Anaerobic bioprocesses towards the conversion of carbon dioxide into bio-based products: as short review.

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The increase in CO_2 in the atmosphere causes a serious problem being the main greenhouse gas of anthropogenic origin. In 2018, the CO_2 accounted for about 81% of the global GHG emissions in the European Union (EU) together with methane and nitrous oxide, which represent 10% and 6% respectively. (Eurostat 2020) The Earth's atmosphere contains several greenhouse gases (GHG), the main ones being water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3), which absorb about 95% of the IR radiation emitted by the Earth's surface. This radiation is then 'trapped' and re-emitted in all directions, so part of it returns to the Earth's surface, heating it (greenhouse effect). In the absence of GHG capable of absorbing IR radiation into the atmosphere, the average temperature of the Earth's surface would be -18°C instead of 15°C (natural greenhouse effect). Consequently, the problem is not the greenhouse effect itself, but the increase in the concentration of GHGs that accentuate this phenomenon. Measurements made in recent decades have shown that the level of radiation escaping into space is decreasing; therefore, heat accumulates on Earth and the energy balance is disturbed. Therefore, it is observed that climate change is caused by the intensification of the greenhouse effect (global warming), caused mainly by the increasing concentration of greenhouse gases in the atmosphere, resulting from anthropogenic activities, pollution and increased industrial activities. (Mielcarek-Bocheńska., 2021) Thus arises the need to reduce GHGs; in fact, one of the objectives of the EU 2020 package on climate and energy is to reduce greenhouse gas emissions by 20% compared to 1990 levels. (COM 2020) In addition to mitigating carbon dioxide (CO_2) emissions into the atmosphere through more sustainable production processes, the trend is to further reduce them through systems that capture it; in this context, the driving force is the EU Emissions Trading System (ETS), which sets a price for carbon and reduces the upper limit applicable to emissions from certain economic sectors each year. In recent months, the progressive increase in the exchange price of CO_2 allowances is increasingly becoming an important cost item for the most energy-intensive and impactful industries (e.g., paper mills, steel mills, textile industries, petrochemicals, etc.). (Capros., 2019; European Commission, ETS) Therefore, climate neutrality is also achievable through the development of new carbon negative bioprocesses, which will allow the permanent removal of carbon dioxide (CO_2) and climate-altering gases from the ecosystem to balance the residual emissions from industrial production activities. In addition, waste, wastewater and activated sludge represent a huge pool of untapped resources and biomass that can represent important economic and environmental burdens, these can be converted into bioenergy and bio-based products through conversion processes, within a circular economy should be considered residual resources. Europe is already a world leader in the sustainable use of natural resources in an essential circular economy to meet most of the Sustainable Development Goals, this allows the dissemination of innovative solutions to exploit organic residues to obtain new and sustainable bio-based products (such as biochemicals, biofuels, etc.) potentially usable as substitutes for current fossil raw materials. (Gontard., 2018) In the face of climate change and progressive environmental degradation, on 11 December 2019 the European Commission established the European Green Deal, which includes a series of policies and objectives aimed at reducing net greenhouse gas emissions until achieving climate neutrality by 2050. (Rekich., 2021; To achieve these goals, Europe needs a net transformation of production cycles and a more sustainable energy supply system as it currently accounts for 75% of the EU's greenhouse gas emissions. (Sartor., 2014; Capros., 2019) The adoption of an energy system based on hydrogen and "biofuels" will pave the way for a more efficient and interconnected energy sector, driven by the dual objective of a cleaner planet with a stronger and more resilient economy. On the other hand, the production of renewable energy must be integrated into the treatment and enhancement of waste water and production waste, promoting recycling with a view to the circular economy. To date, Italy's electricity consumption in sewage treatment plants is about 3,250 GWh / year, which corresponds to about 0.5 billion euros per year, causing about 0.77 Gt of CO_2 emissions, equivalent to 1.57% of global annual greenhouse gas emissions. (Ranieri., 2021; Rekich., 2021) Considering these aspects, the same mission 2 included in the PNRR promotes the transformation of purifiers into "green factories" to allow the recovery of energy and sewage sludge and the reuse of purified wastewater for irrigation and industrial purposes. Today, at European level, this type of waste is treated mainly through anaerobic digestion, in