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Coagulation–flocculation of anaerobically treated sugarcane stillage

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ABSTRACT

Anaerobic digestion applied to stillage usually results in treatment performances. However, effluents from anaerobic reactors still present a residual polluting load due to the presence of organic recalcitrant compounds. Additional treatment methods, such as coagulation–flocculation, may be utilized to improve the final effluent quality. In this study, we assessed the processes of coagulation and flocculation for sugarcane stillage samples previously submitted to anaerobic digestion, aiming to obtain optimal conditions for the physicochemical treatment. Natural corn starch and ferric chloride were tested as coagulants. While starch was considered as not suitable for the treatment for the tested conditions, ferric chloride assays presented satisfactory results. The investigated parameters included coagulant solution dose, rapid mixing gradient and time, flocculation gradient and time, and sedimentation time. Their adjusted values at which better performances obtained were, respectively, $1.6\,\mathrm{g\,L^{-1}}$, 325 rpm, 10 s, 65 rpm, 20 and 20 min. The best color, turbidity, and chemical oxygen demand removal efficiencies were 95, 97, and 65%, respectively. Stillage pH variation to alkaline conditions did not result in improved removal efficiencies. Although relatively high removal efficiencies of constituents were obtained, the final effluent characteristics did not fit regulations of water reuse in the agriculture through fertigation. However, stillage can definitely become more easily managed if better final effluent quality control parameters are achieved, enabling for example effluents discharge in water bodies.

Keywords: Stillage; Anaerobic digestion; Coagulation–flocculation; Reuse; Fertigation

1. Introduction

The challenges and limitations associated with the water availability worldwide demand the establishment of alternative methods to reduce the pressure over the remaining water sources. In this context, the reuse of wastewaters represents an attractive option, as it also recycles nutrients and organic matter. Stillage, the main effluent resulting from ethanol production, is a potential wastewater for the reuse practice due to its high water and nutrient content, such as potassium, calcium, and magnesium. The reuse of stillage in agriculture is usually known as fertigation.

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Fertigation represents the main process used to recycle stillage in Brazil. Under uncontrolled conditions, the land applications of stillage may be problematic, because its low pH value and high sulfate and organic matter concentrations can compromise the soil structure and the surrounding water bodies, besides reducing the agricultural productivity of the crops [1]. Biological processes, especially anaerobic digestion may be successfully applied to the treatment of high-strength wastewaters, resulting in satisfactory removal efficiencies for the biochemical oxygen demand (BOD) [2]. However, most of the biologically treated effluents show some reuse limitations due to the remaining high color and chemical oxygen demand (COD) values, usually associated with recalcitrant compounds, such as melanoidins, tannins, and humic acids [3–6].

Further improvements on the final quality of effluents from anaerobic reactors may be achieved by combining physicochemical methods, such as adsorption and coagulation–flocculation, or advanced oxidation processes (AOPs), which include ozonation, UV-radiation, and Fenton process, for instance. Considering that the application of AOPs to wastewaters in large scales is usually expensive, the conventional methods, specifically coagulation–flocculation, still represent an attractive alternative to be applied on the removal of remaining pollutants in wastewater streams. Coagulation–flocculation is widely employed in treatment plants to remove colloidal particles and natural organic compounds from water and wastewater, representing a well-established treatment technology. Some studies [3,4,6,7,9,11,14] indicate good performances related to the application of coagulation–flocculation treatment on raw or previously digested stillage, with removal efficiencies as high as 90% for color and turbidity and 65% for COD. Although various inorganic and natural coagulants are usually tested, studies [3,4,8,13,14] have demonstrated ferric chloride ($FeCl_3$) as a better coagulant for stillage treatment, specifically among other common salts, such as aluminum and iron sulfates and aluminum chloride.

Based on the need of reusing wastewaters, the objective of this study was to optimize the processes of rapid mixing, coagulation, flocculation, and sedimentation for sugarcane stillage samples previously treated in an anaerobic reactor. The investigated coagulation parameters included coagulant solution dosage (D_c), rapid mixing gradient (G_{rm}) and time (t_{rm}), flocculation gradient (G_f) and time (t_f), and sedimentation time (t_s). In addition, the suitability of the final effluent for reuse in the agriculture through fertigation was discussed.

2. Materials and methods

2.1. Characteristics of the wastewater

Biologically treated stillage samples were obtained from a bench-scale fixed-film anaerobic reactor operated under acidogenic conditions to produce biohydrogen at the Laboratory of Biological Processes (LPB)—São Carlos School of Engineering—University of São Paulo (EESC/USP). Prior to the coagulation–flocculation assays, the samples were mixed to maintain homogeneous conditions and stored at −10°C in freezers. The stillage samples were diluted (1:10) to carry out the experiments, because no results were known from the combination of these processes for this type of effluent, available volume of effluent from the digester was limited, high volume of samples was required during the experiments and stillage availability depended on the sugarcane season (Table 1).

2.2. Coagulation–flocculation methodology

Coagulation–flocculation tests were carried out using a jar test apparatus model 218/6LDB (Nova Ética Produtos e Equipamentos Científicos Ltda, Vargem Grande Paulista, SP, Brazil), which is composed of six jars, each one with a volumetric capacity of 2L. The experiments were conducted at ambient temperatures (20–25°C) at the Laboratory of Treatment and Reuse of Water and Wastewater (LATARE)—Environmental Studies Center—State University of São Paulo (CEA/UNESP). Natural corn starch solution 0.2% (w/v) and ferric chloride (density of $1.414\,\mathrm{g\,mL^{-1}}$ and $FeCl_3$ content of 39.32% [w/w]) were tested as coagulants. The starch solution was prepared by dissolving 2 g of natural corn starch (Unilever Brasil Industrial Ltda, Garanhuns, PE, Brazil) in 1,000 mL of distilled water. The solution was then heated and slightly mixed for 10 min after the boiling point was achieved. Lastly, the solution was kept standing until ambient temperature was reached. Tables 2 and 3 depict the experimental design.

