Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21743

101 (2018) 77–85
January

Treatment of beef cattle feedlot wastewater by electrocoagulation technology

Erick Butler[a,*], Robert E. DeOtte[a], Catherine F.M. Clewett[a], Oliver Mulamba[a], Noel Spaar[a], Yung-Tse Hung[b]

[a]*School of Engineering, Computer Science, and Mathematics, West Texas A&M University, Canyon, TX 79016, USA, emails: erick.ben.butler@gmail.com (E. Butler), rdeotte@wtamu.edu (R.E. DeOtte), cclewett@wtamu.edu (C.F.M. Clewett), omulamba@wtamu.edu (O. Mulamba), noelspaarlives@gmail.com (N. Spaar)*
[b]*Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, OH 44115, USA, email: yungtsehung@yahoo.com*

Received 3 August 2017; Accepted 25 November 2017

ABSTRACT

Regulatory requirements and waste management system operating practices continue to be developed to address environmental concerns regarding cattle feedlots. Cattle feedlot runoff is documented to contain substantial concentrations of salts, nutrients, pathogens, and organic matter, which all present potential pollution problems. This study focused on the efficiency of treating feedlot wastewater using an electrocoagulation process using aluminum electrodes to neutralize particles within the wastewater. The results demonstrated that an efficient removal of total phosphorus (0.58%–100%) and total organic carbon (7.97%–100%) within 30 min electrolysis time from commercial beef cattle feedyard wastewater. Factors such as the initial pH (4.0, 7.0, and 10.0), current density (2.6, 5.4, and 8.0 mA/cm^2), water: wastewater dilution ratio (2:1, 1:2, and raw), and electrolysis time (0–30 min) were observed to have an effect on the efficiency of treatment. Nuclear magnetic resonance (NMR) spectroscopy was used to assess the phosphate molecules formed based on the mentioned factors. The observed patterns assist in setting up and tailoring for specific removal treatments. The findings from this study are vital for the development of methods to generate phosphorus forms capable of being extracted for new products.

Keywords: Concentrated animal feeding operations; Wastewater treatment; Electrocoagulation; Nuclear magnetic resonance spectroscopy; Total organic carbon; Total phosphorus

1. Introduction

The last several decades have ushered in research, waste management operations and regulations addressing the environmental effects of cattle feedlots. Prevention of pollution to water has necessitated a proactive approach establishing efficient methods to control the runoff from rain and snow, maintain feedlot surfaces, handle solid manure, and operating wastewater treatment facilities. Cattle feedlot runoff is documented to contain substantial concentrations of salts, nutrients, pathogens, and organic matter (oxygen demanding) [1,2]. Wastewater generated from beef cattle concentrated animal feeding operations (CAFOs) consists primarily of runoff from rain and snow events. Table 1 summarizes typical characteristics of beef cattle feedlot runoff. This wastewater is usually collected, diverted, or treated to avoid ponding. The wastewater collection system has two parts—settling basins and runoff holding ponds (retention ponds). Settling basins are channels or boxes made from earth or concrete that separate liquids from solids where liquids remain at the top and solids settle to the bottom. This is accomplished by the use of risers or dams within the basins. Liquids from the settling basins move into the retention ponds where irrigation systems dewater wastewater from

---

* Corresponding author.

1944-3994/1944-3986

Table 1
Average physical characteristics of beef cattle feedlot runoff

Parameter	Great Plains [4]	Southern Alberta [5]	North Dakota [6]	Iowa [7]
TDS (mg/L)	NR	1,331	NR	NR
TS (mg/L)	11,231	NR	1,002	14,900
COD (mg/L)	7,853	NR	NR	NR
TN (mg/L)	583	82.2	86.6	483
TP (mg/L)	121	33.3	65.4	170
K^+ (mg/L)	1,020	495	488	NR
Na^+ (mg/L)	443	252	NR	NR
Ca^{2+} (mg/L)	374	84	NR	NR
Mg^{2+} (mg/L)	131	79.1	NR	NR
Cl^- (mg/L)	822	559	NR	NR
EC (mmhos/cm)	6	4	3	NR

NR = Author(s) did not report a value.

the ponds. In some cases such as in semi-arid regions the wastewater evaporates [3].

While the runoff does contain rain and snow water, it still consists of a high concentration of solids and nutrients [8,9]. For example, suspended particulate matter tends to clog irrigation systems such as nozzles and pumps. Other constituents include nitrogen species which are converted to ammonia and then volatilized into the atmosphere or denitrified, potassium, phosphorus, or salinity [10]. Several treatment methods such as physicochemical (adsorption, ion-exchange, chemical precipitation) and biological methods (anaerobic) can be employed for the removal of these constituents [11]. But these methods can generate high costs and may require additional treatment to remove by-products formed from using these methods [12].

However, electrocoagulation (EC) is another treatment method that would be a viable alternative to removing these constituents [13–17]. This treatment method is capable of removing wastes in a short amount of time [18] which can effectively reduce the treatment costs. EC is also a viable treatment option because it is easy to operate and requires little maintenance. It also produces very little sludge and does not require handling of chemical waste [19]. EC has been successful in treating various wastewaters such as metal plating [20], baker's yeast [21], paper industry [22], olive mill [23], and municipal wastewater [24].

1.1. Theory behind electrocoagulation

EC is an electrochemical process that uses polymeric hydroxide metal complexes [25] to neutralize particles within the wastewater [19]. These neutralized particles agglomerate into larger constituents known as flocs which float to the top of the reactor and are skimmed.

