

Vinasse treatment by coupling of electro-dissolution, hetero-coagulation and anaerobic digestion

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Abstract

The distillery vinasse is the most important liquid effluent of the ethanol production process and it is characterized by a high chemical oxygen demand (COD) and high biochemical oxygen demand (BOD); besides its acid pH and dark brown color. Phenol content in vinasse causes inhibitory effects on anaerobic digestion processes and has an adverse environmental impact. An alternative for treating vinasse from distilleries by using the electro-dissolution of iron and a heterocoagulation stage with $\text{Ca}(\text{OH})_2$ as a pretreatment was evaluated. Removals of 92% in phenols and 52% in chemical oxygen demand (COD) were obtained. Then, the pretreated vinasse was undergone to an anaerobic digestion process. Global removals to around 93% in biochemical oxygen demand (BOD_5), 83% in COD, and over 99% in total phenols were obtained. Finally, an eco-toxicological evaluation using *Daphnia pulex* was carried out, and it was found that the coupling treatment increased the medium lethal concentration (LC_{50}) to around 190%.

Keywords: Vinasse, phenols; electro-dissolution; heterocoagulation; anaerobic process; *Daphnia pulex*.

Tratamiento de vinazas acoplado electrodisolución, heterocoagulación y digestión anaerobia

Resumen

La vinaza es el principal efluente del proceso de producción de etanol y se caracteriza por su alta demanda química de oxígeno y alta demanda biológica de oxígeno; además, un pH ácido y por su color marrón oscuro. El contenido de fenoles en la vinaza ocasiona efectos inhibitorios en los procesos de digestión anaerobia y presenta un impacto ambiental adverso. Se evaluó un tratamiento alternativo de vinazas de destilería empleando como pretratamiento una etapa de electrodisolución de hierro y heterocoagulación con $\text{Ca}(\text{OH})_2$ logrando reducciones del 92% en el contenido de fenoles y 52% en la demanda química de oxígeno (DQO). Posteriormente, la vinaza pre-tratada se sometió a digestión anaerobia alcanzando reducciones globales cercanas al 93% en demanda bioquímica de oxígeno (DBO_5), 83% en DQO y mayores al 99% en el contenido de fenoles. Finalmente, se llevó a cabo una evaluación toxicológica empleando *Daphnia pulex* y se encontró que con el tratamiento acoplado la concentración letal media (LC_{50}) se incrementó cerca de 190%.

Palabras clave: Vinazas; fenoles; electrodisolución; heterocoagulación; biodegradabilidad anaerobia; *Daphnia pulex*.

1. Introduction

Vinasse is the main liquid effluent in ethanol-producing industry which generates between 9 and 14 liters of this effluent for each liter of ethanol produced. This wastewater is characterized by a high chemical oxygen demand (COD) *ca* 80,000–100,000 mg L^{-1} and high biochemical oxygen demand (BOD) *ca* 40,000–50,000 mg L^{-1} ; besides its low pH, strong odor, and dark brown color [1]. This effluent presents a high dissolved organic matter content, as well as a considerable quantity of inorganic salts composed by

chlorides, sulfates, phosphates, calcium, magnesium, and potassium [2]. Vinasse is potentially toxic because of its bio-recalcitrant substance contents, such as phenolic compounds, and pigments like melanoidins, which can inhibit the activity of microorganisms present in water sources [3]. Although, liquid vinasse has been used as a fertilizer to improve soils [4]; it also presents adverse environmental impacts, such as salt-enriching of soil, and nutrient runoffs in rainy seasons.

The presence of phenolic compounds deserves special attention because of their high toxicity. They are known as a

kind of pollutants to be prioritized by USEPA [5]. On the other hand, phenol-compound toxicity has been studied by using anaerobic and aquatic organisms [6, 7].

Several technological processes for treating vinasse have been researched; physicochemical treatments as adsorption, membranes, electrocoagulation, electrodialysis, electro-oxidation, chemical oxidation, bio-concentration, etc., and biological treatments including some combinations [8,9]. Particularly, Dávila et al [10] studied a process of electrocoagulation– electroflotation in the treatment of vinasse and was achieved remove only 37% of the total solids by using aluminum anodes and was not studied the effect over phenols content.

