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Biological hydrogen promotion via integrated fermentation of complex agro-industrial wastes

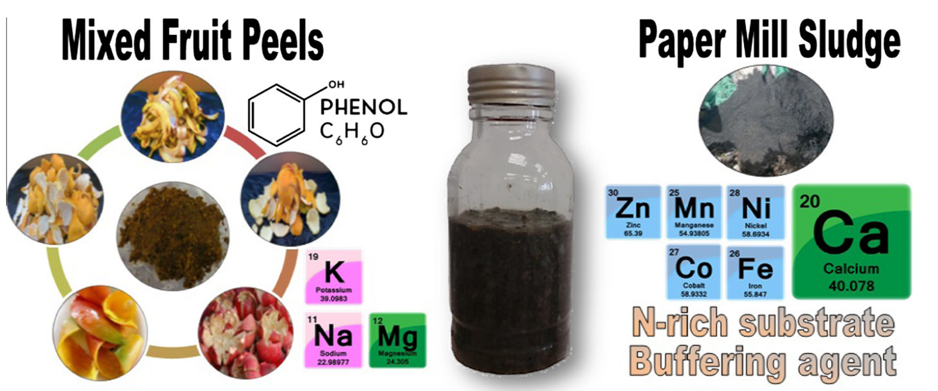
Mohamed Soltan [a], Mohamed Elsamadony [b,*], Ahmed Tawfik [a,*]

[a] Egypt-Japan University of Science and Technology (E-Just), Environmental Engineering Department, P.O. Box 179, New Borg El Arab City, 21934 Alexandria, Egypt
[b] Public Works Engineering Department, Faculty of Engineering, Tanta University, 31521 Tanta City, Egypt

HIGHLIGHTS

- Maximum H_2 production was achieved at 30% MFPs + 70% PMS.
- MFPs/PMS of 30/70 balanced self-originated metals to ideal concentrations.
- PMS supplementation mitigated the inhibition effect of phenolic compound.
- PMS is a good buffering substrate that is able to valorise hydrogenation process.
- Integrated fermentation exhibited the highest net energy gain of 32.2 ± 4.2 $kJ/kg_{feedstock}$.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of phenolic compounds and/or metals in mixed fruit peels (MFPs) and paper mill sludge (PMS) yielded hydrogen production values of 121.6 ± 9.2 and 163.5 ± 13.4 mL, respectively. MFPs contained total phenolic compound concentrations of 2.43 ± 0.11 mg_{GAU}/g, which reduced anaerobic activity. However, the integration of MFPs (30%) into PMS (70%) mitigated the inhibition of hydrogen production and resulted in a 3.01 and 2.24 increase in hydrogen generation compared to the separate fermentation of MFPs and PMS, respectively. Moreover, integrated fermentation of 30% MFPs and 70% PMS synergistically balanced the concentrations of trace metals in terms of calcium, iron, magnesium, manganese, nickel, zinc, sodium, potassium and cobalt at 2016.1 ± 119.3, 473.0 ± 42.6, 243.3 ± 21.7, 23.0 ± 2.7, 14.2 ± 1.3, 109.6 ± 7.5, 113.9 ± 9.1, 888.2 ± 102.4 and 1.2 ± 0.1 mg/kg, respectively. Total ammonia nitrogen and alkalinity values were augmented up to 539.20 ± 28.02 mg/L and 5.23 ± 0.73 $gCaCO_3/L$, respectively, at 70% PMS, which resulted in a limited pH drop of 1.31 ± 0.41. Furthermore, the 30/70 MFP/PMS substance yielded a net energy profit of 32.2 ± 4.2 $kJ/kg_{feedstock}$. This value corresponded to a payback period of 2.6 years compared to 11.5 and 5.4 years for the separate fermentation of MFPs and PMS, respectively.

1. Introduction

Moving towards renewable energy sources requires urgent action worldwide as traditional energy sources are depleted as well as the harmful effects of their utilization such as global climate change [1,2]. Waste to energy conversion is considered a

* Corresponding authors.
E-mail addresses: mohamed.elsamadony@f-eng.tanta.edu.eg (M. Elsamadony), ahmed.tawfik@ejust.edu.eg (A. Tawfik).

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promising approach to overcome organic waste accumulation in the environment and undoubtedly represented a potential renewable energy source [3]. Conversion of bio-wastes into hydrogen is considered a promising replacement for fossil fuels because hydrogen is a superior energy carrier that has water vapour as its sole combustion by-product, is 50% more efficient than gasoline, and has an energy yield 2.75 greater than hydrocarbons [4–6]. Biohydrogen could be easily harvested from organic waste via a highly productive dark fermentation process [7,8]. Of the dark fermentation processes available, solid state fermentation outperformed liquid fermentation through its rapid stabilization of organic matter, digestate volume reduction, high energy potential and ability to provide a clean environment compared to landfills or incineration processes [9,10].