An EC reactor consists of metal electrodes commonly made from either aluminum (Al) or iron (Fe). These electrodes are connected to a power supply on both the anode and cathode sides. Several chemical reactions occur as electricity passes through the reactor. On the anode side, the electrode is oxidized, while on the cathode side water is disassociated into hydrogen gas (H_2) and hydroxyl ions (OH^-). The hydrogen gas floats the neutralized particles to the top of the reactor surface, while the hydroxyl ions react within the oxide ions to form the hydroxide metal complexes [25]. The success of EC relies heavily on the factors such as the current density, spacing between electrodes, number of electrodes, electrolysis time, pH, and electrical conductivity [26]. A summary of the chemical reactions that occur in EC is shown below [25]:

Chemical reactions at the anode:

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3e^- \tag{1}$$

Chemical reactions at the cathode:

$$2\mathrm{H_2O} + 2e^- \rightarrow \mathrm{H_2} + 2\mathrm{OH}^- \tag{2}$$

Alkaline reactions:

$$\mathrm{Al}^{3+} + 3\mathrm{OH}^- \rightarrow \mathrm{Al(OH)_3} \tag{3}$$

Acidic reactions:

$$\mathrm{Al}^{3+} + 3\mathrm{H_2O} \rightarrow \mathrm{Al(OH)_3} + 3\mathrm{H}^+ \tag{4}$$

It is important to emphasize that the aluminum hydroxide complexes (depicted as $Al(OH)_3$ in Eqs. (3) and (4) vary chemically based on the pH. At very low pH values (less than 2), aluminum hydroxide complexes do not precipitate [27]. When the pH value reaches 4–5, monomeric complexes such as $Al(OH)^{2+}$, $Al(OH)_2^{+}$, and $Al(OH)_3$ are formed. As the pH increases, dimeric, trimeric, and polymeric complexes ($Al_2(OH)_2^{4+}$ $Al_3(OH)_4^{5+}$, $Al_6(OH)_{15}$ $^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$) can form. Any pH values greater than 9 generate $Al(OH)_4^-$ [28–29].

In the past, the use of EC to treat CAFO wastewater has been limited. Thapa et al. [30] studied an EC reactor for 30 min by varying the voltage (5, 10, and 15 V) and the electrode configuration (aluminum, iron, and hybrid) to treat nutrient-loaded runoff from feedlot wastewater. The reactor was capable of removing total phosphorus (TP) (100%), chemical oxygen demand (COD) (50%–75%), and total nitrogen (TN) (25%–60%) [30]. Yetilmezsoy et al. [27] integrated EC to polish wastewater treated by an upflow anaerobic sludge blanket (UASB). The authors varied electrolyte concentration, pH, and current density to treat poultry manure wastewater for color and COD. The authors found that an increase in current density increases the removal of color, while a decrease in pH decreases the treatment efficiency [27]. Finally, Şengil and Özacar [31] varied the pH, current density, and salt concentration to treat dairy wastewater using mild steel electrodes. The authors found that at a pH between 6 and 7, the reactor was capable of removing COD and oil–grease concentration at high efficiencies—98% COD and 99% oil–grease [31]. Aitbara et al. [32] used EC to treat dairy wastewater in Algeria. The reactor removed turbidity (98%), COD (90%), BOD_5 and grease (97%), and TP (70%) [32]. Bensadok et al. [33] treated dairy effluent using EC to treat COD (80%), phosphate (59%), and turbidity (96%). As shown, authors have used EC to treat wastewater from the dairy and poultry industries. However, there is very little research completed to evaluate how effective EC is in treating wastewater from beef cattle feedlots.

1.2. Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is a noninvasive technique able to determine the structure and chemical moieties of phosphorus in both solution and solid phase. It is commonly used as an analytical technique for solution phase mixtures and well able to determine the distribution of dissolved and particulate P species in river waters [34], soils, composts, and sludges [35]. Solid-state ^{31}P NMR allows analysis of samples with minimal preparation and very small sample size. In solution phase NMR, resolution is quite good, but quantification is difficult and sample preparation can be quite complex. For solid-state analysis, sample quantification of TP is not difficult, and with spectral deconvolution, the lack of resolution can be alleviated [36].

Therefore, the purpose of this study is twofold—(1) determine the parameters necessary to remove total organic carbon (TOC) and TP using a batch EC at laboratory scale; (2) determine the amount of phosphorus captured from EC sludge using ^{31}P NMR.

2. Methods

2.1. Reactor dimensions

The laboratory scale EC reactor system (Fig. 1) consists of two sets of four bipolar aluminum electrodes with approximate dimensions of 6.25″ × 4.5″ (15.88 cm × 11.43 cm) connected at the anode and cathode side of a direct current (DC) power supply (Mastech Variable Regulated DC Power Supply 0–30 V, 0–20 A). Within the vessel, the electrodes alternate between anode and cathode with spacing between 1″ (2.54 cm). The electrodes are placed in a 6 qt (5.67 L) reactor vessel (approximate dimensions: 5/8″ L × 8 1/4″ W × 4 7/8″ H, 34.6 cm L × 21.0 cm W × 12.4 cm H) with two schedule 40 PVC garden hose adaptors (dimensions: ¾″ × 1/2 ″) and are connected to a schedule 40 PVC ball valve and ½″ garden hose end caps. This setup is situated to minimize the presence of floated material carried by hydrogen gas bubbles in the collected sample. The experiment was outside of a fume hood.

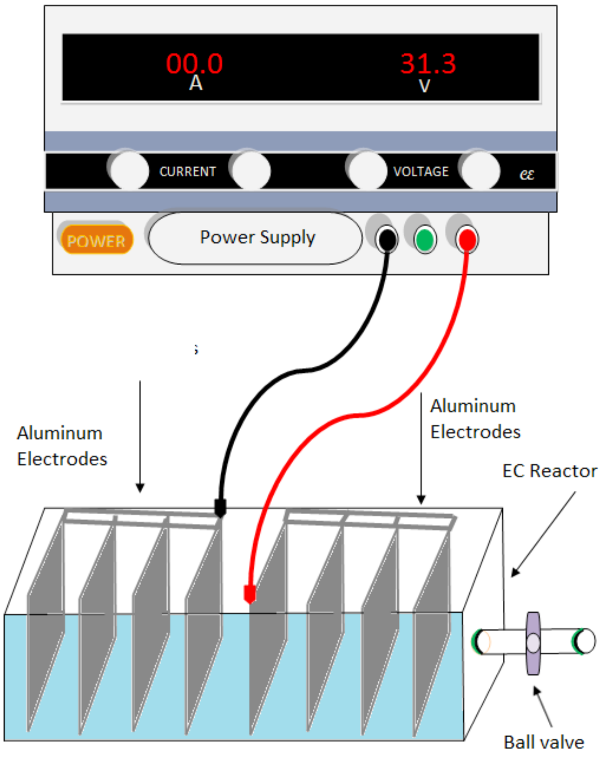

Fig. 1. Setup of laboratory scale EC reactor.