Table 1
Physicochemical basic characteristics of the biologically-treated stillage samples used in the experiments

Parameters	Anaerobically digested stillage	
	Raw	Dilluted (1:10)
COD ($\mathrm{mg\,L^{-1}}$)	12,100–26,400	1,210–2,640
Color (Pt-Co)	6,800–23,600	680–2,360
Turbidity (NTU)	183–1,250	18.3–125
pH	4.93–7.18	4.93–7.18

Table 2
Experimental conditions for the tests based on the use of natural starch solution as coagulant

Coagulation parameter	Test		
	EA_1	EA_2	EA_3
D_c ($mg\,L^{-1}$)	1.0–6.0[a]	1.0–6.0[a]	20.0–120.0[b]
T_{rm} (s)	10	10	10
G_{rm} (rpm)	500	500	500
T_f (min)	30	30	30
G_f (rpm)	50	50	50
T_s (min)	20	20	20

Intervals: [a]1.0 $mg\,L^{-1}$; [b]20.0 $mg\,L^{-1}$. For example, starch solution concentrations of 1, 2, 3, 4, 5 and 6 $mg\,L^{-1}$ were investigated in EA_1.

Due to significantly unstable results, as discussed later, only three tests were performed with starch solution as the coagulant ($EA_1 - EA_3$). For ferric chloride as the coagulant, nine assays were carried out ($EF_1 - EF_9$), such that a different coagulation parameter was optimized in each: coagulant solution dosage ($EF_1 - EF_3$), sedimentation time (EF_4), flocculation time (EF_5), flocculation gradient (EF_6), rapid mixing time (EF_7), and rapid mixing gradient (EF_8). An optimized parameter was considered when the tested conditions resulted simultaneously in the best removal efficiencies for COD, color, and turbidity. Analyses of variance (ANOVA) were also performed to assess the statistical difference between set of data for each test. In EF_9, we investigated the influence of pH on the coagulation process through the variation of stillage's pH values before coagulant addition. pH adjustments were performed by adding sodium hydroxide (NaOH) at a concentration of 0.1 M.

2.3. Analytical methods

The measurements of COD, color, turbidity, pH, as well other physicochemical parameters, were made in accordance with procedures described in the Standard Methods for the Examination of Water and Wastewater [15]. pH measurements were performed using a pH meter model mPA-210P (MS Tecnopon Equipamentos Especiais Ltda, Piracicaba, SP, Brazil). COD and color were monitored using direct reading spectrophotometers (models DR/2000 and DR/2800, Hach Company, Loveland, CO, USA) and turbidity using a portable turbidimeter model 2100P (Hach Company, Loveland, CO, USA). In addition to COD, color, turbidity, and pH, other physicochemical parameters were included to characterize stillage at the end of the experiment, such as: BOD, total suspended solids (TSS), volatile suspended solids (VSS), fixed suspended solids (FSS), total dissolved solids (TDS), potassium (K), total phosphorus (P_{total}), total nitrogen (N_{total}), sulfate (SO_4^{2-}), alkalinity, and electrical conductivity (EC). It was also investigated the concentrations of chlorine (Cl) and iron (Fe) in the samples so that the interferences in the final effluent due to the addition of ferric chloride could be identified. The results obtained after the complete characterization of the samples were used to analyze the suitability of the final effluent for reuse in the agriculture through fertigation. The data used for comparison were obtained in the Guidelines for the Safe Use of Wastewater, Excreta, and Greywater [16].

3. Results and discussion

3.1. Coagulation–flocculation tests using starch solution

Coagulation–flocculation phenomena were significantly unstable for the assays with starch solution as the coagulant. For the same coagulant solution dosages of 1 and 4 $mg\,L^{-1}$, COD removal efficiencies varied from 0 to 72.8% and from 27.7 to 96.6%, respectively. The same erratic pattern for the removal of organic matter could be observed for the tests using starch solution dosages ranging from 1 to 6 $mg\,L^{-1}$, as shown in Table 4. Only for color removal similar

Table 3
Experimental conditions for the tests based on the use of ferric chloride as coagulant

Coagulation parameter	Test								
	EF_1	EF_2	EF_3	EF_4	EF_5	EF_6	EF_7	EF_8	EF_9
D_c ($g\,L^{-1}$)	1.0–25.0[a]	0.5–3.0[b]	1.0–2.0[c]	1.6	1.6	1.6	1.6	1.6	1.6
[Fe^{3+}] ($g\,L^{-1}$)	0.14–35.46	0.07–0.41	0.14–0.27	0.22	0.22	0.22	0.22	0.22	0.22
T_{rm} (s)	10	10	10	10	10	10	6–14[f]	10	10
G_{rm} (rpm)	200	200	200	200	200	200	200	150–400[g]	325
T_f (min)	30	30	30	30	10–35[d]	20	30	30	20
G_f (rpm)	50	50	50	50	50	25–70[e]	50	50	65
T_s (min)	20	20	20	5–30[d]	20	20	20	20	20

Intervals: [a]5.0 $g\,L^{-1}$; [b]0.5 $g\,L^{-1}$; [c]0.2 $g\,L^{-1}$; [d]5 min; [e]25–35–50–60–65–70 rpm; [f]2 s; [g]150–175–200–225–250–275–325–400 rpm.