Anaerobic digestion represents a promissory alternative because it is possible to obtain biogas from vinasse [11]; however, it has been found that phenols content leads to inhibitory effects in microorganisms used [12]. For this reason, anaerobic treatments combined with advanced oxidation pre-treatments have been tried to mitigate this inhibitory effect [13, 14].

A combined process consisting in the electro-dissolution of iron and a posterior stage of heterocoagulation on distillery vinasse was recently evaluated [14]. Were obtained reductions in turbidity of about 99%, in color 83%, and in dissolved organic carbon (DOC) 25%, with electrical power consumption below 0.3 kWh m⁻³. However, the performance of this novel process by operating as a pre-treatment of a biological system had not been assessed up to now.

The aim of this study was to research the performance of the coupling between the electro-dissolution-heterocoagulation and the anaerobic biodegradation of vinasse by using the toxicity indicator *Daphnia pulex*.

2. Materials and methods

2.1. Vinasse characteristics

Vinasse samples were taken from the bottom of the mash column in a local distillery located in Cerrito, Valle del Cauca, Colombia. The distillery produces about 300,000 liter/day of ethanol. The samples were collected every two months during consecutive ten months, and the collecting and preserving procedures followed the standards in APHA et al [16]. The physicochemical characteristics of the sample were determined according to standardized methods for analyzing drinking water and wastewater [16], and the total phenol content according to Folin Ciocalteu's method [17].

2.2. Electrodissolution and heterocoagulation (EH)

An arrangement of seven carbon-steel electrodes (ASTM A36) in a monopolar configuration was used during electro-dissolution; the electrode dimensions were 9 cm long, 6 cm wide, and a gap of 5 mm. The electrode assembly had a 324 cm² anodic area and it was immersed into the vinasse using 800 mL of the sample to 60°C; also, it was used magnetic stirring at 240 rpm. The system was galvanostatically polarized with 1.0 mA cm⁻² by a power source GPS-S 3030D, and an electrical charge of 0.278 Ah L⁻¹ was used in all tests.

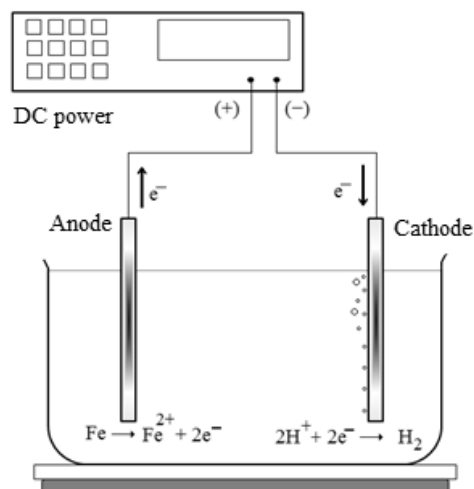


Figure 1. Electro-dissolution cell.

Source: The Authors

Electro-dissolution can be considered as an accelerated-corrosion process that can be achieved by keeping an anodic potential which is higher than the metal equilibrium potential. During this process, the iron cations pass to the vinasse by dissolving sacrificial anodes (Fig. 1). Different to electrocoagulation, the electro-dissolution is carried out keeping pH acid, not only to improve the dissolution kinetic, but also to avoid electrodes passivation. Besides, it is operated to low potentials to avoid the reaction of oxygen evolution in the anode.

A heterocoagulation stage, which is defined as the simultaneous coagulation of several species, was carried out to pH 11.5 using Ca(OH)₂ and 150 ppm of H₂O₂ for oxidizing Fe²⁺ to Fe³⁺ which generates species less solubles. During this stage, a 240 rpm constant stirring was kept for 30 minutes, according to Marriaga [15]. Also, 3 ppm of anionic polyacrylamide (*flopam*) was added; then, the sample was strongly stirred (700 rpm) for 5 seconds. Afterwards, the stirring was stopped and a supernatant was obtained by decantation; then, a second flocculation took place by adding 500 ppm of H₂O₂ and 3 ppm of anionic polyacrylamide (PAM).

2.3. Anaerobic biodegradability

The used anaerobic sludge was obtained from a local effluent treatment plant; these effluents came from an abattoir. Eight 1-liter amber reactors inoculated with 2 g L⁻¹ of volatile suspended solids (VSS) were used. Each reactor was fed with each one of the samples until they reached a concentration in COD of 3.9 gO₂ L⁻¹ of raw vinasse, and 4.5 gO₂ L⁻¹ of pre-treated vinasse by EH. 1 mL of macro and micronutrient solution was provided as well as a 0.5 mL sodium sulphide solution to 10%, and 0.15 mL of yeast extract. The pH for the operation rank between 6.5 and 7.5 units was set up.