fact, there are 15,000 plants in operation. With anaerobic digestion the stylization of organic residues is obtained by recovering biogas (a mixture composed of 50 – 70% methane and 30 – 50% carbon dioxide) which can be used as renewable energy, and digestate used as organic fertilizer. The first industrial applications of biogas production began well over 50 years ago as a means of stabilizing sewage sludge in wastewater treatment plants. The biogas industry expanded in the 70s and 80s when the increased production of different organic materials in agriculture began to represent one of the main sources of greenhouse gases worldwide, in fact anaerobic digestion systems remove the easily degradable carbon present in the raw materials such as slurry and manure and converts them into biogas. This has created the possibility of creating new sustainable biorefineries capable of converting waste products into products with high added value. In addition to the anaerobic digestion exploited for the production of biogas , one of the main anaerobic processes used for the treatment of waste water exploits Anaerobic Sludge Blanket (UASB) Type Up-flow reactors, thanks to its simple design, easy construction and maintenance, low operating costs and ability to withstand fluctuations in pH, temperature and concentration of the influential substrate, are able to anaerobically degrade the organic matter contained in the wastewater with methanogenic bacteria that produce methane gas (CH_4) which will subsequently be collected in the part upper than the reactor, this can later be used as an energy and heat source. (Gontard., 2018; Metcalf., 1991) To increase the energy activity of biogas it is necessary to eliminate the fraction of CO_2 present in it, this combined with the need to reduce CO_2 emissions an atmosphere leads to the development of new biotechnological processes capable of sequestering it. To date, to separate the CO_2 contained in the biogas from the CH_4 mainly uses chemical-physical methods, the CO_2 thus removed from the biogas can be recovered and liquefied to create an extra source of profit for the plant operator. In the future the idea is to recover the present CO_2 of biogas by exploiting microorganisms (hydrotrophic methanogens) able to use hydrogen to reduce CO_2 in CH_4, this process produces a biogas with a higher CH4 content that could reach the quality of the fuel used for vehicles. (IEA Bioenergy 2022) Biotechnological processes that use the metabolisms of microalgae and cyanobacteria for CO_2 fixation are also known, these are arousing more and more interest with a view to reducing global carbon emissions; however, new microalgae and strains of cyanobacteria with tolerance to high temperatures and CO_2 concentrations are essential for the further development of carbon capture based on the use of algae. In the face of this, attention is increasingly emerging towards the metabolism of purple phototrophic bacteria (PPB) which through anoxygenic photosynthesis can accumulate organic substances, nutrients from wastewater as well as assimilate CO_2. (Schipper., 2019; Batstone., 2015) In short, these types of microorganisms in conditions of growth, photoautotrophy and / or chemoautotrophy, through the Calvin-Benson-Bassham cycle (CBB) can assimilate CO_2 as this turns out to be the only source of carbon. During photoheterotrophic growth, the CBB pathway works to allow CO_2 to act as an electron dissipator for excess reducing power generated during oxidation of organic carbon substrates. In the absence of alternative electron acceptors supplied under these growing conditions, the demand for the CBB cycle is directly related to the oxidation state of the supplied carbon source. (Capson., 2020; Gibson., 2002) In order to optimize the biochemical reactions of PPB, the use of microbial electrochemical technologies (METs) is suggested by several authors, providing electric current to microorganisms that use electrodes as electron donors. This is a bio-electrochemical system in which electrons are supplied to microorganisms through a cathode in an electrochemical cell by applying an electric current to promote bioprocesses that hardly occur spontaneously, such as the bioconversion of carbon dioxide. In addition, some authors have reported evidence of CO_2 bioconversion, observing a growth of photosynthetic microorganisms as well as a simultaneous production of volatile fatty acids in the growth medium such as acetate. In addition, they highlighted how these microorganisms can produce polyhydroxyalkanoates usually used to produce biodegradable plastics with characteristics like traditional plastics. (Koku., 2002) The biomass obtained from these processes can also be subsequently used as an alternative and innovative protein food source such as Single Cell Proteins (SCPs), proteins extracted from microbial biomass that can be used for protein supplementation by replacing conventional and expensive protein sources, in view of the continuous growth of global demand for proteins of animal origin in view of the increase in population. (Delamare-Deboutteville., 2019)

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