



Advanced treatment of liquid swine manure using physico-chemical treatment

Pamela Chelme-Ayala^a, Mohamed Gamal El-Din^{a,*}, Richard Smith^b, Kenneth R. Code^c, Jerry Leonard^d

^a Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, Canada

^b Department of Agricultural, Food and Nutritional Science, University of Alberta, Edmonton, Alberta, Canada

^c IOWC Technologies Inc., Edmonton, Alberta, Canada

^d Edmonton Waste Management Centre of Excellence, Edmonton, Alberta, Canada

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ABSTRACT

In this study, liquid swine manure was treated by physico-chemical treatment, including coagulation, flocculation, and sedimentation followed by an oxidation step as a polishing treatment at a bench-scale level. A superabsorbent polymer (SAP) and a mineral and salt formulation able to generate molecular iodine were used as coagulant and oxidant agents, respectively. The results indicated that SAP at a concentration of 1.25 g/L was able to reduce 32% of the initial total suspended solids (TSS) in experiments using supernatant at its natural pH. Following the SAP application, 82% of initial ammonia (NH₃), 78% of initial total organic carbon (TOC), and 93% of the total coliforms were reduced using 40 mg/L of free iodine. In experiments performed with diluted supernatant (five-fold dilution), it was found that SAP at a concentration of 0.5 g/L was capable of reducing 80% of the initial TSS in experiments at pH 11. A leaching study was conducted to assess the safety of sludge disposal. From the leaching tests using non-diluted supernatant, it was found that 24% of the chloride (Cl⁻) and 50% of the phosphate (PO₄³⁻) ions retained in the sludge leached to the ultrapure water after 48 h. Potential contamination due to leaching of NH₃, nitrite (NO₂⁻) and nitrate (NO₃⁻) was found to be statistically insignificant.

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1. Introduction

Livestock industries are growing rapidly along with the human population [1]. Because of this increasing trend, tons of swine manure are being generated annually worldwide. Swine manure contains pig urine and feces as well as water spillage, remains of undigested feed items, antimicrobial drug residues, and sometimes precipitation [2]. Typical swine manure is characterized by a high content of suspended solids and organic matter, high biochemical oxygen demand (BOD), and high phosphorus and nitrogen contents, as well as high levels of microbial population.

Environmental problems caused by swine manure include water contamination and human health concerns due to the presence of microorganisms in animal manures. It has been found that swine manure hosts and reservoirs human pathogenic bacteria, including *Clostridium perfringens*, *Escherichia coli*, and *Salmonella* spp., among others [3]. Other problems associated with swine manure are odours caused by gases produced by decomposing manure in swine manure handling facilities or from land application [4]. Nutrients leaching below the root zone and into groundwater together with nutrients entering

into surface water systems through runoff from manure storage facilities are other concerns caused by improper swine manure management.

Animal waste management may comprise collection, storage, treatment, and utilization. In Canada, manure management considers the storage of manure in earthen or concrete storage tanks during the winter season and the land application in summer [5]. Strategies for swine manure treatment include physical, chemical and biological processes, designed to reduce the contaminants of concern and convert them into usable products such as fertilizer and biogas [6,7].

Physico-chemical methods have been found to be effective processes to remove solids and nutrients from animal manure. Technologies used for solid–liquid separation include the addition of coagulants such as aluminum sulphate (alum) or ferric chloride (FeCl₃) [8,9]. The presence of metal salts in the sludge, the large amount of chemical needed as well as the large amount of sludge generated may limit the application of the inorganic salts [10,11]. One of the synthetic organic polymers most commonly used for the sedimentation of swine manure is polyacrylamide (PAM). Vanotti and Hunt [11] reported total suspended solid (TSS) removal efficiencies higher than 90% with PAM concentrations of 26–79 mg/L applied to liquid swine manure containing 1.5–4.1 g TSS/L. Chitosan, a natural polycationic polymer has also been used for solid–liquid separation of dairy manure [12].