A sludge pattern without substrate was developed at the same time to correct methane content caused by the sludge. The anaerobic biodegradability was evaluated for 30 days in terms of the COD daily removal. 3 mL of the solution were

Table 1.
Physicochemical characteristics of vinasse

Parameters	Samples				
	I	II	III	IV	V
pH	4.29	4.70	4.14	4.35	4.10
COD, mg O ₂ L ⁻¹	82,758	89,000	92,800	84,375	76,250
BOD ₅ , mg O ₂ L ⁻¹	18,408	19,442	31,416	36,847	13,514
BOD ₅ /COD	0.22	0.22	0.34	0.33	0.18
Total phenols, mg GA L ⁻¹	257	332	230	320	390
Total hardness, mgCaCO ₃ L ⁻¹	18,750	14,000	34,000	25,000	33,000
Calcium, mg L ⁻¹	6,007	4,805	6,888	4,800	6,408
Conductivity, mS cm ⁻¹	14.31	21.20	17.91	20.90	18.65
VFA, mg HAc L ⁻¹	6,846	5,344	9,368	10,449	7,566
TS, mg L ⁻¹	51,140	68,595	69,954	69,200	65,113
TSS, mg L ⁻¹	1,731	1,438	1,576	1,417	1,588
TDS, mg L ⁻¹	49,409	67,157	68,378	67,783	63,525

Source: The Authors

daily removed from the anaerobic reactor. The pH, the soluble COD, and methane production were measured with the volumetric method by liquid-displacement (NaOH 3%), using an experimental gasometer designed at the laboratory. The effectiveness determination of the applied treatment systems was evaluated by determining effluent toxicity using *Daphnia pulex*.

2.4. Toxicity evaluation with *Daphnia pulex*

Firstly, the rank of sensibility of the indicator organism was established before performing the bio-trial, using K₂Cr₂O₇ as a toxic of reference. The bio-trials set-up was achieved taking a rank of 5 concentrations of each sample three times, in which less than 24-hour-old newborn/neonate were exposed. The pH was kept in a rank from 7.0 to 7.5, and the oxygen dissolved between 6.93 and 8.86 mgO₂ L⁻¹. After 48-hours exposure time, the mean lethal concentration LC₅₀ was calculated, using the statistical software from EPA probit v1.5.

3. Results and discussion

The physicochemical characteristics of the vinasse used in the tests are summarized in Table 1.

The COD and BOD₅ values found indicate that vinasse is an effluent with a high organic-matter content, and susceptible to be degraded only between 18% and 34%. The high total solid content is also relevant, in which more than 97% are found as dissolved solids represented mainly as inorganic salts; besides, it presents high hardness (14,000-34,000 mg L⁻¹) and high electrical conductivity, which diminishes power consumption during the electrodisinfection.

The phenol total content (measured in milligrams of galic acid per liter) fluctuated between 230 and 390 mg GA L⁻¹; this variation could be related to the different varieties and the ripeness degree of the sugar cane used to obtain the cane juice. In this sense, Larrahondo [18] points out that sugar cane juices are made of phenolic compounds, which can be simple or complex as flavonoids that are highly soluble in water. Vinasse composition also depends on the raw material used in the fermentation process, i.e. juice,

molasses, syrup or a mixture of them; it also depends on the type and efficiency of fermentation and distillation stage as well as the varieties and the ripeness time of cane [19].

In general, it was found that the parameter values exceeded the legal discharging limits (Table 1), according to act 1594, 1984 (Ministerio de Agricultura Colombiano) e.g the discharge limit for total phenols is 0.2 mg L⁻¹.

3.1. Electro-dissolution and hetero-coagulation (EH)

In this stage, the flocculant polymer (PAM) accomplished the function of increasing the size of the generated flocs during the hetero-coagulation. Due to that the insoluble aggregates of ferric species formed have negatives superficial charges, the calcium cations are attracted to the surface of these species and modifies the superficial charge of them to positive values. For this reason, the branched anionic polymer used can act as flocculant of this system.