2.2. Wastewater collection and run procedures

Wastewater was collected from feedyard C (approximately 20 miles northeast of Hereford) on four different dates in a 5-gal (18.9 L) bucket during each visit. At the feedyard, the researcher waded in the pond with rubber boots with two buckets. One bucket was used for collection for the pond and another was used as a reservoir. During sampling, the mouth of the bucket was pointed upstream to avoid extra sediment in the sample and keep the bucket from touching the bottom of the pond. Table 2 lists the weather conditions during each visit to the feedyard. Please note that the conditions include the high, low, 3-h average between nine and noon, a 7-d precipitation total before collection, and the average highs and lows during that same time frame. Table 3 includes the raw wastewater characteristics. This table includes TP, total dissolved solids (TDS), total suspended solids (TSS), and TOC. These characteristics are the average initial concentrations for each run prior to treatment. The parameter matrix is displayed in Fig. 2.

The wastewater was brought back to the laboratory where it was used almost daily to avoid major decomposition of constituents. To design the run protocol, a full factorial design (3^3) was created, varying the wastewater concentration by volume using the following dilution ratios expressed as the volume of wastewater to the volume of dilution water (no dilution, 2:1, 1:2) to simulate potential conditions of dilution found within a retention pond, initial pH (4.0 ± 0.02, 7.0 ± 0.02, and 10.0 ± 0.02) adjusted by sodium hydroxide (NaOH) and hydrochloric acid (HCl), and current density (2.6, 5.4, and 8.0 mA/cm^2). 4 L of wastewater were used for each run.

2.3. Data analysis

The pH was measured using a benchtop pH meter (Sper Scientific, (Scottsdale, AZ), 860031), TP (Standard Methods 4500DP-Persulfate Digestion and Vanadomolybdophosphoric Acid Colorimetric method) (APHA et al. [37]) by a Hach

Table 2
Average raw wastewater characteristics of water collected from feedyard C

Parameter	Concentration
TP (μg/L)	2,222
TSS (mg/L)	1,033
TDS (mg/L)	6,886
TOC (mg/L)	1,129

Table 3
Recorded weather data from the nearest NOAA weather station

Station					KHRX (Hereford Municipal)	
Date	High (°F)	Low (°F)	3-h Average (nine to noon, (°F))	7-d Total precipitation before collection (in)	7-d Average high before collection (°F)	7-d Average low before collection (°F)
25-Aug	85 (29.4°C)	56 (13.3°C)	69.9 (21.1°C)	0.08	88.4 (31.3°C)	61.9 (16.6°C)
7-Sep	86 (30°C)	68 (20°C)	72.5 (22.5°C)	1.88	83.3 (28.5°C)	65.1 (18.4°C)
19-Sep	91 (32.8°C)	52 (11.1°C)	73 (22.8°C)	0.25	81.3 (27.4°C)	60.3 (15.7°C)
10-Oct	87 (30.6°C)	57 (13.9°C)	68.1 (20.1°C)	0	78.7 (25.9°C)	46.4 (8°C)

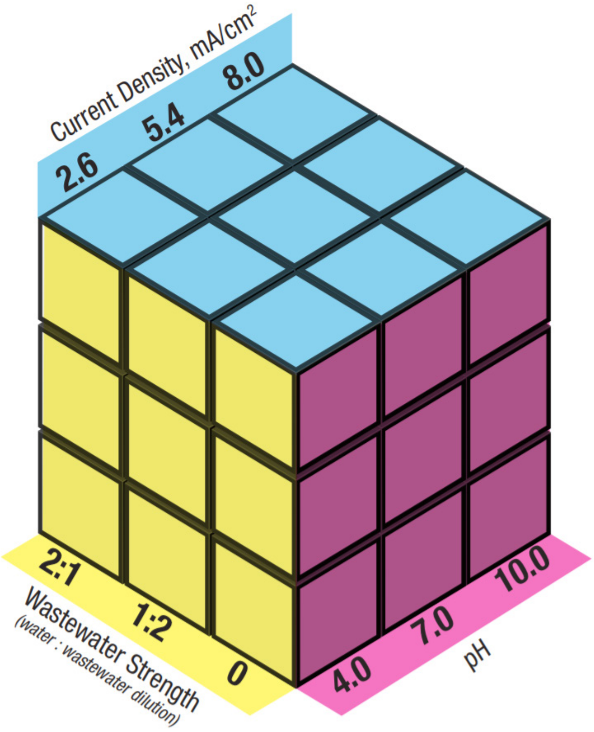

Fig. 2. Graphical representation of parameter matrix.

DR6000 UV–Vis Spectrophotometer with RFID Technology at 470 ± 1 nm wavelength, and the TOC by a TOC analyzer (Shimadzu (Kyoto, Japan) TOC-LCPH, ASI-L 40 mL, SSM-5000A). The total solids and TSS were measured using standard methods (Standard Methods 2540B – Total Solids Dried at 103°C–105°C, Standard Methods 2540D- total solids dried at 103°C–105°C) [37]. Data was collected for each run prior to the run and also after 5, 10, 20, and 30 min of treatment. Determination of TOC and TP removal was done by running the sample through instrumentation three times and averaged. The results for TP and TOC removal are reported in this study. Eqs. (5) and (6) summarize the treatment efficiency of TOC and TP:

$$\text{TOC removal}(\%) = \left(\frac{\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}}}{\text{TOC}_{\text{initial}}}\right) \times 100 \quad (5)$$

$$\text{Total phosphorus removal}(\text{TP},\%) = \left(\frac{\text{TP}_{\text{initial}} - \text{TP}_{\text{final}}}{\text{TP}_{\text{initial}}}\right) \times 100 \quad (6)$$

2.4. NMR analysis

Room temperature, solid-state NMR measurements were taken on a Avance III HD spectrometer (Bruker Biospin, Billerica, MA) using a double resonance (MAS) probe and operating at a ^{31}P NMR frequency of 161.97 MHz. Dried samples were weighed into 4 mm zirconium rotors and capped with Kel-F caps. The samples were spun at a rate of 5.0 kHz. Direct spectra were acquired using a 4 µs pulse, 4,096 data points, 512 signal averages, and a recycle delay of 20 s. The recycle delay was chosen to ensure full relaxation and maximum signal. Spectra were line broadened by 50 Hz and chemical shifts were measured relative to an $NH_4H_2PO_4$ secondary external standard. Quantitative data was calculated for both the standard and the pH dependent samples by integrating the signal from –150 to 100 ppm using the automated baseline correction of the TopSpin 3.5 pl 5 software (Bruker Biospin, Billerica, MA).

