Journal of Hazardous Materials 349 (2018) 45–50

Contents lists available at ScienceDirect

Journal of Hazardous Materials

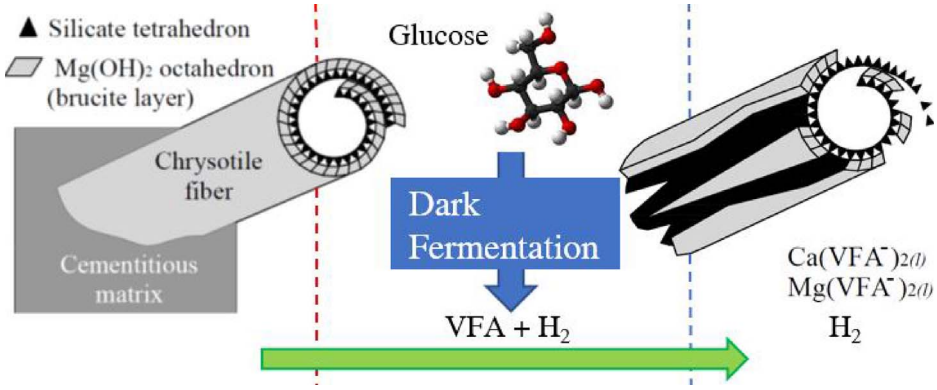
journal homepage: www.elsevier.com/locate/jhazmat

Dark fermentation process as pretreatment for a sustainable denaturation of asbestos containing wastes

Danilo Spasiano

Dipartimento di Ingegneria Civile, Ambientale, Edile, del Territorio e di Chimica, Politecnico di Bari, Via E. Orabona, 4, 70125, Bari, Italy

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Dark fermentation
Glucose
Asbestos
Eternit, hydrogen
Hydrothermal treatment

ABSTRACT

A cement asbestos compound (CAC) sample was detoxified by a treatment train based on a dark fermentation (DF) process followed by a hydrothermal phase, which led to the complete degradation of the chrysotile fibers. During the biological pretreatment, the glucose was converted in biogas rich in H_2 and volatile fatty acids (VFA). The latter caused the dissolution of all the Ca-based compounds and the solubilisation of 50% brucite-like layers of chrysotile fibers contained in the CAC suspended in the bioreactor (5 g/L). XRD analysis of the solids contained in the effluents of the DF process highlighted the disappearance of the chrysotile fiber peaks. However, a complete destruction of all the asbestos fibers is hard to prove and a hydrothermal treatment was carried out to dissolve the "brucite" layers still present in solution. Due to the presence of the VFA produced during the DF, a complete destruction of chrysotile fibers was achieved by a 24 h hydrothermal process performed with a $[H_2SO_4]$/[CAC] ratio 50% lower than that adopted in a previous finding. Consequently, the DF pre-treatment can contribute to lower the H_2SO_4 and the energy consumption of a CAC hydrothermal treatment, due to the production of VFA and H_2.

1. Introduction

The treatment and the management of asbestos containing wastes (ACW) is increasingly attracting the attention of the scientific community and the political world. Indeed, during the last two decades, many processes, aimed to the asbestos denaturation, were proposed as alternative to the ACW landfilling. In particular, vitrification by plasma gun [1,2] or Joule heating [3], thermal [4–6], mechano-chemical [7,8] and chemical [9–12] treatments have been shown to be effective at destroying asbestos fibers by generating non-harmful, and sometime

E-mail address: danilo.spasiano@poliba.it.

https://doi.org/10.1016/j.jhazmat.2018.01.049
Received 7 September 2017; Received in revised form 22 January 2018; Accepted 23 January 2018

reusable, by-products. As a consequence of these new scientific findings, in 2013, the European Parliament not only has encouraged the development of action plans for asbestos removal and management, but also promoted and supported *"research into, and technologies using, eco-compatible alternatives, and to secure procedures, such as the inertisation of waste-containing asbestos, to deactivate active asbestos fibers and convert them into materials that do not pose public health risks"* [13]. The reason why the EU Parliament has undertaken these actions is not only related to the large number of deaths due to asbestos related illness, e.g. the WHO estimated 1.07×10^6 worldwide deaths during the 2004 [14–16], but also to asbestos airborne releases from the damaging of asbestos containing products after natural and made-man disasters. For example, the generation of large volumes of asbestos containing debris, occurred after the 2005 Katrina hurricane, the 2011 Tohoku earthquake, and the terroristic attack to the World Trade Center [17–19].

Unfortunately, the innovative treatments, briefly outlined above, have been adopted only few times at industrial scale because of their high cost, generally related to the large consumption of energy and/or reagents. In fact, the only two plants that can treat ACW are the Inertam and GeoMelt®, which adopt the vitrification treatment by plasma gun and Joule heating respectively [1,20]. In particular, the Inertam plant, opened in 1999 in France, can treat 8×10^3 tons ACW per year and produces, as an end-product, a rocklike material, which is sold as quartz and basalt replacement in the construction industry for 10 €/ton. On the other hand, due to the high process temperature (1600 °C) the minimum cost for the ACW treatment in this plant is 1.0×10^3 €/ton. Consequently, with the aim of reducing the costs related to the energy consumption, it has been recently proposed a thermochemical process, which can treat 5 g of a cement asbestos compound (CAC) suspended in 10 mL solution containing 2.5 g of sulfuric acid (5 N) at 100 °C for 24 h [21]. This process is effective because the chrysotile ($Mg_3Si_2O_5(OH)_4$), the most used asbestos fibrous silicate minerals, when suspended into an acidic solution undergo to a denaturation process consisting in the dissolution of the brucite-like layer ($Mg(OH)_2$) with a consequent release of Mg^{2+} ions (1) [22–24]:

$$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 \rightarrow 3Mg^{2+} + 3SO_4^{2-} + 2SiO_2 + 5H_2O \quad (1)$$

