	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_5	FeO
Kao_CC31	11,94	0,04	0,21	35,63	48,83	0,05	2,32	0,05	0,03	0,01	0,89	0,00

Chemical analysis (Table 1) of kaolinitic clay shows amounts of SiO_2 and Al_2O_3 higher than 80 wt%.

Table 2

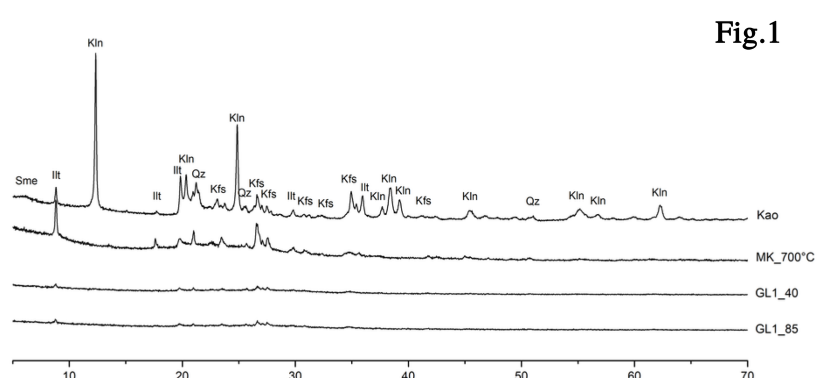
Sample	LOI	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_5	FeO
FDN	47,16	0,15	0,55	37,77	4,23	6,24	0,12	2,95	0,07	0,01	0,73	0,00

In Table 2 the chemical composition (wt%) of sludge (FDN). Sludge shows low SiO_2 content and Al_2O_3 and P_2O_5 as main oxides.

Chemical analyses

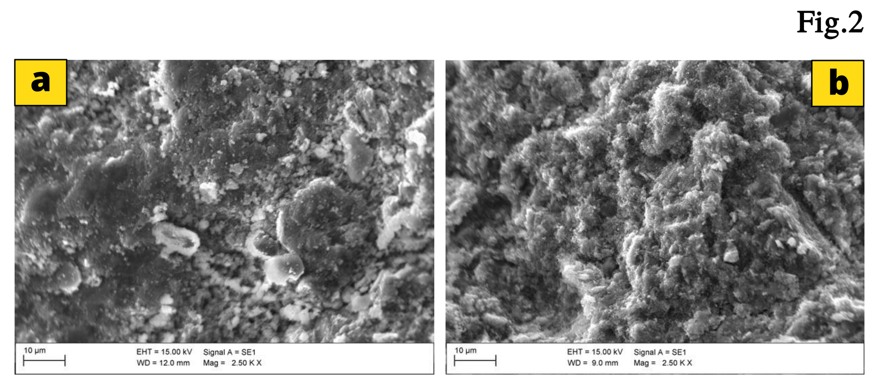
Mineralogical analyses

Fig.1



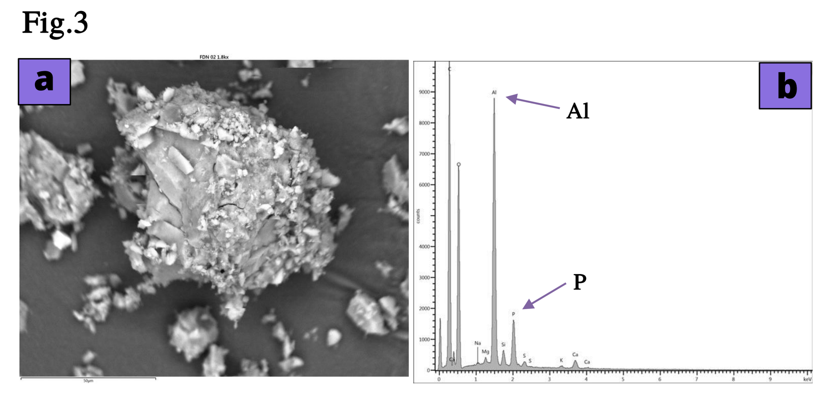
Mineralogical analyses (Fig.1) of kaolinitic clay (Kao) shows quartz, kaolinite, illite, smectite and feldspars as main crystalline phases. After heating to 700°C (MK_700°C) the main peaks of kaolinite disappear due to dehydroxylation of the mineral; dehydration of smectite is also observed from X-ray diffraction pattern. Geopolymer samples cured at 40°C for 24 hours (GL1_40) and 85°C for 5 hours (GL1_85) show the absence of new secondary phases and the formation of an extended amorphous hump indicating the occurrence of geopolymerization reaction.