3. Results and discussion

Because of the variation in collection dates, the raw data were normalized.

3.1. Total phosphorus removal

The general understanding throughout literature is that EC removes phosphorus through polymerization. Following the formation of metal hydroxides (in this case aluminum hydroxide), phosphate ions present within the wastewater chemically react to form insoluble metal hydroxide phosphate thereby decreasing TP present in the reactor [29]. Eqs. (7) and (8) summarize this reaction [38]:

$$3Al^{3+} + 2PO_4^{3-} + 3H_2O \rightarrow Al(OH)_3(PO_4)_{2(s)} + 3H^+ \quad (7)$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_{4(s)} \quad (8)$$

These aluminum hydroxide complexes are unique because they have large surface areas and are capable of trapping colloids [39]. Fig. 3 depicts the results of phosphorus removal vs. current density at initial pH values of 4.0, 7.0, and 10.0.

Beginning at the pH of 4.0, phosphorus removal at 2:1 dilution was 100% at current densities 2.6, 5.4, and 8.0 mA/cm^2. However, at the 1:2 dilution ratio it appears that an increase in current density decreases the removal of phosphorus specifically from 2.6 mA/cm^2 (55.30%) to 5.4 mA/cm^2 (50.98%). But when there was no dilution the maximum removal was at 2.6 mA/cm^2 (16.27%) and no removal at 5.4 and 8.0 mA/cm^2. This seems to indicate that at a pH of 4.0, phosphorus removal is independent of current density for highly diluted water, more efficient at low current densities for slightly diluted water, and is most efficient at a low current density for raw wastewater.

Second, when the pH was 7.0, phosphorus removal at 2:1 dilution was most efficient at 2.6 mA/cm^2 (100%) and 8.0 mA/cm^2 (97.54%) but not as efficient at 5.4 mA/cm^2 (89.50%). However, at the 1:2 dilution ratio an increase in current density decreases the removal of phosphorus from 2.6 mA/cm^2 (89.05%) to 8.0 mA/cm^2 (10.72%). But for the raw wastewater, the maximum removal was at 8.0 mA/cm^2 (14.16%), no removal at 5.4 mA/cm^2, and removal was limited at 2.6 mA/cm^2 (0.58%). Therefore at a pH of 7.0, phosphorus removal is independent of current density, as removal efficiency decreases as current density increases for slightly diluted water, and is more efficient at a high current density than any other current density for raw wastewater.

Finally, at the pH of 10.0, phosphorus removal at 2:1 dilution was most efficient at 2.6 and 5.4 mA/cm^2 (100%) and 8.0 mA/cm^2 (90.95%). However, the 1:2 dilution ratio high phosphorus removal occurred at 2.6 mA/cm^2 (97.80%) and 8.0 mA/cm^2 (93.65%) in contrast with 5.4 mA/cm^2 (46.82%). When there was no dilution the maximum removal was at 5.4 mA/cm^2 (95.67%), little removal at 2.6 mA/cm^2 (31.08%), and no removal at 8.0 mA/cm^2. Therefore at a pH of 10.0, phosphorus removal is independent of current density. The EC reactor was most efficient at 2.6 and 8.0 mA/cm^2 for slightly diluted water, and is very efficient at 5.4 mA/cm^2 density for raw wastewater.

Summarizing the results from this experiment, phosphorus removal at a 2:1 dilution ratio appears irrespective to current density or pH as removal ranges between 89.50% and 100%. Water at 1:2 dilution and raw wastewater appear to be driven by the initial pH of the wastewater sample. In general, the concentration of the wastewater determines how well the reactor is capable of removing phosphorus from wastewater. This is caused by adsorption where phosphate ions adsorb onto the hydroxide flocs. In general, the amount of available flocs effects the removal of phosphate from the wastewater [38]. Therefore, it is important to select conditions based on the dilution of the wastewater in order to generate the desired phosphorus removal.

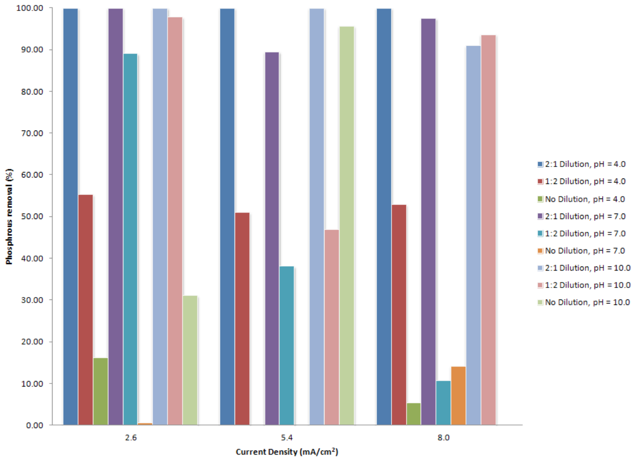

Fig. 3. Phosphorus removal vs. current density.

3.2. Phosphorus uptake in flocculent

The chemical shift of the ^{31}P NMR signal is a reflection of the chemical environment surrounding the nucleus. Thus, the chemical shift varies with pH, due to the degree of protonation which shields the ^{31}P nucleus. A positive chemical shift indicates a greater nuclear shielding component compared with the reference compound. The chemical shift for the P uptake by the flocculent shows two things – one of the chemical form is not changing depending on pH, and the P is more highly protonated even in the solid phase [40]. This result is not completely expected if the P is in a crystalline phase.