Table 4
Comparison between the treatment performances obtained in EA_1 and EA_2

Starch solution dosage ($mg\,L^{-1}$)			1.0	2.0	3.0	4.0	5.0	6.0
Removal efficiency (%)	COD	EA_1	72.8	61.4	68.7	27.7	0	20.5
		EA_2	0	26.4	7.9	96.6	34.1	79.5
	Color	EA_1	30.0	25.0	25.0	30.0	22.5	10.0
		EA_2	46.5	44.4	46.5	43.4	44.4	45.4
	Turbidity	EA_1	0	0	0	13.7	0	0
		EA_2	19.4	21.2	14.7	0	0	10.6

results could be observed, especially in EA_2, where an average treatment efficiency of 45.1% was obtained. However, the removal levels for color and mainly turbidity (Table 4) were not satisfactory, as the purpose of the treatment system included the reuse of stillage. For the assays using coagulant solution dosages in the range of 20–120 $mg\,L^{-1}$, coagulation–flocculation showed poor performances, as the maximum COD and turbidity removals reached 47.1 and 22.9%, respectively. In this case, it was not observed color removal. Particularly regarding to turbidity, some studies indicated that the selection of the best type of starch for coagulation–flocculation depends directly on the raw water turbidity [17]. Thus, the poor turbidity removals observed in this study might be related to the starch selected rather than to other factors, such organic content and pH.

Probably, the low performance of the coagulation process using starch may be associated to the nonionic character of the tested polymer, as the interparticle bridging mechanism was unable to destabilize the colloidal particles present in the stillage samples. The inefficiency of this coagulation mechanism could be particularly related to the application of inadequate mixing to the jars, as insufficient mixing velocities tends to hinder the contact between the polymer chains and the colloidal particles. Better treatment performances could be achieved by activating the starch previously to coagulation–flocculation tests, for instance, by introducing small amounts of ionic or hydrophobic groups into the chains already separated due to the heating [18].

The use of natural coagulants (e.g. starch, chitosan, and tannins) in wastewater treatment plants is environmentally advantageous in comparison with inorganic salts, as they may be easily degraded and consequently do not increase the polluting potential of the treated effluents. High treatment performances may also be observed in these cases, i.e. considering coagulation–flocculation applied to stillage, the use of processed moringa seeds (*Moringa oleifera*) as coagulants resulted in color removals of up to 64% [19]. Other studies based on the use of tannin, chitosan, and also moringa as coagulants presented color and turbidity removals greater than 90%, as well as reductions of 45% in the COD of raw stillage samples [14,20]. Even for the simultaneous use of natural and inorganic coagulants, the amount of salts employed may be significantly reduced as the natural compounds act like flocculant aids [21]. Thus, further investigations using starch as the sole coagulant and/or flocculant aid in the treatment of stillage should be carried out based on the potentialities previously discussed.

3.2. Coagulation–flocculation tests using ferric chloride

As for the ferric chloride as the coagulant, the average removal efficiency values were 81.5, 87.2, and 42.7%, respectively, for color, turbidity, and COD (Table 5). Other values, depicting coagulation performances, are presented in Fig. 1. Coagulation–flocculation optimal conditions are also depicted in Table 5, enabling the establishment of relations between the process parameters and COD, color, and turbidity removal efficiency values. A great effect of the ferric chloride concentrations can be noted on the process performance (Fig. 1(a–c)). Coagulant overdoses result basically in two effects on the effluent characteristics: first, it is observed an electrical stabilization (repolymerization) of the colorant colloidal organic particles, especially melanoidins. In addition, the residual iron in excess contributes to a high-colored effluent [3,8,14]. The best performances were observed for a ferric chloride solution dose of 1.6 $g\,L^{-1}$ (Table 5).

Removal efficiencies stopped increasing after 20 min of sedimentation (Fig. 1(d)). Color and turbidity removal efficiencies were not strongly affected by the variation of flocculation time, while COD removal efficiencies presented its best value for t_f equal to 20 min (Fig. 1(e)). The flocculation gradient also did not result in a significant effect on the removal efficiencies of color and turbidity (Fig. 1(f)), but the value of 65 rpm (Table 5) can be indicated as the best one based on the COD removal efficiency.

Table 5
Removal efficiency ranges for the optimized coagulation parameters

Assay		EF1	EF2	EF3	EF4	EF5	EF6	EF7	EF8	Optimized assay[a]
Coagulation parameter		Dc ($g\,L^{-1}$)	Dc ($g\,L^{-1}$)	Dc ($g\,L^{-1}$)	ts (min)	tf (min)	Gf (rpm)	trm (s)	Grm (rpm)	–
		0–5.0	1.0–2.0	1.6	20	20	65	10	325	
Removal efficiency ranges (%)	COD	12.3–36.9	0–59.5	30.2–40.7	12.9–32.6	1.8–46.0	14.9–43.3	38.4–41.7	32.0–53.3	64.6 ± 2.5
	Color	0–79.0	0–78.4	14.6–95.1	36.1–80.7	65.9–72.0	63.3–78.9	78.8–82.4	64.7–80.9	51.2 ± 3.4
	Turbidity	0–83.7	0–90.3	29.3–96.5	0–85.8	79.2–84.4	67.7–78.2	89.0–94.6	65.0–90.3	70.3 ± 3.6

[a] Additional assay designed with the adjusted parameter values.

The rapid mixing parameters, like the flocculation parameters, do not seem to have a significant effect on the coagulation–flocculation process (Fig. 1(g)). In similar studies [3,4], it was also observed that the coagulation process efficiency and the sedimentation characteristics of the aggregates formed during the processes were not directly influenced by the rapid mixing time.

However, slightly higher performances were obtained for higher rapid mixing gradient values (Fig. 1(h)), being the 325 rpm value reported as the better one (Table 5). Rapid mixing gradient can have a relatively strong effect on the coagulation–flocculation processes, as variations on the mixing intensity affect the settling properties of the flocs and consequently the turbidity removal efficiency [3]. Lower gradients accelerate the settling rates of the flocs, but at the same time, the supernatant quality is deteriorated by leaving floating aggregates.