Fig.2



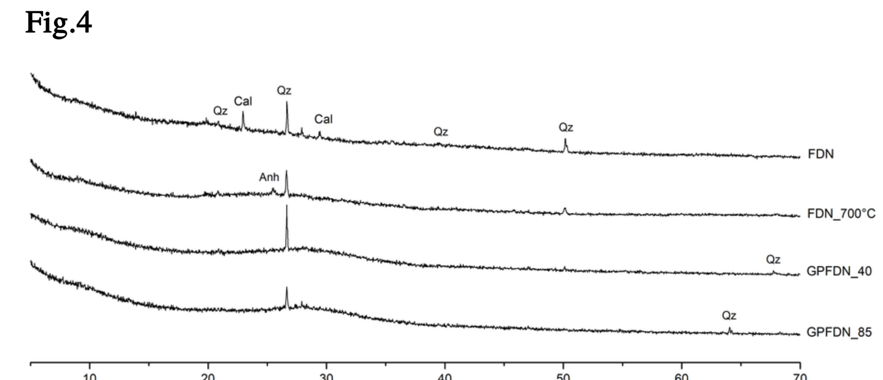
Morphological analyses by SEM-EDS (Fig.2) of MK-geopolymer cured at 40°C for 24 hours (a) and MK-geopolymer with 5 wt% of hydrogen peroxide (b), showing well developed amorphous matrices in both samples.

Fig.3



Chemical-morphological analyses by SEM-EDS (Fig.3) of magnified single granule of wastewater sludge (a) and correspondent EDS spectrum (b), showing aluminium and phosphorus as the main chemical components.

Fig.4

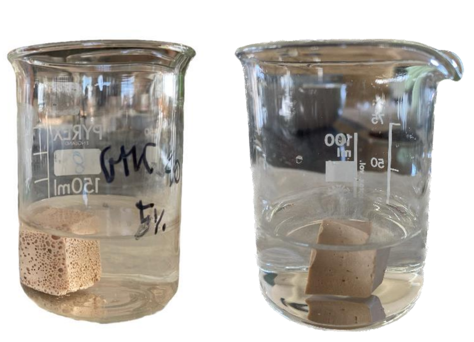


Mineralogical analysis (Fig.4) of wastewater sludge (FDN) shows a large amorphous hump, and calcite and quartz as crystalline phases. In the heated sludge (FDN_700°C) the anhydride phase occurrence and the calcite phase disappearence was observed. Geopolymer samples cured at 40°C for 24 hours (GPFDN_40) and 85°C for 5 hours (GPFDN_85) are characterized by the absence of secondary phases and the formation of an extended amorphous hump 20 to 40 °2ϑ, indicating that the geopolymerization was successful.