Phosphorous compounds must be mineralized before P is available for plant uptake [41]. Usually, phosphatase enzymes are responsible for P mineralization in soil. It is hoped that if the phosphorus can be mineralized by a physical process, the flocculent will be useful as an inexpensive fertilizer.

Fig. 4 presents the ^{31}P NMR spectra of flocculent by initial pH after 30 min of treatment. Solid-state NMR analysis of the flocculent showed one species of phosphorus compounds. For the pH 7 sample, this peak is located at –7 ppm chemical as referenced to $NH_4H_2PO_4$ (+0.8 ppm compared with phosphoric acid). The peak shifts from a value of –9.5 ppm at a pH of 4 to –5.7 ppm at a pH of 10. This peak is assigned to pyrophosphates [42,43]. It is possible that these are crandallite [$(CaAl_3(OH)_5(PO_4)_2]$ crystals [41,44], but further evidence of Ca availability and more selective NMR pulse sequences would be required to verify this assumption. The pyrophosphates are water soluble, but they are generally not considered efficient fertilizers for plant nutrition.

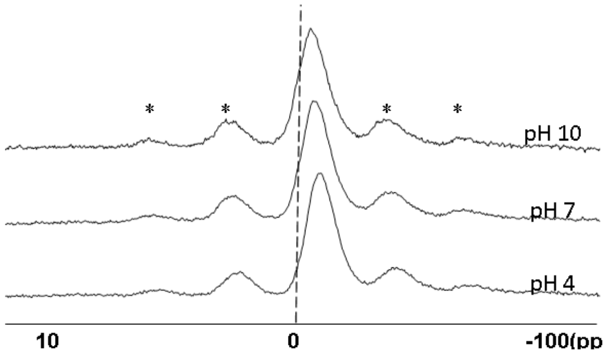

Fig. 4. ^{31}P NMR spectra of flocculent by initial pH after 30 min of treatment. The vertical line shows 0 ppm. Asterisks "*" denote spinning side bands.

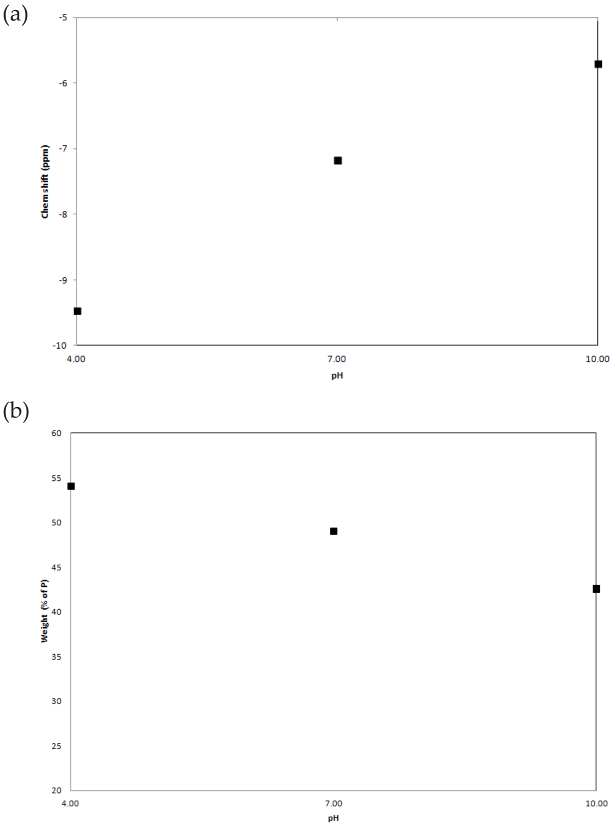

Fig. 5. (a) Chemical shift as a function of pH. (b) Weight % of phosphorus as a function of pH.

Uptake of P in the flocculent is most efficient at low pH. Fig. 5(a) shows the chemical shift as a function of pH, while Fig. 5(b) describes percent of P by weight as a function of pH as measured with NMR. The weight % of phosphorus for the standard compound is shown at 0 ppm. At low pH nearly 55% of the flocculent is phosphorus. At higher pH this is reduced to 43 wt. %.

3.3. Total organic carbon removal

The following section summarizes the effects of current density, wastewater dilution, and pH on the removal of TOC. Fig. 6 depicts the results of TOC removal vs. current density at initial pH values of 4.0, 7.0, and 10.0.

When the initial pH value is 4.0, TOC removal at 2:1 dilution decreased as the current density increased (100% at 2.6 mA/cm^2 and 52.78% at 8.0 mA/cm^2). At the 1:2 dilution ratio TOC removal increased from 44.19% at 2.6 mA/cm^2 to 68.13% at 5.4 mA/cm^2 but then decreased to 15.15% at 8.0 mA/cm^2. When there was no dilution, TOC removal decreased as the current density increased. This seems to indicate that at a pH of 4.0, TOC removal was most efficient at low current densities for very diluted and raw wastewater, but is more efficient at a slightly higher current density.

At a pH of 7.0, TOC removal at 2:1 dilution decreased as the current density increased (76.78% at 2.6 mA/cm^2 and 49.65% at 8.0 mA/cm^2). At the 1:2 dilution ratio TOC removal was 52.73% for both 2.6 and 5.4 mA/cm^2 but then decreased to 17.02% at 8.0 mA/cm^2. When there was no dilution, TOC removal increased with an increase in current density. In summary when treatments were made at a pH of 7.0, TOC removal was most efficient at low current densities for very diluted water and slightly diluted wastewater, but most efficient at higher current densities for raw wastewater.