It should be pointed out that preliminary tests aiming to find the ideal ferric chloride dose must be performed when new batches of stillage are sampled. Different characteristics in its composition result in the need of obtaining correct doses of coagulant. Wastewater quality is one of the main factors that influence optimal conditions of coagulation [3,4,6]. Though stillage from different feedstocks present some basic common characteristics, wide ranges of variations are also common for parameters like COD, color, and solids content. Even for stillage streams generated in the same distillery, qualitative variations are expected, representing one of the main limiting factors to establish global patterns for coagulation–flocculation treatment plants. The type and efficiency of the previous biological treatment also affects the optimal conditions of coagulation.

A performance comparison of ferric chloride– and aluminum sulfate–based coagulation–flocculation treating stillage samples is presented in Table 6. Even though high removal efficiencies are usually verified (average values of 67, 85 and 90% for COD, color and turbidity, respectively), it can be noted significant variations in the coagulant doses, ranging from 1.6 to $20\,g\,L^{-1}$ and from 1.1 to $10.0\,g\,L^{-1}$, respectively,for ferric chloride and aluminum sulfate. Usually, the greater the organic content and the color in wastewater, the greater the coagulant dosage required to destabilize the physicochemical properties of the colloidal particles [4]. However, as discussed earlier, low and high doses will affect negatively the performance of the process.

The treatment performances associated with coagulation–flocculation listed in Table 6 may be considered as high as the ones obtained after the application

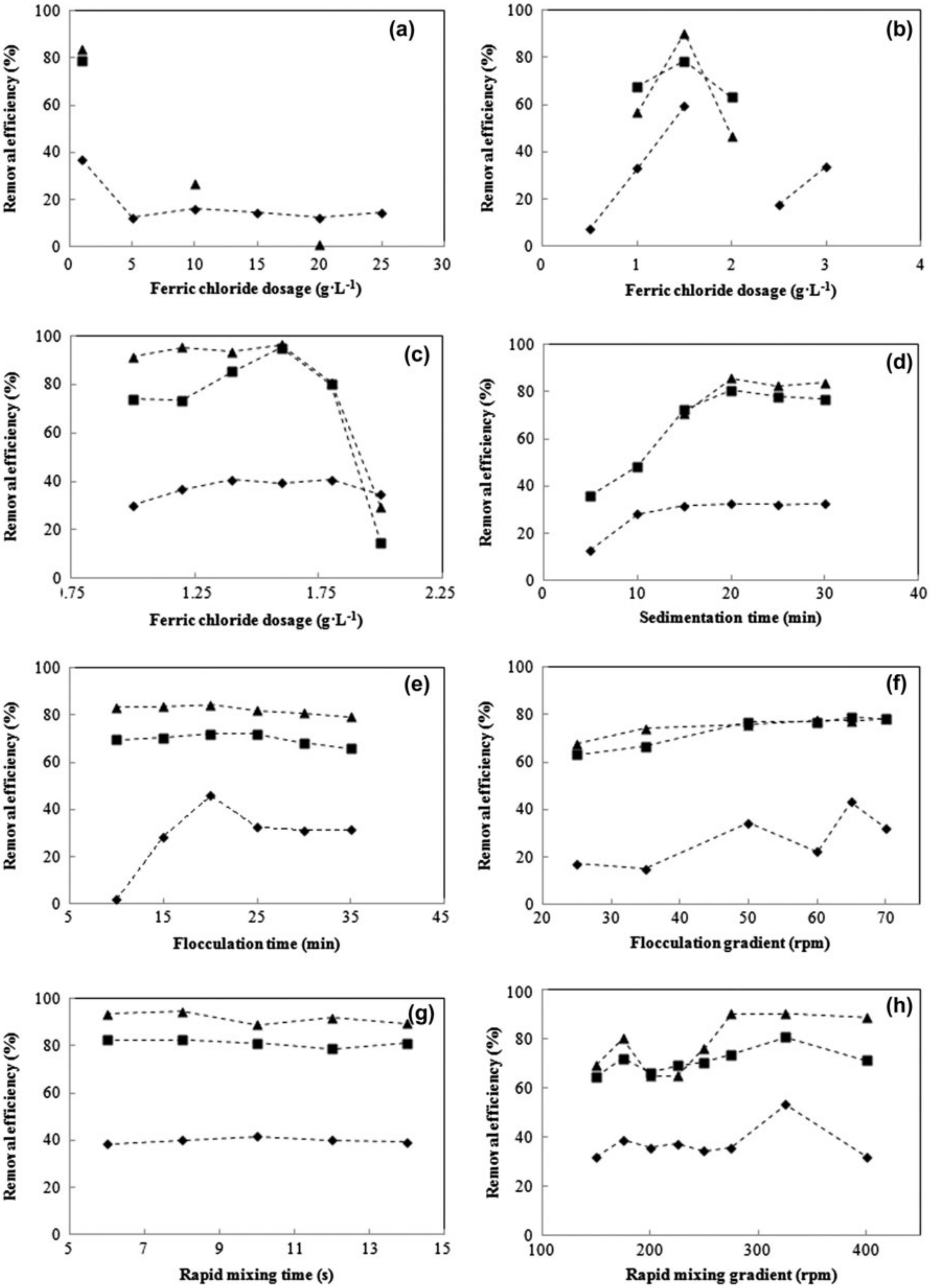

Fig. 1. Variations of the removal efficiencies (COD [◆], color [■] and turbidity [▲]) in the optimization assays: (a) ferric chloride solution dose (EF_1); (b) ferric chloride solution dose (EF_2); (c) ferric chloride solution dose (EF_3); (d) sedimentation time (EF_4); (e) flocculation time (EF_5); (f) flocculation gradient (EF_6); (g) rapid mixing time (EF_7); (h) rapid mixing gradient (EF_8). 253 × 347 mm (300 × 300 DPI).