Lignocellulosic materials including MFPs and paper mill sludge (PMS) are the most abundant bio-wastes on the earth and their annual production amounted to 50 billion tons [11]. Approximately, 9.0 million tons per year of mixed fruit peels (MFPs) are generated in Egypt [12]. Dumping and burning such waste in open areas results in serious environmental problems such as ground water, air pollution and smog formation [13]. Meanwhile, MFPs represent a profitable option for energy conversion via solid state fermentation because they are cheap, abundant renewable, and inedible [14]. However, hydrolysis of solid wastes into soluble organics is the rate-limiting step process [15]. In addition, the sole fermentation of MFPs results in various potential inhibitors, which need to be addressed and overcome to enhance the formation of hydrogen. Low hydrogen productivity from fruit peels has been previously identified by Vijayaraghavan et al. [16], who harvested only 1.22 L $H_2/L_{reactor}$/day from MFP waste via an anaerobic contact filter process. Nathoa et al. [17] also obtained a maximum hydrogen productivity value of 0.71 L $H_2/L_{reactor}$ from the sole fermentation of banana peels. This is because fruit cultivation concentrates antimicrobial compounds in the peels to protect fruit from microbial attacks [18]. These compounds negatively affect anaerobic activity during the anaerobic digestion process and shift substrate degradation pathways to volatile fatty acid accumulation, causing digester instability [19]. Moreover, MFPs suffer from the lack of buffering capacity, nitrogen content and the proper micronutrients to efficiently carry out the hydrogen formation process [20]. Therefore, the need to upgrade the hydrogen formation process of MFPs has been emerged to increase the hydrogen produced and enhance the substrate's utilization. One way to do this is through integrated fermentation in which different organic substrates with complementary characteristics are combined to increase the substrate degradation efficiency and improve hydrogen productivity [21]. Substrate integration represents a feasible solution to overcome the limitations of individual substrates via the mitigation of their repressive effects within the fermented media. These include the presence of macro and micronutrients, the carbon to nitrogen (C/N) ratio, alkalinity, the presence of inhibitor compounds, and the organic loads and solid content. This process is also an economically viable solution to the separate fermentation of individual substances [22,23]. Earlier research carried out by Tenca et al. [24] emphasized the limitations of the sole fermentation of fruit and vegetable mixed waste (FVMV) associated with the process's instability. However, integrated fermentation with alkali rich materials such as swine manure promoted higher hydrogen formation efficiency rates. An FVMV to swine manure ratio of 35/65 resulted in maximum hydrogen productivity and an hydrogen content of 3.27 ± 0.51 L H_2/L day and 42 ± 5%, respectively. These values surpassed those obtained in those aforementioned studies that used fruit peels as the exclusive H_2-producing substrate. However, Mussoline et al. [25] demonstrated that using paper mill sludge (PMS) as a supplemental substrate to rice straw yielded performance values that surpassed other biological, chemical and thermal pre-treatment methods. In which, approximately 3.0 million cubic meters of paper mill sludge are annually produced in Egypt and mainly dumped in a desert causing serious environmental problems [12,26]. Therefore, paper mill sludge (PMS) represents an ideal candidate for integrated fermentation with MFPs, particularly because its high $CaCO_3$ levels [27] and low carbon to nitrogen (C/N) ratio make it a good buffering agent that is able to improve the anaerobic productivity of hydrogen and preclude ammonia inhibition [28]. Furthermore, PMS contains microbes already adapted for the biodegradation of lignocellulosic waste residues, which will undoubtedly enhance the fermentation process as well as supply anaerobic bacteria with essential trace metals such as iron, cobalt and nickel during the fermentation process [25]. Han et al. [15,29] used a combination bioprocess to develop hydrogen production from food waste and waste bread. The proposed bioprocess could effectively accelerate the hydrolysis rate, improve raw material utilization and enhance hydrogen yield from organic solid wastes. In addition, Han et al. [30] proved that their proposed method achieved a payback period of 5 years. Therefore, the aim of this study is to investigate the practicability of the proposed integrated fermentation bioprocess of MFPs with PMS at different volumes in order to: (1) investigate the hydrogen potential of the integrated fermentation of MFPs and PMS, (2) explore the synergistic effects that result in an increase in hydrogen production, (3) identify the metabolic pathways of the sole and integrated fermentation of MFPs and PMS, and (4) analyse the energetic and economic outcomes of both processes to evaluate the added value of the various substrate combinations.

2. Materials and methods

2.1. Agro-industrial wastes

Mixed fruit peels (MFPs) and paper mill sludge (PMS) have been selected and tested to identify their hydrogen production via a dry anaerobic digestion process. MFPs from Faragalla Manufacturing Company (Alexandria, Egypt) were harvested daily. The MFPs, which included orange, tangerine, banana, pomegranate and mango in equal weights, were blended and then crushed into small particles using an electrical grinder to avoid the dilution of the waste. The MFPs were preserved at 4 °C to prevent self-biodegradation. The crushed MFPs were sieved using a stainless steel sieve (2.0 mm) before conducting the batch experiments. Paper mill sludge (PMS) was collected from a sink (3-m width and 3-m depth) in the Aldar Albydaa factory (Alexandria, Egypt). The recycled waste paper was blended with water and lime to maintain a paste and then passed through a centrifuge device to remove impurities. It was then bleached and placed into a rolling drying machine at a temperature of 135 °C. The physicochemical characteristics of MFPs and PMS are presented in Table 1.

2.2. Mixed culture bacteria

Anaerobes used as an inoculum were obtained from the sludge thickener chamber of Alexandria city's wastewater treatment plant. The inoculum sludge was further concentrated by allowing it to settle for 24 h; and the supernatant was discarded. Furthermore, the concentrate was filtered through sieve No. 10 (2.0 mm apertures) to eliminate coarse particles. Afterwards, the inoculum was enhanced via incubation under anaerobic conditions for 90 days. The anaerobes were pre-heated at 90 °C for 30 min to inhibit the bioactivity of methane-producing microbes and to harvest spore-forming anaerobes [31]. The mixed liquor suspended solids (MLSS) concentration, mixed liquor volatile suspended solids (MLVSS) concentration and the pH of the adapted

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