pH measurement

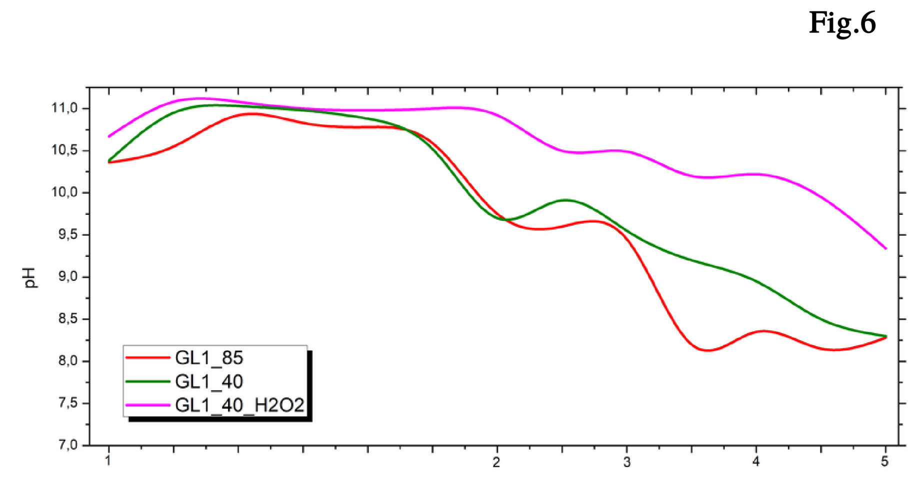
Integrity test

Fig.5



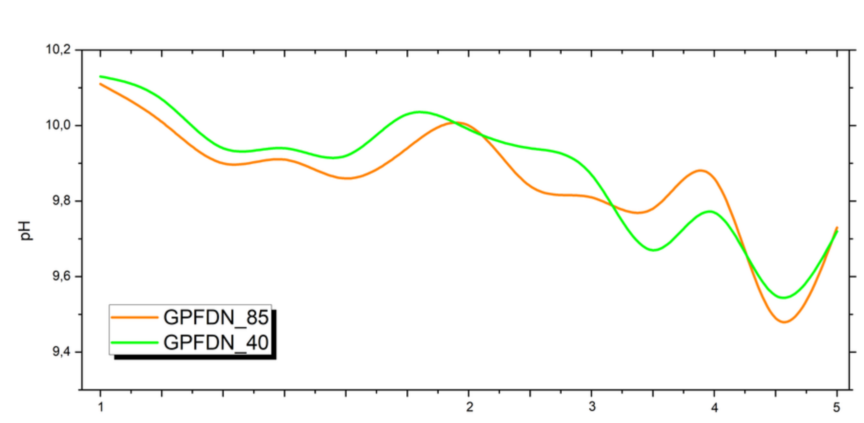
A test of integrity in water (Fig.5) was performed on MK-geopolymer samples, including the porous one, which showed undamaged surfaces after five days of immersion in distilled water.

Fig.6



The figure (Fig.6) shows the pH variation of water after immersion of MK-based geopolymers GL1_85 and GL1_40 and the porous sample (GL1_40_H2O2) for a control time of 5 days. As evidenced, leaching leads to different pH values: the water in which was immersed porous geopolymer achieves pH above 9 after 5 days, whereas for the other samples pH decrease until 8.

Fig.7



The figure (Fig.7) shows the pH variation of water containing sludge-based geopolymers (GPFDN_85 and GPFDN_40). Leaching leads the water pH to values slightly below 10 after 5 days, observing a marginally lower pH for the sample cured at 85°C for 5 hours.

Fig.8

A test of integrity in water (Fig.8) was performed on FDN-based geopolymers, showing undamaged surfaces after five days of immersion in distilled water.

Preliminary results

According to the analyses, the formulations with metakaolin and peroxide, as well as the formulation with wastewater treatment sludge, allow to obtain geopolymer samples with extended amorphous structures (one of the main characteristic of geopolymers). All the investigated formulations gave geopolymer samples showing good integrity in water, which is a key feature for the application in wastewater treatments. Samples cured at 40°C, will result preferable with a view of energy saving during preparation of the samples.

Next steps

Future investigations will be focused to the optimization of preparation and curing parameters of the obtained geopolymers, both from MK and WWTS precursors, in order to test their efficiency in removal pollutant, mainly ammonium, from wastewater. Tests will be performed in a first instance in laboratory using test solutions and then in real conditions at the experimental lines. Mechanical, microstructural and porosimetric investigations will be also performed for the comprehensive characterization of geopolymers.