Table 6
Treatment efficiencies associated to coagulation-flocculation of biologically treated stillage using ferric chloride and aluminum sulphate as coagulants

Reference	Wastewater[a]		Coagulant	Dosage ($g\,L^{-1}$)	Removal efficiency (%)		
	COD ($g\,L^{-1}$)	pH			COD	Color	Turbidity
–	1.2–2.6	4.9–7.2	Ferric chloride	1.6	64.6	51.2	70.3
[3]	1.75–1.80	8.0–8.2	Ferric chloride	6.5	89.0	98.0	nd
			Aluminum sulphate	8.0	66.0	86.0	nd
[4]	4.5	7.4	Ferric chloride	2.4–3.2	80.0	88.0	nd
			Aluminum sulphate	1.1–1.5	50.0	89.0	nd
[6]	8.52	8.4	Ferric chloride	20	84.0	98.4	99.2
[7]	nd	6.0	Ferric chloride	1.7	53.0	60.0	nd
			Aluminum sulphate	2.5–3.3	30.0	70.0	nd
[8]	0.95–1.00	7.9–8.1	Ferric chloride	3.5	85.0	96.0	nd
			Aluminum sulphate	5.0	64.0	89.0	nd
[10]	nd	3.0–4.5	Ferric chloride	3.2	nd	96.5	nd
[12]	8.52	8.4	Ferric chloride	16.0–20.0	65.0	98.4	99.2
[13]	46.7–48.7	nd	Ferric chloride	10.0	88.0	97.7	99.1
			Aluminum sulphate	10.0	82.1	99.3	99.1
[14]	35.1–58.4	3.5–4.5	Ferric chloride	3.0	37.0	62.0	76.0

[a] Characteristics of stillage after biological treatment and before coagulation-flocculation.
nd: Data not reported.

of some advanced treatment processes to stillage. For instance, the association between ultrasound and aerobic degradation resulted in COD removals close to 60% [22,23]. Some examples of AOPs applied to stillage in association with biological and/or physicochemical methods are listed in Table 7. Although some treatment performances reach up to 100% in color and turbidity removal [6,24,26] (Table 7), the values obtained with conventional coagulation–flocculation indicate its suitability to efficiently treat stillage, including the processes based on the use of natural coagulants [20].

The composition of the effluents at their various stages can be seen in Table 8. The COD, color, and turbidity removal efficiencies were 65, 51, and 70%, respectively, for an additional assay that was designed with the adjusted parameter values. An interesting finding refers to the low BOD removal efficiency after coagulation–flocculation ($\sim$18%). Based on the COD/BOD ratio values, obtained for the digested stillage and the final effluent (respectively, 1.3 and 0.56), it is possible to associate a sharper removal of inorganic material (and difficult to remove organic material) in the physicochemical process compared with the biological one, indicating that the application of both processes complement each other in terms of removing a variety of constituents. Higher levels of the chlorine and iron elements were detected in the final effluent, as anticipated, due to the addition of the coagulant. The increase in the concentration of metals in wastewaters and the reduction in pH values are pointed as one of the main disadvantages of coagulation–flocculation [4,5].

The influence of pH on the coagulation–flocculation process was also investigated during the experiments, as it is an important factor to control the reactions and the predominant chemical species in coagulation–flocculation process [3,4,6]. The literature reports optimal ranges in which certain coagulants are recommended to be used, such that for ferric chloride, these values usually vary from 5.0 to 8.5. However, stillage pHs are lower than those reported. Considering the optimal pH range for coagulation with ferric chloride, stillage pH values ranging from 5.4 to 10.6 (Table 9) were investigated in an assay designed with the previously reported optimized parameters. The pH correction did not result in satisfactory treatment performances for the studied conditions, since the removals related to Jar1 (stillage without adjustment of initial pH) were better than in the other jars. The deficiencies in color removal observed in jars 4, 5, and 6 may be related to the repolymerization of the melanoidins (auto-aggregation effect) due to the increase in pH [3].

As ferric ions require lower pH values ($\approx$5.0) to use organic functional groups as ligands, due to the predominance of positively charged ferric hydrolyzed species [5,34,35], the better treatment performances obtained for the slightly acidic conditions may be explained. However, as shown in Table 6, some

Table 7
Recent research studies based on the application of advanced oxidation processes to stillage

Reference	Advance oxidation process (italic)	Removal efficiencies (%)
[6]	Anaerobic digestion + coagulation-flocculation + *eletrochemical oxidation*	COD > 95%; color ≈ 100%; turbidity ≈ 100%
[14]	Coagulation-flocculation + *TiO_2/UV radiation photocatalysis*	COD = 59–68%
[22]	*Ultrasound* + aerobic digestion	COD = 60%
[23]	*Ultrasound + aerobic digestion*	COD = 50–60%
[24]	*Ozonation* + aerobic digestion + *ozonation*	COD = 79%; color ≈ 100%
[25]	Thermal pretreatment + *ozonation* + aerobic digestion	COD = 45.6%
	Thermal pretreatment + *ozonation* + aerobic digestion	COD = 13%
[26]	*Ozonation* + electrocoagulation	COD = 83%; color ≈ 100%
[27]	*TiO_2/UV_{solar} photocatalysis* + activated sludge	COD = 71%; BOD = 86.4%
[28]	*Electrofenton*	COD = 92.6%

Table 8
Removal efficiencies after coagulation-flocculation of anaerobically digested stillage applying optimal conditions