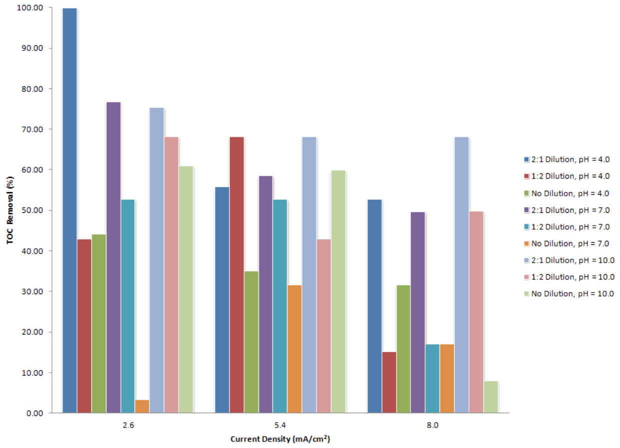

Fig. 6. TOC removal vs. current density.

When the initial pH is 10.0, TOC removal decreased as current density increased (75.45% at 2.6 mA/cm^2 and 68.19% at 8.0 mA/cm^2). At the 1:2 dilution ratio, TOC removal decreased from 2.6 to 5.4 mA/cm^2, but increased at 8.0 mA/cm^2. For undiluted wastewater TOC removal decreased as current density increased (61.04% at 2.6 mA/cm^2 to 7.97% at 8.0 mA/cm^2). In general when treatments were made at a pH of 10.0, TOC removal was most efficient at low current densities for all wastewater strengths, but indicated patterns of decreasing TOC removal for very diluted and raw wastewater.

In summary, TOC removal of very diluted wastewater is dependent upon pH as results indicated very efficient treatment for wastewater at a pH of 4.0. EC was not as effective in the removal of TOC as it was when the pH was 4.0. For slightly diluted wastewater and raw wastewater, a higher pH is more effective in the removal of TOC.

Current density is also important to consider. It was shown at several pH values that low current density optimizes treatment for very diluted and raw wastewater. Slightly diluted wastewater seems to be less dependent on current density and more on pH as there were no similar patterns observed for an increase in current density across the varying pH values. The results from this study indicated that current density and the strength of the wastewater as a major factor in selecting the optimum parameter for effectively removing TOC from beef cattle feedlot wastewater.

Overall, there are varying parameters that initiate high phosphorus and TOC removal rates at each wastewater strength. The following summarizes the trends of varying current density and pH values to achieve maximum phosphorus and TOC removal by wastewater strength:

- For very diluted samples (2:1 dilution), the pH and current density are immaterial in achieving maximum phosphorus removal efficiency. However, maximum TOC removal efficiency is best found at 2.6 mA/cm^2 and at a pH of 4.0. It also appears that as the current density increases, maximum TOC removal decreases.

- Maximum phosphorus removal of slightly diluted samples (1:2 dilution ratio) appears to occur at current densities of 2.6 and 8.0 mA/cm^2. The pH seems to be the driving factor of maximum phosphorus removal at this wastewater strength. This is because as the pH increases, the maximum phosphorus removal increases. On the other hand, maximum TOC removal remains the same from 2.6 to 5.4 mA/cm^2 but decreases at 8.0 mA/cm^2, while the optimal pH values are 4.0 and 10.0.
- The maximum treatment efficiency of phosphorus in undiluted samples appears to occur when the current density is 5.4 mA/cm^2 and pH is 10.0. For maximum TOC removal, an increase in current density decreases TOC removal when the initial pH is 4.0 and 10.0. Maximum treatment of TOC occurs when the initial pH is 10.0 and the current density is below 5.4 mA/cm^2.

3.4. Effects of electrolysis time on treatment efficiency

The study on the effects of electrolysis time and treatment performance has been well documented [30,45–49]. From these studies, it has been observed that the treatment time necessary for high performance is dependent upon the constituent being removed. For example, Zuo et al. [49] found that only 30 min was necessary to remove fluoride by EC, while Şengil and Ozacar [31] only required 1 min of treatment to remove COD from a wastewater sample.

In order to determine the effects of electrolysis time on treatment efficiency, the results from three runs were identified. These runs had both high phosphorus and TOC removal efficiencies (TOC removal ranged from 58.87% to 73.54%; phosphorus removal ranged from 90.94% to 97.98%). The experimental parameters of all three runs had a pH of 10.0 but varied in dilution and current density. Fig. 7(a) is the $TOC_t/TOC_{initial}$ vs. treatment time, while Fig. 7(b) is $phosphorus_t/phosphorus_{initial}$ vs. treatment time. The legends of these figures provide the experimental parameters.

From the results, it was determined that an increase in electrolysis time reduces the phosphorus and TOC concentrations. Attour et al. [39] states that treatment efficiency is directly related to either temporary increasing the current density during treatment or lengthening the treatment time when applying a constant current density. The results from this experiment appear to confer with the sentiments of the authors as an increase in electrolysis time improves treatment efficiency. It also appears that an electrolysis time of 30 min is sufficient to reduce the phosphorus and TOC concentrations. Nevertheless, the results of several experimental conditions as outlined in the previous sections suggest that an electrolysis time of 30 min was not sufficient in effectively removing phosphorus and TOC concentrations. There are some instances that longer retention times are more appropriate to increase treatment efficiency. Future studies should be done to identify when longer retention times are appropriate.

