Sludge recovery from industrial wastewater treatment

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Industries produce significant quantities of sludge from wastewater treatment. Industrial sludges have different composition, depending on the specificities of each industrial activity (Lee *et al*., 2018). In Portugal, some of the polluting industries that produce large amounts of effluents and sludges are food, chemical, textile, paints, resins, pharmaceuticals, tanneries, paper, metallurgy and mining.

Most industrial sludges are considered wastes or even hazardous wastes. Nowadays, the wastewater treatment sludges go to composting, anaerobic digestion, incineration or landfill. Therefore, with proper treatment industrial sludge can be considered valuable material resources contributing to the sustainable circular economy of the wastewater treatment sector (Elalami *et al*., 2019).

The present work has the objective to identify and evaluate different sludge treatment/valorisation methodologies, being given priority to the valorisation in detriment of the elimination operation, like incineration or landfill. The industrial sludges were from a wastewater treatment plant from a resin industry, after dehydration operation by a press (Figure1). These sludges have a high variety of components, notably the high levels of calcium, magnesium, pH and dry and organic matters (Table 1).

Table 1. Industrial sludges characterization.

Parameter	Units	Valor
Dry Matter	% (m/m)	78.4
Organic Matter	% (m/m)	56.8
pH	Sorensen scale	12.7
Magnesium	g Mg/kg	1,130
Calcium	g Ca/kg	80,030

Figure 1. Dehydrated industrial sludges

For valorisation of industrial sludge several solutions were tested such as: application in anaerobic digestion aiming the production of biogas and allowing energy recovery, use in the preparation of adsorbents for the treatment of industrial wastewater, utilization of sludge to replace cement for mortar production, application of heterogeneous catalysts to produce biodiesel and clinker production (cement).

The anaerobic digestion option for treat the industrial sludge was applied in order to evaluate the substrate biodegradability by the biochemical methane potential (BMP) tests, that are worldwide applied to gauge the biodegradability of different substrates or mixture of substrates (Kafle *et al*., 2016, Cabrita *et al*., 2016). The BMP tests are essentially based on the incubation of a quantity of substrate and anaerobic inoculum, on the measurement of the volume of biogas produced and the determination of its composition by GC, in order to obtain the specific methane production.

The anaerobic reactors used were glass recipients, with a volume of 500 mL, sealed with butyric rubber stopper, with a glass tube of about 10 cm, which had a Teflon septum at the end to allow the biogas collection during the tests. In the BMP tests, two substrate mixtures were analysed, consisting of industrial sludge (IS) and mixed sludge - primary and secondary (MS), from a municipal wastewater treatment plant (WWTP) located in central Portugal. The two mixtures of sludge applied as substrates were composed of 80% MS and 20% IS and 90% MS and 10% IS.

The adsorption tests consist in the preparation of solid adsorbents, mixtures of industrial sludge with sludge from water treatment to remove dyes from industrial wastewater. For the adsorption tests, four mixtures were made with LI and dehydrated sludge from water treatment (LSW), with the following proportions: 50% IS and 50% LSW; 40% IS and 60% LSW; 33% IS + 67% LSW; 25% IS + 75% LSW. However, after testing these mixtures with distilled water and agitation, it was found that only the mixture with 25% IS + 75% LSW was a solid material with mechanical strength not to break down during adsorption test and promoting solid / liquid separation. Therefore, the with mixture with 25% IS + 75% LSW was applied as an adsorbent in the dye adsorption tests.

As adsorbate, four dyes were selected because they are used in large quantities in the textile and food industries. The dyes chosen were rhodamine-B (RB), mordant orange 1 (MO1), methylene blue (MB) and mordant blue 9 (MB9). To quantify the adsorbates concentration, the spectrophotometric method was applied, with calibration curves for each dye with concentrations between 1 and 100 mg/L. Thus, for each dye, six different concentrations were tested in 100 ml flasks, with a useful volume of 30 mL and with agitation. The adsorbent mass ranged was from 0.5 to 3 g.

In mortar production tests, industrial sludges were used to partially replace (≤10%) the amount of cement. The industrial sludges were previously crushed and sieved with the 500 µm sieve, so that only the fraction with a particle size less than 500 µm was used in the tests. In these tests five mortars mixtures were done, cement was partially replaced by industrial sludge, using different sludge percentages, 0, 1, 2.5, 5 and 10%. In the five mortars obtained the flexural and compressive strength were evaluated. The experimental procedure was based on the standard NP EN 191-1: 2006.

In the biodiesel production tests, industrial sludges were used to produce heterogeneous catalysts. The sludges were crushed and subjected to two pre-treatments, drying at 70 ºC (oven), for 24 h and calcination at 850 ºC (muffle), for 3 h. The production of biodiesel was carried out through a transesterification reaction of used cooking oils, with methanol, in the presence of a solid catalyst (industrial sludge).

The biodiesel produced passed through a purification procedure in which three steps were carried out: washing, centrifuging and drying in order to guarantee a product with maximum purity. The purified biodiesel was analysed to check some parameters, such as density, acidity index and chemical composition by FTIR analysis.

Analysing the results from anaerobic co-digestion, it was possible to verify the anaerobic reactors, with 90% MS and 10% IS, had the highest specific production with around 0.487 L CH_4 / gVS, estimating the energy production of about 4 kWh / kg VS, equivalent to 2 kWh / kg industrial sludge and corresponding to an economic return of € 308 / ton of sludge. Thus, it is possible to apply anaerobic co-digestion to industrial sludge with other substrates, namely municipal WWTP sludge with energy recovery.

In the production of adsorbents for dyes removal efficiencies were obtained from 50 to 80% for MB9, RB and MO1 dyes and 30% for MB dye. In these tests, the Langmuir and Freundlich isotherms were applied, and it was verified that the Langmuir isotherm describes with a better adjustment of the experimental data.

Regarding the production of mortars, it was found that the compressive and flexural strength decreased with the increase of the sludge fraction (1, 2.5, 5 and 10%) in cement replacement, obtaining 2.73 to 4.46 MPa for flexural strength and 17.12 to 38.14 MPa for compression, lower than normal values for mortars (42.5 MPa).

In the production of heterogeneous catalysts for biodiesel production, high conversions were obtained, and characteristics like the biodiesel obtained by homogeneous catalysis were observed.

The FTIR results of biodiesel are identical to those of biodiesel produced by homogeneous catalysis, concluding that the use of industrial sludge, with thermal pre-treatment, as a catalyst in the production of biodiesel is possible, with high conversions expected.

Regarding the application of industrial sludge as a raw material for clinker, an intermediate product of cement, it was not possible to carry out laboratory tests due to the lack of the specific equipment required. Thus, only an analysis to compare the physical-chemical composition of the sludge with the usual raw materials in the production of clinker was made. Due to the fact of industrial sludges were made up mostly of calcium, it would probably be possible to apply it.

Therefore, it was concluded that the most promising industrial sludge treatment / recovery hypotheses are anaerobic co-digestion and the production of heterogeneous catalysts for biodiesel production. As future work, it's also possible to study the application of industrial sludges in the mortar production by replacing the sand, due to the sludges particle size after crushing.

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