Alginate beads with humic acids extracted from anaerobic digestate of sewage sludge

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The wastewater production is rising all over the world as a consequence of the increasing of population and industrialization (Hong et al., 2009). A recent study estimated that approximately 330 km^3 of wastewater are produced worldwide yearly (Mateo-Sagasta et al., 2015). For purification purposes, different treatment strategies can be carried out, producing sewage sludge (SS) as main residue, which is stabilized mostly via anaerobic digestion (Liu et al., 2012). A study of the European Commission revealed that Europe produced 17 kg per capita of dry sludge per year (European Commision, 2017). SS is really rich in terms of plant nutrients such as nitrogen and phosphorous (Cristina et al., 2019); for this reason, agricultural reuse is the principal solution in many countries (Epstein, 2002). Furthermore, some studies revealed that SS can contain humic acids (HA) (Adani and Tambone, 2005), that are defined as "the portion of the soil organic matter which is soluble in base and insoluble in mineral acid and alcohol" (Steelink, 1963). Beneficial effects of HA on soil quality and plant growth are well known in literature (Tan and Nopamornbodi, 1979). On the other hand, SS can retain many pollutants, such as heavy metals (Healy et al., 2016). Within a circular economy approach, the first aim of the present work was to implement an HA extraction protocol from sewage sludge anaerobic digestate (SSAD), to purify it from heavy metals and other unwanted substances. Secondly, HA quantification was conducted on SSAD and on the extract as well as on commercial HA. Thirdly, encapsulation in alginate beads was tested as potential formulation of HA extract. Finally, HA beads were used in a greenhouse experiment in order to evaluate effects on plant growth and biomass.

- The exploited SSAD came from "La Farfana" wastewater treatment plant (WWTP) of Santiago (Chile), one of the biggest WWTP in Latin America (3.7 million equivalent people). The extraction protocol exploits, as raw matter, SSAD with a mean dry biomass of 25.58%. In order to obtain an adequate liquefaction of the digestate, water was added to reach 13% of dry biomass. Successively, KOH and $K_4P_2O_7$ were added to reach a final concentration of 0.01 M each. Next, a steady and slow mixing was carried out for five hours at room temperature. Subsequently, the mixture was neutralized to pH 7 with H_3PO_4. Finally, a centrifugation (40', 3500 g) was performed in order to separate humins (pellet) and the HA extract (supernatant). With the purpose of evaluating the quantity of HA, Lamar method (Lamar et al., 2014) was applied on SSAD, HA extract and commercial HA. Afterwards, alginate beads containing the HA extract were created using encapsulator Buchi B-390. A stirred solution of $CaCl_2$ 0.6 M was used as hardening bath. Moreover, lyophilized HA extract and an alginate beads were investigated through FESEM-EDX to understand humic acids structure and beads shape, and to get qualitative information on the chemical composition. Finally, a pot experiment in greenhouse was performed. Chilean lettuce plants (*Lactuca sativa* L.) were transplanted in pots of 30 cm of diameter filled with a sandy soil. Next, half of the pots (9 replicates) were treated with alginate-extract beads and the second half was no treated (control). Finally, after 70 days, dry matter of the epigean and hypogean part of plants were weighted separately.

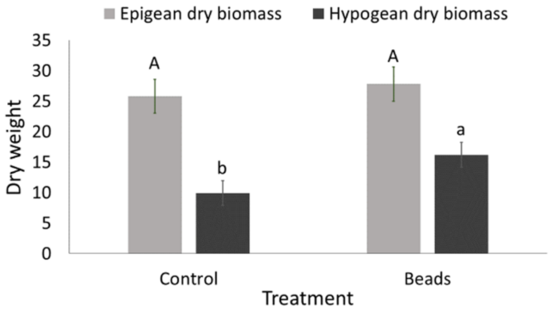
- Lamar method revealed that HA concentration in SSAD was 12.53% dry matter basis (d.m.b.) (Table 1). In the extract the HA percentage rose to 26.87% (d.m.b.). Commercial HA reached 77.87% of HA (d.m.b.). These results confirmed the presence of HA in SSAD and validated the HA extraction technique. FESEM and EDX confirmed that no heavy metals passed into the extract and, consequently, in beads. The same analyses showed also that an abundant part of the beads surface area was still constituted by NaCl, meaning that the exchange reaction from sodium to calcium alginate occurred only partially. The greenhouse experiment revealed that the use of HA beads caused an increase in epigean and hypogean biomass production. Statistical analysis partially confirmed these results; in fact, only the hypogean biomass of lettuce treated with HA beads were significantly higher than control (Figure 1).

- One of the most important outcomes of this work is the possibility of HA extraction from SSAD. Despite the HA% of the extract is lower than commercial HA, it is important to underline that normally HA derive from non-renewable resources such as peat, lignite and leonardite, while in this case HA derived from a waste. Furthermore, the extraction protocol allowed to separate heavy metals from the extract, yielding a successful separation of interesting compounds from potential pollutants. Concerning the encapsulation technique, although it showed good performance in the greenhouse experiment, it should be more investigated in order to reduce the NaCl presence. Finally, this work represents a good example of application of circular economy since a high value-added product was obtained from a waste.

Table 1. Dry matter mean percentages and humic acid mean percentages measured in sewage sludge from anaerobic digestate (SSAD), extract of SSAD (Extract) and commercial humic acids (Commercial HA). d.m.b.: dry matter basis.

Parameter	Dry matter %		% HA (d.m.b.)	
	Mean value	Standard dev.	Mean value	Standard dev.
SSAD	25.58	± 0.49	12.53	± 1.60
Extract	1.13	± 0.02	26.87	± 0.35
Commercial HA	83.95	± 0.08	77.87	± 1.46

Figure 1. Mean dry epigean and hypogean biomasses of Lactuca sativa L. grown on sandy soil with beads treatment and without beads treatment. Different letters indicate differences between treatments that are significant at P < 0.05 (Tukey HSD). Error bars represent standard error. Upper-case letters refer to statistical analysis applied to epigean dry biomass samples and lower-case letters refer to statistical analysis applied to hypogean dry biomass samples.



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