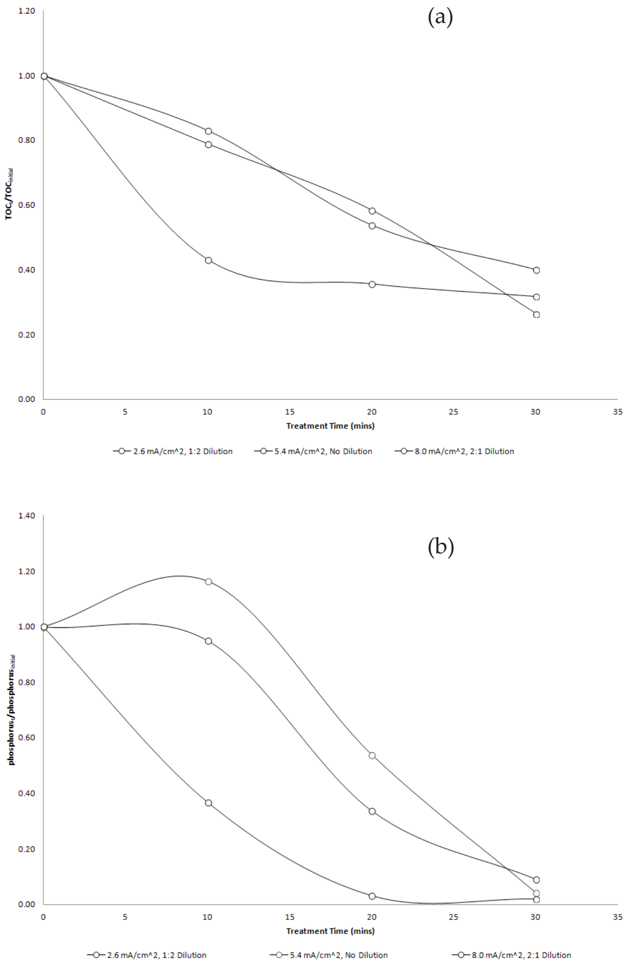

Fig. 7. (a). TOC vs. treatment time. (b) Phosphorus vs. treatment time.

4. Conclusions

The study has demonstrated that the EC setup has been capable of removing TP and TOC from beef cattle feedyard wastewater. It has been determined that treatment is dependent on the initial pH, current density, wastewater strength, and electrolysis time. There are different patterns of behavior that exist between the treatment of phosphorus and TOC at various wastewater strengths. These patterns exist when examining the initial pH and current density. Ultimately, one must consider the wastewater condition in order to determine the removal efficiency of a particular parameter. Finally, NMR analysis determined the presence of ^{31}P in flocculants generated after 30 min of treatment. The NMR results are valuable because they confirm that phosphorus is adsorbed onto the surface of the hydroxide complexes. These observations are vital for the development of methods to generate phosphorus forms capable of being extracted for new products.

Acknowledgments

Special thanks to United States Department of Agriculture (USDA-ARS) Ogallala Aquifer Program for providing the funds necessary to conduct this research under cooperative agreement 58-6209-2-076, Improving Water Productivity and New Water Management Technologies to Sustain Rural Economies – WTAMU. This work was also supported in part by NSF-MRI proposal 1428605.

References

[1] D.L. Reddel, G.G. Wise, Water Quality of Storm Runoff of a Texas Beef Feedlot, Texas Agricultural Experiment Station, PR-3224, College Station, 1974.

[2] United States Environmental Protection Agency, Development Document for Proposed Effluent Limit Guide and New Source Performance Standards for Feedlot Point Source Category, EPA-440/I-73/004, United States Environmental Protection Agency, Washington, D.C., 1973, pp. 59–64.

[3] D.H. Vanderholm, D. Day, A. Muheling, Y.-T. Hung, E. Butler, Natural Resources and Control Processes, Springer International Publishing, Switzerland, 2016, pp. 1–71.

[4] J.M. Sweeten, J. Hatfield, B. Stewart, Animal Waste Utilization: Effective Use of Manure as a Soil Resource, Lewis Publishers, Boca Raton, 1998, pp. 125–155.

[5] J.J. Miller, B.P. Handerek, B.W. Beasley, E. Olson, L.J. Yanke, F.J. Larney, T.A. McAllister, B.M. Olson, L.B. Selinger, D.S. Chanasyk, P. Hasselback, Quantity and quality of runoff from a beef cattle feedlot in southern Alberta, J. Environ. Qual., 33 (2004) 1088–1097.

[6] S. Rahman, T. Scherer, A. Rahman, J. Lang, Water Quality of Runoff from Beef Cattle Feedlots. Available at: https://www.ag.ndsu.edu/publications/environment-natural-resources/water-quality-of-runoff-from-beef-cattle-feedlots/wq1667.pdf 2013 (Accessed 1 June 2017)

[7] L.M. Pepple, D.S. Andersen, R.T. Burns, L.B. Moody, Physical and chemical properties of runoff effluent from beef feedlots in Iowa, Trans. ASABE, 54 (2011) 1079–1084.

[8] J. Sweeten, Agricultural and Food Processing Wastes Proceedings of the Sixth International Symposium on Agricultural and Food Processing Wastes, American Society of Agricultural Engineers, Chicago, 1990, pp. 168–184.

[9] J. Sweeten, Cattle Feedlot Waste Management Practices for Water and Air Pollution Control, Texas Agriculture Extension Service, 1990.

[10] R.N. Clark, A.D. Schneider, B.A. Stewart, Analysis of Runoff from Southern Great Plains Feedlots, Trans. ASAE, 18 (1975) 319–322.

[11] D. Franco, J. Lee, S. Cohen, Removal of phosphate from surface and wastewater via electrocoagulation, Ecol. Eng., 108 (2017) 589–596.

[12] S. Tchamango, C.P. Nanseu-Njiki, E. Ngameni, D. Hadjiev, A. Darchen, Treatment of dairy effluents by electrocoagulation using aluminum electrodes, Sci. Total Environ., 408 (2010) 947–952.

[13] N. Bektaş, H. Akbulut, H. Inan, A. Dimoglo, Removal of phosphate from aqueous solutions by electro-coagulation, J. Hazard. Mater., 106 (2004) 101–105.

[14] A.A. Bukhari, Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater, Bioresour. Technol., 99 (2008) 914–921.

[15] F.R. Espinoza-Quiñones, M.M. Fornari, A.N. Módenes, S.M. Palácio, F.G. da Silva, N. Szymanski, A. Kroumov, D.E. Trigueros, Pollutant removal from tannery effluent by electrocoagulation, Chem. Eng. J., 151 (2009) 59–65.

[16] E. Lacasa, P. Cañizares, C. Sáez, F.J. Fernández, M.A. Rodrigo, Removal of nitrates from groundwater by electrocoagulation, Chem. Eng. J., 171 (2011) 1012–1017.

[17] H. Inan, E. Alaydın, Phosphate and nitrogen removal by iron produced in electrocoagulation reactor, Desal. Wat. Treat., 52 (2014) 1396–1403.

[18] E. Butler, Y.-T. Hung, O. Mulamba, The effects of chemical coagulation on the decolorization of dyes using response surface methodology (RSM), Appl. Water. Sci., 7 (2016) 1–16.