Coagulation–flocculation is a conventional physico-chemical treatment process used to separate the suspended solids from the

* Corresponding author at: 3-093 Markin/CNRL Natural Resources Engineering Facility, Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta T6G 2W2, Canada. Tel.: +1 780 492 5124; fax: +1 780 492 8198.
E-mail address: mgamalel-din@ualberta.ca (M. Gamal El-Din).

liquid phase. The objective of this study was to investigate whether the coagulation/flocculation process utilizing a superabsorbent and a new mineral and salt formulation called CupriDyne™ were effective and applicable processes for the treatment of liquid swine manure. To achieve that, the optimum treatment conditions and most effective chemical doses to yield higher removal efficiencies, in terms of TSS and nutrient removal efficiencies, were evaluated. The levels of fecal and total coliforms as well as the acute toxicity of the untreated and treated samples were also determined. To investigate the safety of disposal of the sludge generated from the coagulation/flocculation process, a leaching study was conducted as the last phase of this research.

2. Materials and methods

2.1. Chemicals and materials

CupriDyne™ superabsorbent (SAP) and CupriDyne™ tablets were provided by IOWC Technologies Inc. (Canada). Chemicals used for preparing solutions and eluents were of reagent grade and were used without further purification. The raw swine manure was obtained from the Swine Research and Technology Centre at the University of Alberta, located in Edmonton, Alberta, Canada. The swine manure samples after collection were transported and stored in the laboratory cooling room at 4 °C until they were used.

2.2. Experimental methods

The coagulation/flocculation and sedimentation experiments were performed using the standard jar test apparatus (Phipps and Bird™ 6-place paddle stirrer apparatus) [13,14]. The jar test was set-up at room temperature for all trials. The sample pHs were adjusted using 1 M sodium hydroxide (NaOH) or 1 M hydrochloric acid (HCl). The first phase (Phase 1) of this study involved the determination of optimum conditions using the CupriDyne™ SAP based on the maximum TSS removal efficiency. The most important parameters affecting the coagulation/flocculation processes such as mixing intensity, mixing time, and polymer dose were determined. A settling period of 1 h was used in all jar tests to determine the effect of SAP on solids and nutrient removal.

The supernatant generated during coagulation/flocculation treatment, under the optimum conditions, was used in the second phase (Phase 2) of this study. The supernatant was treated using CupriDyne™ tablets as an oxidizing agent by generating iodine in water. The optimum conditions were determined based on the maximum total organic carbon (TOC) and ammonia (NH₃) removal efficiencies. The CupriDyne™ technology is reported to generate free iodine by dissolving potassium iodide (KI) and copper sulphate (CuSO₄) in water. Free iodine has been found to be an effective disinfectant [15]. Therefore, to test the disinfection efficacy, the levels of fecal and total coliforms were determined before and after treatment. The Microtox® bioassay was used to determine the acute toxicity of the untreated and treated samples.

The sludge generated from the coagulation/flocculation process, under optimum conditions, was used in a leaching test. The sludge generated was dried at room temperature and then ultrapure water was added to the previously dried sludge to simulate rainfall runoff. After a certain period of contact with the dried sludge, the water was collected and analyzed to test the leaching of nutrients and other elements.

2.3. Analytical methods

During the experiments, the raw and treated liquid swine manure samples were characterized by various water quality parameters including pH, TSS, total phosphorus (TP), total Kjeldahl

nitrogen (TKN), nitrite (NO₂⁻), nitrate (NO₃⁻), BOD over a five-day period (BOD₅), and chemical oxygen demand (COD) according to the Standard Methods [16]. The concentrations of sulphide (S²⁻) ion in the liquid swine manure were measured using the methylene blue method [16]. The levels of NH₃, hydrogen sulphide (H₂S), and carbon dioxide (CO₂) gases were taken from inside the jar test using a portable Eagle™ gas detector (RKI Instruments).

