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AN INVESTIGATION INTO THE USE OF SODIUM ALGINATE AS A CHELATING LIGAND FOR TREATMENT OF TANNERY GASEOUS WASTE

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ABSTRACT

Gaseous emissions arise from tannery effluent storage chambers that are left untreated. This is a common practice in most Nigerian tanneries which leads to release of toxic gases like hydrogen sulphide. In this study sodium alginate was employed as a polymeric chelating ligand in the desulphurization of biogas produced from the anaerobic digestion of tannery fleshing and tannery waste water. The soaking liquor from the tannery's beam house was used as diluent, anaerobic microbes from cow cud was used as inoculum, and cow-dung was added as co-substrate in the ratio 1:2 of fleshing to cow dung in order to boost methane concentration. The mesophilic temperature ranges of 30 ºC – 38 ºC and pH of 5.5 – 6 for the optimal growth of anaerobes were maintained. The ability of minute concentrations of sodium alginate (0.01% wt/v) introduced from the onset of the anaerobic digestion cycle, to increase methane concentration and decrease hydrogen sulphide concentration was ascertained. Methane concentration increased significantly from 45 %v/v to 70.1 %v/v corresponding to a heating value of $2.3795 \times 10^4 MJ/m^3$ while hydrogen sulphide concentration decreased from 532 ppm to 0 ppm. In addition, retention time was seen to decrease with the inclusion of alginates.

KEYWORDS

Sodium alginate, tannery fleshing, anaerobic digestion, sulphide reduction, methane booster

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INTRODUCTION

Despite its economic viability, the tanning industry suffers environmental shortcomings in terms of hazardous pollutants all of solid, liquid and gaseous states. A detailed overview of the tanning industry reveals the beam house to be a major culprit of the odoriferous pollutants due to the organic load (Thomas, 2018). This characteristic foul odour is due to high sulphide load and putrefaction of fleshing which constitute a major part of the solid waste. These waste are generated after the unhairing process with sodium sulphide and hydrosulphide. Fleshing is a type of animal tissue waste generated during the preparatory leather processing stage in relatively large quantities about 50-60 % (Hafiz *et al*., 2012). They consist mainly of fat, proteins, and residual chemicals such as lime and sulphide used in the unhairing process. When solid waste and waste liquors are left untreated in storage chambers (soak away), they create conditions suitable for anaerobic digestion (biomethanation).

The use of sodium sulphide and sodium hydrosulphide in tannery for unhairing and liming processes, result in sulphide concentrations varying from 10 – 5000 mg/l. This is as a result of remnant chemicals in the processed skin or hide (pelt) during the tannery's unhairing process which goes into the waste stream liquor (Minas *et al*., 2017). Under alkaline conditions, sulphides remain largely in solution. Nevertheless, when pH of the effluent drops below 9.5, hydrogen sulphide gas evolves from the effluent which keeps increasing as the pH drops further. At concentrations of 150 – 750 ppm it can lead to severe health effects and consequently death (Lutsenko and Egorova, 2023).

$$S^{2-} + 2H^+ \rightarrow H_2S$$

The gas characterized by a rotten egg smell causes severe odour problem. Hydrogen sulphide gas has eminent pollution hazards and when in contact with water vapour in raw biogas or in burner applications forms sulfuric acid, which is very corrosive to engine components. Various desulfurizing technologies include the Claus process, the use of carbonaceous based materials as adsorbents, membrane separation, the use of metal oxides, the use of impregnated sorbents and biological desulfurizing methods. Sodium alginate is a polysaccharide sourced from marine algae and bacteria with vast applications. It has a heteropolymeric structure that combines manuronic (M)/guluronic (G) residues and a sequence based on its source. It has found uses in agricultural, biomedical, food, textile and pharmaceutical industries amongst others due to its biocompatibility, zero toxicity, chelating and human degradable attributes (Martínez-Cano *et al*., 2022).