Parameter	Raw stillage[a]	Digested stillage	Coagulated stillage	Removal efficiency (%)
COD (mg L^{-1})	1,500–8,490	1,400	495	64.64
BOD (mg L^{-1})	600–3,900	1,080	890	17.59
COD/BOD	1.96–2.49	1.30	0.56	–
TSS (mg L^{-1})	150–1,500	36.0	28.0	22.22
VSS (mg L^{-1})	120–1,000	28.0	21.0	25.00
FSS (mg L^{-1})	nd	8.0	7.0	12.50
TDS (mg L^{-1})	4,300–5,600[b]	1,000	660	35.93
K (mg L^{-1})	120–783	342.4	364.5	−6.51
P_{total} (mg L^{-1})	1–29	Analysis in course		–
N_{total} (mg L^{-1})	15–161	Analysis in course		–
SO_4^{2-} (mg L^{-1})	60–640	190.0	160.0	15.79
Color (Pt-Co)	1,700–4,700[b]	820	400.0	51.22
Turbidity (NTU)	200–950[b]	37.2	11.0	70.30
Alcalinity (mg $CaCO_3$ L^{-1})	9–137[b]	68.5	146.2	−113.50
EC (dS m^{-1})	6.7–8.7[b]	1.05	1.20	−14.28
Cl (mg L^{-1})	nd	<0.01	0.04	−300.00
Fe (mg L^{-1})	7.9	0.73	16.75	−2,294.52
pH	3.7–5.0	5.61	4.58	–

[a] Reference values for raw stillage in dilution 1:10. References: [2,29–33]22930313233.

[b] Parameters determined experimentally in raw stillage from sugarcane for comparison.

nd: Data not reported; Negative removal efficiency values indicate an increase in final concentrations in relation to the initial ones.

studies indicate average-to-good coagulation performances for both acidic and basic conditions [3,6,10,14], suggesting that the analysis of a broader pH range could also result in high treatment performances for more acidic conditions. Probably, the variations in the patterns of influence expected for pH over coagulation are strongly related to the characteristics of the organic fraction present in the wastewater. Thus, the coagulant dose still represents a dominant factor in relation to the other parameters.

3.3. Suitability of treated stillage for reuse in agriculture

Suitability of stillage land application after anaerobic digestion and coagulation–flocculation process for reuse in the agriculture was investigated, using comparison data from the Guidelines for the Safe Use of Wastewater, Excreta, and Greywater [16]. Based on the concentrations reported in Table 8, pH (4.58), dissolved solids (660 mg L^{-1}), BOD (890 mg L^{-1}), and iron levels (16.75 mg L^{-1}) represented the main limiting factors to use stillage as a crop fertilizer. Excessive

Table 9
Removal efficiencies for coagulation-flocculation with variation of pH

Physicochemical and coagulation parameters		Stillage after coagulation-flocculation					
		Jar1	Jar2	Jar3	Jar4	Jar5	Jar6
pH (after adjustment with NaOH)		5.4[a]	7.0	8.3	8.9	10.0	10.6
pH (after coagulant addition)		4.3	4.8	5.3	5.0	5.0	5.0
Removal efficiency (%)	COD	17.36	9.92	18.18	12.40	3.31	3.31
	Color	68.18	37.88	22.73	–	–	–
	Turbidity	72.46	8.21	22.22	–	–	–

[a] pH of digested stillage without NaOH adjustment.

organic matter ($BOD > 400\,mg\,L^{-1}$) and dissolved solids ($TDS > 500\,mg\,L^{-1}$) levels may obstruct soil pores and stimulate the development of anaerobic populations in the root zone. In addition, organic overloads may reduce dissolved oxygen in groundwater to extremely low levels. As a direct consequence, the capacity of soil in reducing the polluting load of wastewaters is compromised, as well as a greater physical instability is verified, since aerobic microbial activity is negatively affected. For instance, studies in arid regions reported a microbial activity loss of 44.9% in soils fertigated with fresh beet-molasses stillage [36,37].

With respect to pH, recommended values for agricultural reuse of wastewater range from 6.5 to 8.5 [16]. Lower pH values combined with high organic matter contents tend to affect the mobility of metals in solution, so negative environmental effects over water sources may be generated. Low pH values also affect soil microbial activity and long-term wastewater applications result in significant changes in the subsurface buffering system. Considering the effects of iron, the recommended limits in wastewater for irrigation reaches $5\,mg\,L^{-1}$ [16,38]. Excessive iron levels may contribute to soil acidification and also result in essential nutrients losses, such as phosphorus and molybdenum. For free chlorine residual, recommended limits in wastewater for irrigation are inferior to $1\,mg\,L^{-1}$. In this case, the chlorine levels ($0.04\,mg\,L^{-1}$) determined in stillage samples after coagulation–flocculation fit into the established pattern, but severe damage may be verified in sensitive plants at levels as low as $0.05\,mg\,L^{-1}$.

Considering specifically the problems related to the presence of iron in wastewater, its removal from the coagulated stillage could be obtained through the application of processes associated with adsorption phenomena, using materials such as activated carbon, zeolites, and even vegetable wastes [39,40]. In addition, some extra advantages could be observed due to the use of these processes, as it should be possible to remove other toxic metals eventually present in stillage, such as cadmium and lead.

pH adjustment could also result in the removal of iron from stillage, once the ferric ion (Fe^{3+}) is very insoluble at neutral to slightly basic pH [34,41]. Thus, iron could be precipitated to low concentrations by adding alkalizing substances to stillage after coagulation–flocculation. Other more sophisticated processes (e.g. ion exchange and membrane filtration) may also be employed [40], but the selection of the best treatment method, including the previous stages of anaerobic digestion and coagulation–flocculation, depends on a balance that includes practical (technical), economic and environmental aspects.