[19] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, J. Hazard. Mater., 84 (2001) 29–41.

[20] M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M.R. Qtaishat, M. Alkasrawi, Heavy metal ions removal from metal plating wastewater using electrocoagulation: kinetic study and process performance, Chem. Eng. J., 260 (2015) 749–756.

[21] M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M.R. Qtaishat, M. Alkasrawi, COD reduction of baker's yeast wastewater using batch electrocoagulation, Environ. Eng. Manage. J., 13 (2014) 3153–3160.

[22] M. Al-Shannag, W. Lafi, K. Bani-Melhem, F. Gharagheer, O. Dhaimat, Reduction of COD and TSS from paper industries wastewater using electro-coagulation and chemical coagulation, Sep. Sci. Technol., 47 (2012) 700–708.

[23] W.K. Lafi, M. Al-Anber, Z.A. Al-Anber, M. Al-Shannag, A. Khalil, Coagulation and advanced oxidation processes in the treatment of olive mill wastewater (OMW), Desal Wat. Treat., 24 (2010) 251–256.

[24] M. Al-Shannag, K. Bani-Melhem, Z. Al-Anber, Z. Al-Qodah, Enhancement of COD-nutrients removals and filterability of secondary clarifier municipal wastewater influent using electrocoagulation technique, Sep. Sci. Technol., 48 (2013) 673–680.

[25] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

[26] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage., 90 (2009) 1663–1679.

[27] K. Yetilmezsoy, F. Ilhan, Z. Sapci-Zengin, S. Sakar, M.T. Gonullu, Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: a post-treatment study, J. Hazard. Mater., 162 (2009) 120–132.

[28] G. Mouedhen, M. Feki, M.D.P. Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, J. Hazard. Mater., 150 (2008) 124–135.

[29] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, Ind. Eng. Chem. Res., 42 (2003) 3391–3396.

[30] A. Thapa, S. Rahman, M.S. Borhan, Remediation of feedlot nutrients runoff by electrocoagulation process, Am. J. Environ. Sci., 11 (2015) 366–379.

[31] I.A. Şengil, M. Ozacar, Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes, J. Hazard. Mater., 137 (2006) 1197–1205.

[32] A. Aitbara, C. Mouna, H. Sabir, J.P. Leclerc, Continuous treatment of industrial dairy effluent by electrocoagulation using aluminum electrodes, Desal. Wat. Treat., 57 (2016) 3395–3404.

[33] K. Bensadok, N.E. Hanafi, F. Lapicque, Electrochemical treatment of dairy effluent using combined Al and Ti/Pt electrodes system, Desalination, 280 (2011) 244–251.

[34] B.J. Cade-Meun, J.A. Navartnam, M.R. Wallbridge, Characterizing dissolved and particulate phosphorus in water with ^{31}P nuclear magnetic resonance spectroscopy, Environ. Sci. Technol., 40 (2006) 7874–7880.

[35] B.J. Cade-Menun, Characterizing phosphorus in environmental and agricultural samples by P-31 nuclear magnetic resonance spectroscopy, Talanta, 66 (2005) 359–371.

[36] B.J. Cade-Menun, C.M. Preston, A comparison of soil extraction procedures for P-31 NMR spectroscopy, Soil Sci., 161 (1996) 770–785.

[37] American Public Health Association (APHA), American Water Works Association, Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 22nd ed., American Public Health Association, Washington, D.C., 2006.

[38] B.M.B. Ensano, L. Borea, V. Naddeo, V. Belgiorno, M.D.G. de Luna, F.C. Ballesteros, Removal of pharmaceuticals from wastewater by intermittent electrocoagulation, Water, 9 (2017) 85.

[39] A. Attour, M. Touati, M. Tlili, M.B. Amor, F. Lapicque, J.P. Leclerc, Influence of operating parameters on phosphate removal from water by electrocoagulation using aluminum electrodes, Sep. Purif. Technol., 123 (2014) 124–129.

[40] S. Vasudevan, J. Lakshmi, J.K. Jayaraj, S. Ganapathy, Remediation of phosphate-contaminated water by electrocoagulation with aluminum, aluminum alloy and mild steel anode, J. Hazard. Mater., 164 (2009) 1480–1486.

[41] D.A. Crouse, H. Sierzputowska-Gracz, R.L. Mikkelsen, Optimization of sample ph and temperature for phosphorus-31 nuclear magnetic resonance spectroscopy of poultry manure extracts, Commun. Soil Sci. Plant Anal., 31 (2000) 229–240.

[42] *P.A. Moore, T.C. Daniel, A.N. Sharpley, C.W. Wood, Poultry manure management: environmentally sound options, J. Soil Water Conserv.,* 50 (1995) 321–327.

[43] Z.R. Hinedi, A.C. Chang, R.W.K. Lee, Characterization of phosphorus in sludge extracts using P-31 nuclear magnetic resonance spectroscopy, J. Environ. Qual., 18 (1989) 323–329.

[44] L.M. Condron, E. Frossard, R.H. Newman, P. Tekely, J.L. Morel, Nuclear Magnetic Resonance Spectroscopy in Environmental Chemistry, Oxford University Press, New York, 1997.

[45] W.F. Bleam, P.E. Pfeffer, J.S. Frye, P-31 Solid-state nuclear magnetic resonance spectroscopy of aluminum phosphate minerals, Phys. Chem. Miner., 16 (1989) 455–464.

[46] A. Gürses, M. Yalçin, C. Doğar, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, Waste Manage., 22 (2002) 491–499.

[47] N. Daneshvar, H. Ashassi-Sorkhab, A. Tizpar, A, Decolorization of orange II by electrocoagulation method, Sep. Purif. Technol., 31 (2003) 153–162.

[48] B. Merzouk, B. Gourich, A. Sekki, K. Madani, M. Chibane, Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique: a case study, J. Hazard. Mater., 164 (2009) 215–222.

[49] Q. Zuo, X. Chen, W. Li, G. Chen, Combined electrocoagulation and electroflotation for removal of fluoride from drinking water, J. Hazard. Mater., 159 (2008) 452–457.