Sodium alginate can be used to produce matrices in the form of hydrogels in order to prevent unfavourable environmental conditions and provide suitability for reuse. Studies have found that the alginate polymers act like a giant chelating ligand (similar to Ethylenediaminetetraacetic (EDTA) (Mohammadi *et al*., 2013), Diaminocyclohexane-N, N-tetra-acetic acid (CDTA 1:2) (Belmont-Sanchez *et al*., 2020), Nitrilotri-acetic acid (NTA) and 5-sulphosalicyclic acid (SSA) (Nwokem *et al*., 2017). Chelating ligands are molecules that can form several bonds with a single metal ion. Most researchers focused on the use of alginates for removal of heavy metals from tannery wastes nevertheless, this study was aimed at reducing sulfide load from the tanning waste stream.

Dublein and Steinhauser (2008) suggested the direct inclusion of sodium alginate in the concentration of 0.01 %wt/v into the digester to reduce sulphide concentration to about 20 ppm. Cheirsilp *et al*. (2017) reported that immobilizing the microalgae Nannochloropsis sp. in alginate beads for use in phytoremediation of industrial effluents yielded significant increase in biomass and lipid production, as well as nitrogen and phosphorus removal and CO_2 mitigation. El-Tayieb *et al*. (2013) reported the use of calcium alginate beads as an efficient treatment route in the removal of heavy metal ions and toxic pollutants from tannery wastewater.

Anaerobic digestion is a microbiological process of decomposition of organic matter, in the absence of oxygen, common to many natural environments and largely applied today to produce biogas in airproof reactor tanks, commonly named digesters. A wide range of microorganisms are involved in the anaerobic process which has two main end products: biogas and digestate. It is considered to be one of the best treatment methods since it converts the biomass to safe products, it requires low energy and inputs and an operates at relatively low hydraulic retention time at high organic loading rates. An anaerobic biodegradation of the proteinous substrate (fleshing) can be estimated using the following stoichiometric relationship:

$$C_aH_bO_cN_d + \frac{4a-b-2c+3d}{4}H_2O \rightarrow \frac{4a-b-2c+3d}{8}CH_4 + \frac{4a-b-2c+3d}{8}CO_2 + dNH_3 \quad ....$$

Where a, b, c and d are constants.

The energy content of biogas in Btu/ft^3 was calculated from the lower heating value (LHV) of methane (Equation 1), since the combustion of methane produces heat energy:

$$LHV_{biogas} = LHV_{CH4} \times F_{CH4} \quad ... (1)$$

Where LHV_{CH4} is 9111 Btu/ft^3 at standard conditions 15^oC and 1 atm, F_{CH4} is the fraction of methane in biogas.

METHODOLOGY

This work considered anaerobic co-digestion process of tannery fleshing and cow dung to produce reduced sulfide gas. The tannery fleshing was sourced from the tannery at Nigerian Institute of Leather and Science Technology, Zaria, Kaduna State, dried and pulverized to 5 mm. The cow dung was collected from an abattoir in Zango, Zaria and sun dried for 5 days. Cow cud was used as an innoculum. Anaerobic conditions were maintained with a total hydraulic retention time of 50 days, at mesophilic temperature and pH ranges. A batch method of loading was undertaken. Constituent gases in the biogas produced were analyzed daily for their concentration using Biogas 5000 gas analyzer and volume of daily gas production was measured using downward water displacement method. The biogas 5000 analyzer provided an accurate and consistent method of monitoring the composition of the biogas produced from each digester. It operates on the principle of infra-red (IR) absorption for the measurement of CH_4, H_2S, O_2 and CO_2 as a percentage composition of the entire gas. The soaking liquor from the beamhouse was used as diluent while sodium alginate of 0.01 % w/v was added to the digester from the onset of the anaerobic digestion.

RESULTS AND DISCUSSION

Initial sulfide concentration in the raw fleshing was measured, which gave 532 ppm. An assay on the properties of the beam house liquid effluents from major beamhouse processes were taken and presented in Table 1. The concentrations of certain parameters above which methanation can be inhibited was reported by Ye *et al*. (2005).