Though some parameters tended to limit the reuse of the stillage samples in agriculture, it is important to emphasize that the direct application of raw stillage in the soil should amplify the negative environmental impacts discussed earlier, as well as may cause different ones. For instance, yet considering the effects of iron, though its level in coagulated stillage ($16.75\,mg\,L^{-1}$) was higher than the maximum level recommended for irrigation waters ($5\,mg\,L^{-1}$), it is common to obtain iron levels as high or even higher in raw sugarcane stillage samples, such as $60.2\,mg\,L^{-1}$ [28] and $97.5\,mg\,L^{-1}$ [42]. Thus, treating stillage before its agricultural reuse is imperative to obtain a safer recycling of water and nutrients. In addition, the association between coagulation–flocculation and anaerobic processes may also result in energetic gains, based on the energetic potential of biogas due to the presence of methane.

4. Conclusions

The expected increase in ethanol production and consequently in the generation of stillage associated with the high water consumption in agricultural activities demand environmentally safer methods to manage stillage in sugarcane to ethanol industry. Anaerobic digestion followed by coagulation–flocculation may represent an attractive mean to reduce the high polluting load of stillage and also to recycle water and nutrients, since optimized operational conditions are employed in the treatment plants. Thus, considering the results related to coagulation–flocculation obtained in this study some conclusions are described:

(1) For the experimental conditions applied and the characteristics of the wastewater analyzed in this study, natural corn starch could not be used as a coagulant in the anaerobically digested stillage treatment, due to an erratic performance. However, based on the advantages of using natural coagulants in wastewater treatment plants, as well as on some COD removal values obtained in this study (≈97%), additional analysis should be performed to assess other types of starch as coagulants and/or floculant aids in stillage treatment;

(2) Coagulant dose was the main factor of influence on the ferric chloride coagulation–flocculation process performance;

(3) The parameters and their optimized values included: ferric chloride solution dose of $1.6\,\mathrm{g\,L^{-1}}$, rapid mixing gradient of 325 rpm, rapid mixing time of 10 s, flocculation gradient of 65 rpm, flocculation time of 20 min, and sedimentation time of 20 min;

(4) The adjustment of stillage pH values for slightly basic conditions before coagulant addition did not result in satisfactory performances. Better treatment performances were obtained without wastewater pH adjustments, in slightly acidic conditions, which is compatible with the optimal pH range for coagulation with ferric chloride. However, further investigations using a broader pH range should be carried out to provide a better understanding on the influence of pH over the coagulation–flocculation of the stillage sampled in this study;

(5) Based on the wastewater reuse regulations in the agriculture, the method of managing stillage through fertigation yet should not be practiced. Concentration values of BOD, TDS and iron, as well as the low pH of stillage, after coagulation–flocculation still tended to limit its application as a soil fertilizer. It is possible that a more efficient combined (biological and physicochemical) process could enable the safe reuse of the wastewater;

(6) Though the practice of reusing the treated stillage in agriculture was discarded for the studied conditions, the quality of the final effluent can definitely become more easily managed in the sugarcane to ethanol industry if better final effluent quality control parameters are achieved, enabling for example effluents discharge in water bodies.

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References

[1] I.P. Willington, G.G. Marten, Options for handling stillage waste from sugar-based fuel ethanol production, Resour. Conserv. 8 (1982) 111–129.

[2] A.C. Wilkie, K.J. Riedesel, J.M. Owens, Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks, Biomass Bioenergy 19 (2000) 63–102.

[3] G.Z. Liang, Y. Wang, Y. Zhou, H. Liu, Z. Wu, Variables affecting melanoidins removal from molasses wastewater by coagulation/flocculation, Sep. Purif. Technol. 68 (2009) 382–389.

[4] D. Ryan, A. Gadd, J. Kavanagh, M. Zhou, G. Barton, A comparison of coagulant dosing options for the remediation of molasses process water, Sep. Purif. Technol. 58 (2008) 347–352.

[5] D. Ryan, A. Gadd, J. Kavanagh, G.W. Barton, Integrated biorefinery wastewater desing, Chem. Eng. Res. Des. 87 (2009) 1261–1268.

[6] T. Zayas, V. Romero, L. Salgado, M. Meraz, U. Morales, Applicability of coagulation/flocculation and electrochemical processes to the purification of biologically treated vinasse effluent, Sep. Purif. Technol. 57 (2007) 270–276.

[7] M.P. Arturo, B.M. Roberto, I. Kuppusamy, Floculación–coagulación como pos tratamiento del efluente de un reactor anaerobio que trata vinazas tequileras, in: Actas del 25 Congresso Interamericano de Ingenieria Sanitaria y Ambiental, AIDIS, Ciudad de México, 1996, pp. 1–7 [t2].

[8] G.Z. Liang, Y. Wang, Y. Zhou, H. Liu, Z. Wu, Stoichiometric relationship in the coagulation of melanoidins-dominated molasses wastewater, Desalination 250 (2010) 42–48.

[9] V.P. Migo, M. Matsumara, E.J.D. Rosario, H. Kataoka, Decolorization of molasses wastewater using an inorganic flocculant, J. Ferment. Bioeng. 75 (1993) 438–442.

[10] V.P. Migo, E.J.D. Rosario, M. Matsumara, Flocculation of melanoidins induced by inorganic ions, J. Ferment. Bioeng. 83 (1997) 287–291.

[11] R.A. Pandey, S. Malhotra, A. Tankhiwale, S. Pande, P.P. Pathe, S.N. Kaul, Treatment of biologically treated distillery effluent—a case study, Int. J. Environ. Stud. 60 (2003) 263–275.

[12] T. Zayas, V. Romero, M. Meraz, L. Salgado, Tratamiento de agua residual con alta carga orgánica y color provenientes del processo de vinaza, in: Memorias del 5 Congresso Internacional y 11 Nacional de Ciencias Ambientales, UAEM, Oaxtepec Morelos, 2006, pp. 1–7.