Using the EH pretreatment (Table 2), the oxidizable compounds content, which was measured as COD, was decreased between 29-52%. BOD₅ behavior was variable, increasing and decreasing depending on sample. However, the general trend was the increasing in the proportion of biodegradable organic matter (BOD₅/COD) from 0.18-0.24 to 0.46-0.63. Total solids (TS), total suspended solid (TSS) and total dissolved solids (TDS) were also reduced to 27-65%, 13-76% and 27-64% respectively. Likewise, the total hardness was diminished between 20% and 55%; nevertheless, the dissolved calcium content was maintained or tended to increase due to Ca(OH)₂ addition during hetero-coagulation.

Finally, a slight increasing of content of volatile fatty acids (VFA) was observed, nearly to 18%; this indicates that part of the long-chain organic acids were transformed to shorter-chain ones during the EH pretreatment [20]. The VFA in vinasse is attributable to reactions due to bacterial contamination and are performed during the fermentation. In these reactions are produced organic acids mainly acetic, propionic and butyric acids.

Table 2.
Physicochemical characteristics of pre-treated vinasse

Parameters	Samples				
	I	II	III	IV	V
pH	8.24	7.65	8.41	8.54	7.81
COD, mgO ₂ L ⁻¹	40,569	43,000	53,165	45,652	54,375
BOD ₅ , mgO ₂ L ⁻¹	-----	23,220	25,950	30,704	28,838
BOD ₅ /COD	-----	0.54	0.46	0.63	0.52
Total Phenols, mg GA L ⁻¹	50	60	36	24	30
Total hardness, mgCaCO ₃ L ⁻¹	8,500	10,000	26,400	29,000	26,400
Calcium, mg L ⁻¹	2,403	7,208	5,720	6,800	5,720
Conductivity, mS cm ⁻¹	19.98	19.42	22.50	20.90	21.50
VFA, mg HAc L ⁻¹	9,248	6,846	9,968	10,449	9,487
TS, mg L ⁻¹	18,120	47,185	45,688	50,728	41,825
TSS, mg L ⁻¹	410	838	1,367	1,088	825
TDS, mg L ⁻¹	17,710	46,347	44,321	49,640	41,000

Source: The Authors

The most remarkable result during the pretreatment was the decreasing of total-phenol content, which was between 80% and 92%. These removals are higher than those obtained by Siles et al (40%-65%) [13], and those reported by Martin et al (65%-83%) [14]. Both studies used ozone as oxidizing agent in the pretreatment and, in these cases, the initial phenol concentrations were 450-660 ppm, respectively.

Although the mechanism governing the heterocoagulation can be very complex, it is possible to realize that to pH alkaline, insoluble salts precipitation like phosphates, and calcium and iron carbonates are caused [21, 22]. It is also valid to foresee the simultaneous coagulation of ferric species [23], iron hydroxysalts [24], besides organic matter adsorption caused by the presence of $\text{Ca}(\text{OH})_2$ y $\text{Mg}(\text{OH})_2$ in suspension [25]. Therefore, the phenol-content reduction and COD could be attributed to the adsorption influence on generated insoluble species.

Also, applying hydrogen peroxide during treatment at alkaline pH generates the hydroperoxyl ion (HOO^-). The hydroperoxyl ion converts chromophore groups rich in electrons e.g carbonyl groups with conjugated phenolic, to its counterpart non-chromophore due to that is a strong nucleophile. This can explain the significant reduction of color in the pretreated vinasse.

3.2. EH and anaerobic biodegradability

Based on literature values and references [26, 27], the inoculum characterization showed that the sludge employed as a inoculum complies all requisites and minimum characteristics for the anaerobic treatment with respect to TS, VTS, stability and EMA.

The treatment was evaluated in terms of filtered-COD content reduction. Fig. 2 shows the biodegradability behavior related to COD daily reduction. The degradation process began rapidly, which suggests that the inoculum appropriately adapted with raw and pretreated vinasse. At the beginning, the COD removal rate was higher in raw vinasse; however, from the tenth day of digesting, the COD removing rate in pretreated vinasse was much higher than