Table 1: Properties of beamhouse liquors

Parameter (mg/l)	**Inhibitory concentrations (Ye, *et al*., 2005)**	**Soaking liquor**	**Liming liquor**	**Deliming liquor**
BOD_5	100	90	40	10
COD	3,000 – 7,000	4,000	8,000	5,000
Chloride	5,000	4,549	1,250	650
Sulphide	100 – 150	25	26	448
Ammonia-N	1.5 – 3.0	1.0	0.2	0.6
Calcium	8,000	1,619	2,024	3,063

The soaking liquor was thus found appropriate as a diluent for biomethanation as it had all its property concentrations below the inhibitory concentrations. Reuse of one of the tannery waste streams is advantageous in waste water treatment and for economic benefits.

Effect of co-substrate blend ratio and addition of sodium alginate at a fixed volume

In order to achieve commercially acceptable biogas from anaerobic digestion of tannery fleshing, a co-substrate- cow dung which is rich in carbon was added to the digesting reactor. Also, sodium alginate of 0.01 %wt/v was included to individual digesters with fleshing and cow dung in different ratios – 1:0, 1:0.5, 1:1, and 1:2. The results of methane and hydrogen sulfide concentration from the co-digestion were reported in Figure 1.0 and 2.0 respectively.

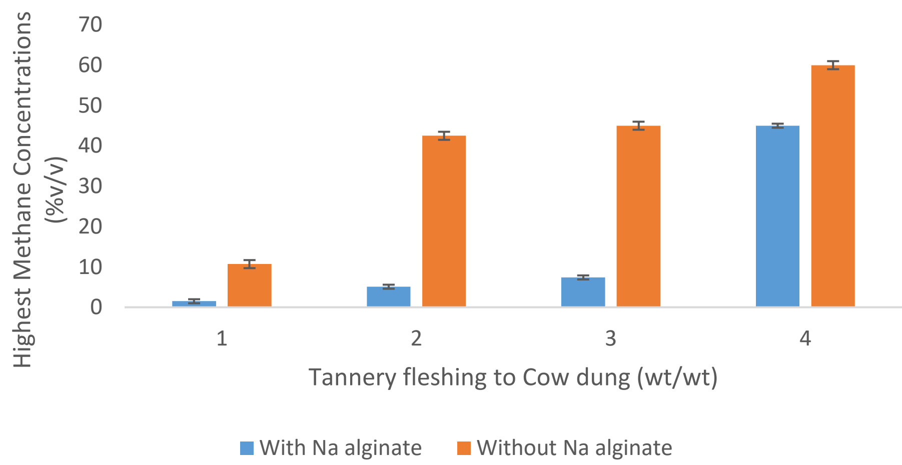

Figure 1.0: Effect of Sodium Alginate on Highest Methane Concentration from Co-substrate Ratios.

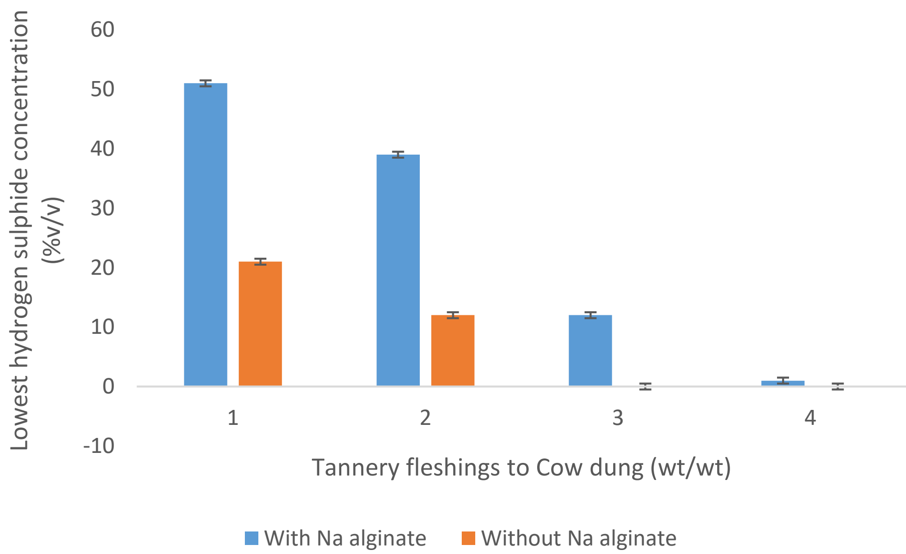

Figure 2.0: Effect of Sodium Alginate on Lowest Methane Concentration from Co-substrate Ratios.