The concentrations of ions were determined using a Dionex ICS-2500 ion chromatography (IC) system, equipped with an IonPac® AS14A column (4 × 250 mm) and IonPac® AG14 guard column (4 × 50 mm) for anions, and a Dionex ICS-2000 IC system with an IonPac® CS12A column (4 × 250 mm) and IonPac® CG12A guard column (4 × 50 mm) for cations. Mobile phases for the chromatography system were 20 mM methanesulphonic acid (CH₃SO₃H) for the cation mode and 8 mM sodium carbonate (Na₂CO₃) combined with 1 mM sodium bicarbonate (NaHCO₃) for the anion mode.

The concentrations of ions in the sludge after Phase 2 were determined by mass balance of the ion concentrations in the raw samples and the ion concentrations in the supernatant. The percentage of ions leaching to the water was calculated by determining the amount of ions in the water (IC analyses) and the ion concentrations in the sludge.

The toxicity of the samples before and after treatment was determined using the Microtox® bioassay [17,18]. The test involved the use of luminescent bacterium (*Vibrio fischeri*). A model 500 Microtox® analyzer (Azur Environmental, USA) was used to measure the light emitted by the bacterium as a result of its normal metabolic processes. Freeze-dried bacteria, reconstitution solution, diluent and an adjustment solution were all obtained from Osprey Scientific Inc. (Edmonton, Canada). The toxicity of the liquid swine manure on *Vibrio fischeri* was measured after 5 and 15 min of exposure. The volume of sample (in percentage) that caused a 20% and an 80% decrease in luminescence was reported as the inhibition concentration IC₂₀ and IC₈₀, respectively, by using the Microtox® Omni Software. The toxicity of phenol (C₆H₅OH) standards was measured as a quality control prior to the analysis of samples.

2.4. Statistical analysis

All experiments were conducted in triplicate ($n=3$), with each sample being injected twice on the ion chromatography system. Significant difference among treatment means were evaluated using a least significant difference (LSD) test at the 5% level.

3. Results and discussion

Preliminary (gravity) settling has been described as an effective and economic liquid swine manure treatment process that allows the separation of readily settleable solids from the liquid manure [9,19]. In this study, the raw liquid swine manure was allowed to settle for at least 24 h prior to any experiment. The results showed that the initial TSS (2325 ± 315 mg/L, $n=3$) in the raw manure decreased by 38% after 2.5 h, 41% after 24 h, and 66% after 19 days of natural settling, as displayed in Fig. 1. In a study by Zhu et al. [9], TSS removal efficiency of 75% after 24 h of settling at initial raw manure TSS concentration of 5800 mg/L was reported. TSS reduction of 14% was reported after 5 h of settling [20]. This preliminary settling of liquid swine manure can be classified as type II settling, where the particles can flocculate as they settle, especially during the initial settling hours [21].

Swine manure characteristics vary significantly depending on several factors, including water consumption, dietary method, on-site operation, seasonal conditions, housing system and waste handling methods [22]. The primary-settled swine manure (supernatant) in the present study had a density of 976 ± 6 g/L ($n=4$), pH

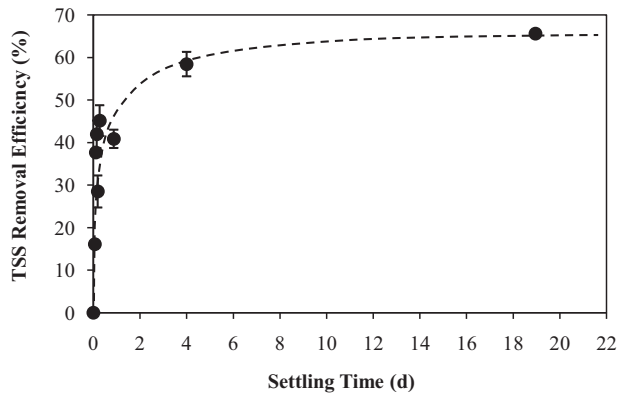


Fig. 1. Natural settling of liquid swine manure. Experimental conditions: $TSS_i = 2325 \text{ mg/L}$, $pH_i = 7.36$, standard error = 0.6–3.8% ($n = 3$). Subscript i denotes initial condition.