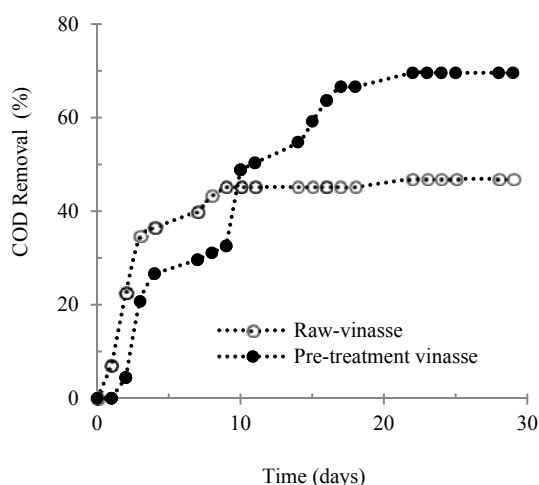


Figure 2. COD daily removal during anaerobic process. Source: The Authors

Table 3. Parameters evaluated during the treatments

Parameter	RV	EHV	EHBV	Removal (%)
pH	4.35	8.54	7.45	NA
COD, $\text{mgO}_2 \text{L}^{-1}$	84,375	45,652	14,159	83.2
$\text{BOD}_5, \text{mgO}_2 \text{L}^{-1}$	36,847	30,704	2,649	92.8
BOD_5/COD	0.33	0.63	0.19	NA
Total phenols, mgGA L^{-1}	320	24	<0.89*	>99

*Detection limit. Source: The Authors

Table 4. Toxicity with *Daphnia pulex*

Sample	LC_{50} (%v/v)		
	RV	EHV	EHBV
1	4.08	5.36	11.63
2	3.73	5.14	11.53
3	4.13	5.05	11.52
4	3.90	5.07	11.42
Average	3.96	5.15	11.53
RV, %	4.0	2.3	0.74

Source: The Authors

the raw vinasse. At the end of treatment, COD removal rates near to 47% for raw vinasse and 70% for pretreated vinasse were obtained. This shows that the raw vinasse is more resistance to degradation than pretreated vinasse, which can be attributed to higher phenol-compound content and to a low BOD_5/COD relationship [28].

Table 3 shows the results of raw-vinasse (RV) physiochemical characterization, the pretreatment vinasse using electro-dissolution and hetero-coagulation processes (EHV), and the vinasse treated through coupling treatments (EHBV).

The most remarkable result was the 99% reduction in total phenols content, whose final concentration was below the detection limit of the used technique. On the other hand, the biodegradable organic matter content, measured as BOD_5 , was reduced nearly 93%, and the oxygen chemical demand was reduce to nearly 83%.

3.3. Toxicity evaluation using *Daphnia pulex*

The sensitivity range of *Daphnia* colony compared to $\text{K}_2\text{Cr}_2\text{O}_7$ was between 0.405 and 0.557 ppm on 20 analyzed samples and a standard deviation of 0.036. The variation coefficient reached an average of 7.49%, lower than the maximum variability value (RV 30%) established by the USEPA. In the tests, the pressure generated was 75% higher than expected. The results of the toxicity tests using *Daphnia pulex* are summarized in Table 4.

The obtained results show that raw vinasse presented the highest toxicity with median lethal concentration (LC_{50}) of 3.96 v/v. By applying the electro-dissolution-hetero-coagulation (EHV), LC_{50} magnitude increased in about 30% in comparison to the results obtained in raw vinasse. This toxicity decrease would be mainly associated to phenol-content reduction.

Coupling electro-dissolution, heterocoagulation and anaerobia digestion (EHBV) LC₅₀ magnitude increased in about 190% in comparison to the results obtained in raw vinasse. This indicates that the coupling treatment effluent presented lower toxicity than raw vinasse.

4. Conclusions

A novel treatment for vinasse was evaluated using as pretreatment a stage of electro-dissolution of iron and hetero-coagulation with Ca(OH)₂ and a posterior biological treatment. During the pretreatment was obtained decreasing of phenol content of 92%, the chemical oxygen demand decreased 52%, and the volatile fatty acids content increased 18%. Afterwards, the pretreated vinasse was subjected to anaerobic digestion and was reached a global diminution close to 93% in BOD₅; 83% in COD and up to 99% in phenol content. In addition, a toxicological evaluation with *Daphnia pulex* was carried out and it was found an increasing of 190% in the median lethal concentration (LC₅₀) after the proposed coupling.

It were found promissory results by using iron electro-dissolution and hetero-coagulation as a pretreatment of anaerobic digestion to remove phenolic compounds and to enhance the degradation of distillery vinasse.

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