However, CACs, which generally contain only 8–15%$_{w/w}$ of asbestos fibers, are characterized by the presence of calcium compounds, as calcium carbonate ($CaCO_3$), portlandite ($Ca(OH)_2$) and calcium silicates, that compete with asbestos fibers in the reaction with the acids (2) [21]:

$$CaCO_{3(S)} + H_2SO_{4(L)} \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \quad (2)$$

Consequently, a large amount of acids is consumed for the dissolution of the CAC cement matrix. For this reason, a recently published paper suggested to employ the dark fermentation (DF), a biological anaerobic process, of biodegradable substrates as pretreatment for the hydrothermal denaturation of the asbestos fibers contained in the CAC [25]. In particular, the DF of glucose was proven to produce H_2 and VFA (3) [26,27], which can dissolve the cement matrix of 5 g/L fiberglass reinforced composite (4), simulating a CAC, suspended into the solution [25].

$$C_6H_{12}O_{6(L)} + \text{inoculum} \xrightarrow[\text{anaerobic conditions}]{T = 35°C;} aCO_{2(G)} + bH_{2(G)} + cVFA_{(L)} \quad (3)$$

$$Ca^{2+}_{(S)} + 2VFA_{(L)} \rightarrow Ca(VFA^-)_{2(L)} + 2H^+_{(L)} \quad (4)$$

In addition, besides the cement matrix, the VFA could also dissolve the brucite-like layers of chrysotile fibers contained in the CAC (5), thus further minimizing the amount of acid required during the hydrothermal treatment.

$$Mg_3Si_2O_5(OH)_{4\,(s)} + 6VFA_{(L)} \rightarrow 3Mg(VFA^-)_{2(L)} + 2SiO_2 + 5H_2O \quad (5)$$

As a result, the adoption of the DF of biodegradable compounds, as pretreatment of a hydrothermal phase, seems to be a promising solution to reduce the costs of the hydrothermal CAC denaturation because: i) it produces bio-H_2, a renewable source of energy, which could be used to reduce the energy necessary for the hydrothermal process; ii) it produces a large quantity of organic acids, as acetic, butyric, lactic, valeric, and propionic acid, which may reduce the consumption of reagents during the hydrothermal phase; iii) since agro-food wastes could be used as biodegradable compounds during the DF pretreatment, the whole process would be able to simultaneously treat two types of wastes. Furthermore, the effluents of the acid-infused hydrothermal treatment could be further processed, since the VFA produced during the DF pretreatment should still be present in solution. For example, with the aim of both stabilizing the effluents of the whole process and producing CH_4 as another source of energy, an anaerobic digestion (AD) treatment could be carried out. The coupling of DF and AD has been suggested in many studies [28–30] and it has been demonstrated that the net energy produced at the end of these two processes could be higher than 250 kJ/L_{sol}. Moreover, a temperature increase of the DF pretreatment from 35 °C to 55 °C would favor the hydrogen production [31,32] and the dissolution rate of the CAC [25]. However, an increase of the operative temperature during the biological pretreatment would increase the energy requirement for heating and maintenance costs [26,33].

To this purpose, this study is focused on the adoption of the mesophilic DF of glucose, which would simulate a by-product deriving from sugar refinery [34,35], as pretreatment of a hydrothermal denaturation a real CAC sample.

2. Materials and methods

2.1. Materials

HPLC grade acetonitrile was purchased from Carlo Erba. Sulfuric acid (98%), nitric acid (70%), hydrochloric acid (35%), hydrogen peroxide (30%), and anhydrous glucose (99.5%) were purchased from Sigma Aldrich. All reagents and organic solvents were used as received. In all the experiments, distilled water was used as solvent.

The digestate withdrawal from the mesophilic anaerobic digestion (AD) plant of the dairy farm "Davide Colangelo" located in Capaccio (Salerno, Italy) was used for the preparation of DF inoculum. In particular, the total solids (TS), volatile solids (VS) and the pH of the AD sludge were equal to 48.2 g/L, 25.9 g/L and 7.8 respectively. The Mg^{2+} and Ca^{2+} concentration were equal to 302 ppm and 1298 ppm respectively. Moreover, no VFAs were detected.

A company handling hazardous waste provided the Eternit slate sample. In particular, the Eternit sample, was stored, cleaned, and milled with the procedure elsewhere described [21]. Finally, the sample was sieved to get a particle size below 2.0 mm, dried at 105 °C, and characterized by SEM (Fig. 1a and b), EDX (Table S1) and XRD analysis (Fig. 1c). In particular, the EDX mapping of the main elements of the CAC sample, reported in Fig. S3, highlights an accumulation of magnesium on the chrysotile fibers.

With regard to the elemental composition of the CAC sample, EDX analysis revealed a concentration of calcium and magnesium respectively equal to 30%$_{w/w}$ and 3.1%$_{w/w}$. These values were also validated by means of a wet digestion procedure, according to the EPA method 3050 [36]. In agreement with the EDX analysis, the weight percentages of Ca and Mg evaluated with the EPA standard method were 29.9%$_{w/w}$ and 3.0%$_{w/w}$ respectively.

2.2. DF experimental apparatus

The DF tests were carried out with an inoculum obtained after a