[13] H.H.S. Lima, A.F. Bezerra, E.G.S. Rodrigues, E.F. Jaguaribe, R.F. Sena, Tratamento físico químico da vinhaça com uso de carvão ativado do bagaço da cana de açúcar, In: Anais do Encontro Nacional de Educação, Ciência e Tecnologia, UEPB, Campina Grande, 2012.

[14] R.P. Souza, Redução da toxicidade da vinhaça: tratamento combinado coagulação/floculação/fotocatálise, M.Sc. diss., State University of Maringá, Maringá, Brazil, 2010.

[15] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, APHA, Washington DC, 2005.

[16] WHO, Guidelines for the Safe use of Wastewater, Excreta and Greywater, WHO, Geneva, 2006.

[17] J.R. Campos, M.B.S. Vieira, L.H. Villela, Comparação da eficiência de amido de diversas fontes naturais quando empregado como auxiliar de floculação de águas para abastecimento, Revista DAE 144 (1984) 144–149.

[18] G.X. Xing, S.F. Zhang, B.Z. Ju, J.Z. Yang, Recent advances in modified starch as flocculant, in: The Proceedings of the Third International Conference on Functional Molecules, Dalian University of Technology, Dalian, 2005, pp. 13–18.

[19] R.K. Prasad, Color removal from distillery spent wash through coagulation using *Moringa oleifera* seeds: Use of optimum response surface methodology, J. Hazardous Mater. 165 (2009) 804–811.

[20] F. Girardi, Tratamento de vinhaça utilizando coagulantes naturais, M.Sc. diss., State University of Maringá, Maringá, Brazil, 2009.

[21] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, IWA Publishing, London, 2006.

[22] P.C. Sangave, A.B. Pandit, Ultrasound pre-treatment for enhanced biodegradability of the distillery wastewater, Ultrason. Sonochem. 11 (2004) 197–203.

[23] P.C. Sangave, A.B. Pandit, Ultrasound and enzyme assisted biodegradation of distillery wastewater, J. Environ. Manage. 80 (2006) 36–46.

[24] P.C. Sangave, P.R. Gogate, A.B. Pandit, Combination of ozonation with conventional aerobic oxidation for distillery wastewater treatment, Chemosphere 68 (2007) 32–41.

[25] P.C. Sangave, P.R. Gogate, A.B. Pandit, Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater, Chemosphere 68 (2007) 42–50.

[26] P. Asaithambi, M. Susree, R. Saravanathamizhan, M. Matheswaran, Ozone assisted electrocoagulation for the treatment of distillery effluent, Desalination 297 (2012) 1–7.

[27] J.S. Carrocci, R.Y. Mori, O.L.C. Guimarães, R.F.S. Salazar, M. F. Oliveira, A.L.C. Peixoto, H.J. Izário Filho, Application of heterogeneous catalysis with TiO_2 photo irradiated by sunlight and latter activated sludge system for the reduction of vinasse organic load, Engineering 4 (2012) 746–760.

[28] Y. Yavuz, EC and EF processes for the treatment of alcohol distillery wastewater, Sep. Purif. Technol. 53 (2007) 135–140.

[29] S.R. Bianchi, Avaliação química de solos tratados com vinhaça e cultivados com alfafa, M.Sc. diss., Federal University of São Carlos, São Carlos, Brazil, 2008.

[30] W.J.B.M. Driessen, M.H. Tielbaard, T.L.F.M. Vereijken, Experience on anaerobic treatment of distillery effluent with the UASB process, Water Sci. Technol. 30 (1994) 193–201.

[31] S.K. Goyal, R. Seth, B.K. Handa, Diphasic fixed-film biomethanation of distillery spentwash, Bioresource Technol. 56 (1996) 239–244.

[32] S. Mohana, B.K. Acharya, D. Madamwar, Distillery spent wash: treatment technologies and potential applications, J. Hazard. Mater. 163 (2009) 12–25.

[33] S.M. Prada, M. Guekezian, M.E.V. Suárez-Iha, Metodologia analítica para a determinação de sulfato em vinhoto, Quim. Nova 21 (1998) 249–252.

[34] H.W. Ching, T.S. Tanaka, M. Elimelech, Dynamics of coagulation of kaolin particles with ferric chloride, Water Res. 28 (1994) 559–569.

[35] M. Kang, T. Kamei, Y. Magaram, Comparing polyaluminum chloride and ferric chloride for antimony removal, Water Res. 37 (2003) 4171–4179.

[36] M. Tejada, J.L. Gonzalez, Effects on two beet vinasse forms on soil physical properties and soil loss, Catena 68 (2006) 41–50.

[37] M. Tejada, J.L. Moreno, M.T. Hernandez, C. Garcia, Application of two beet vinasse forms in soil restoration: Effects on soil properties in an arid environment in southern Spain, Agr. Ecosyst. Environ. 119 (2007) 289–298.

[38] USEPA, 2004 Guidelines for water reuse: EPA 625/R-04/108, USEPA, Cincinnati, 2004.

[39] G. Anusha, Removal of iron from wastewater using bael fruit shell as adsorbent, in: Proceedings of the Second International Conference on Environmental Science and Technology, IACSIT Press [IPCBEE vol. 6], Singapore, 2011, pp. 258–260 [v2].

[40] F. Fu, Q. Wang, Removal of heavy metals ions from wastewaters: a review, J. Environ. Manage. 92 (2011) 407–418.

[41] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid. Interf. 100–102 (2003) 475–502.

[42] A.P. Mariano, S.H.R. Crivelaro, D.F. Angelis, D.M. Bonotto, The use of vinasse as an amendment to ex-situ bioremediation of soil and groundwater contaminated with diesel oil, Braz. Arch. Biol. Technol. 52 (2009) 1043–1055.