The highest methane concentration of 7.4 %v/v was obtained from the blend of fleshing to cow dung ratio 1:1 without sodium alginate, whereas the same ratio of co-substrate blend with sodium alginate gave highest methane concentration of 45 %v/v which is an approximate increase of six (6). There was an approximate increase of one and half (1.5) times when sodium alginate was added to the blend of fleshing to cow dung ratio 1:2 as compared to when it wasn't added. The blend of fleshing to cow dung ratio of 1:0.5 without sodium alginate had a highest methane concentration of 42.5 %v/v which translates to eight (8) times increase of methane concentration. The control substrate of fleshing only (fleshing to cow dung ratio 1:0) without sodium alginate had a highest methane concentration of 1.5 %v/v without and 10.7 % v/v with sodium alginate. The highest methane concentration of 60 %v/v obtained from fleshing to cow dung ratio of 1:2 with the addition of sodium alginate.

Considering the minute quantity of the alginate added (0.01% wt/v), it is most probable that sodium alginate is acting as a co-factor in promoting the activities of the microbes responsible for the methanation of fleshing and not as an additional carbon source. Preferred techniques for increasing the concentration of methanogens in anaerobic digester sludge include the addition of chelating ligands to the sludge in order to increase the solubility of inorganic nutrients (Kroll, 1952). Marvin (1989) reported that addition of certain chelating ligands like alginates, to anaerobic digestion system results in increased production of methane (varying from 5 to 20%) as well as destruction of solids. This is due to trace metals like Fe, Ca, Mg, S and Co in the substrate solubilized by the addition of chelating ligands thereby increasing their availability to methanogenic bacteria which require them for growth. He found out that iron and sulphur are particularly important for the rapid development of the bacteria. Recently, Mohammed *et al*. (2019) reported a significant increase in total cumulative biogas volume and methane volume upon the inclusion of alginate extracted waste as substrate and co digesting with rice straw. They explained that this was due to enhanced substrate degradation. Also, Fang *et al*. (2021) reported enhanced methane recovery from waste activated sludge by alginate-degrading consortia.

A complete desulphurization of biogas on addition of sodium alginate was brought about by a chemical complexing process. Bio-polyelectrolytes like sodium alginate and chitosan have been reported to chelate metal ions due to large amounts of primary amine groups and carboxylic acid groups in their molecular chain structure (Hassan *et al*. 2017). Here, hydrogen sulphide comes in contact with the metal chelate formed as a result of alginate reacting with metals in the substrate, to bring about the reduction of

Mn^+ to $M^{(n-1)+}$ and the oxidation of H_2S to form elemental sulfur with the release of H^+ ions; thus the concentration of H_2S gas produced within the digesters is reduced. The reaction is further depicted below:

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)}$$

$$H_2S_{(aq)} + M^{x+}Chelant^{y-} \rightarrow S\downarrow + 2H^+ + 2M^{(x-1)}Chelant^{y-}$$

Where "x" denotes the charge of the metal cation

"y" denotes the charge of the chelant anion and

"M" represents the metal ion

From the above, the elemental sulfur released after the chelating process was further solubilized by the alginate for consumption as a trace mineral for the methanogenic bacteria. Thus, evolving a biogas free of hydrogen sulfide.

CONCLUSION

The reuse of the wastewater from the pre-tanning operation – soaking, was observed to be a viable option for tannery effluent treatment. Sodium alginate was useful for enhancing the degradation of tannery solid waste (fleshing) and for desulphurization. More environmentally safe approaches to tackling the management of solid, liquid and gaseous tannery waste should be researched on. Also, encapsulating appropriate methanogenic bacteria that can degrade tannery effluent in alginate beads should be further studied.

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