of 7.4 ± 0.5 ($n = 7$), conductivity of 15.7 ± 0.1 ($n = 3$) mS/cm, COD of $10,888 \pm 399 \text{ mg/L}$ ($n = 3$), and TSS of $1550 \pm 260 \text{ mg/L}$ ($n = 8$). The levels of TSS were consistent with those of typical TSS values of primary-settled swine liquid manure [11,23].

3.1. Optimization of mixing speed and mixing time

Coagulation and flocculation are the processes designed to remove suspended solids by the destabilization and the formation of settleable flocs, respectively. It has been found that the most important factors affecting the performance of coagulation/flocculation process are the water pH, mixing intensity, mixing time, coagulant dose, and coagulant type. Jar tests were used to determine the optimum mixing velocity gradient (G), measured in s^{-1} , and mixing time (t), measured in s, based on the maximum TSS removal efficiency. The experiments were also performed using diluted supernatant (two- to five-fold dilutions). The results indicated that the highest TSS removal efficiency was achieved using 300 s of rapid mixing at a velocity gradient of $220 s^{-1}$ (agitator paddle speed of 3.33 rps), representing a Gt value of 60,000. This value is in the range recommended for rapid mixing of wastewaters 10,000–100,000 [24]. Typically, a jar test involves of a rapid mixing period that starts with the addition of the coagulant to simulate coagulation (i.e., destabilization) followed by a period of slow mixing to simulate flocculation. In this study, the combination of rapid and slow mixings was not as effective as the single period of rapid mixing. It was also found that the slow mixing at 0.33 rps for 300 s recorded the lowest TSS removal efficiency. The results also indicated that increasing mixing speed did not enhance the TSS removal efficiency. At 5.33 rps, the initial TSS was reduced by 20% after 300 s of mixing.

Fig. 2 shows the effect of mixing time on the TSS removal efficiency. The results showed that 81.6% of TSS was removed using 300 s of rapid mixing at 3.33 rps. Although wastewaters usually coagulate more rapidly than surface waters, longer rapid-mixing times are required because of the high levels of TSS [21]. Rapid mixing times higher than 720 s caused a decrease in the TSS removal efficiency. Sievers [25] reported that 720 s of rapid mixing at velocity gradient of $12.9 s^{-1}$ was the optimum mixing time to reduce the turbidity of diluted swine manure using chitosan as coagulant, whereas 360 s of rapid mixing was used to achieve the optimum turbidity removal using $FeCl_3$.

Flocculation [14] may occur through two different processes: charge neutralization and bridge formation [26]. Charge neutralization reduces the repulsive forces between charged particles through the addition of metal ions. In bridging, organic polymers adsorb the destabilized particles and build bridges between them.

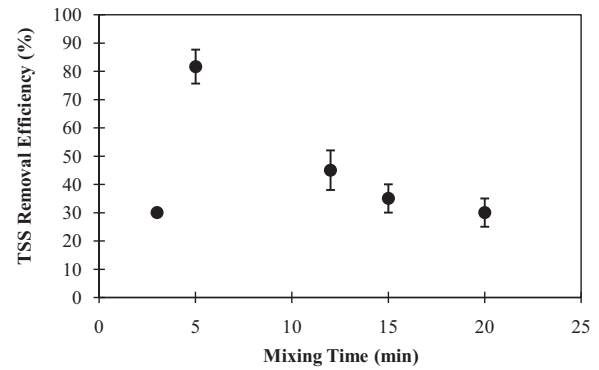


Fig. 2. Effect of mixing time on TSS removal efficiency. Experimental condition: dilution factor = 1:5, $TSS_i = 200 \text{ mg/L}$, $pH_i = 11.1$, mixing speed = 3.33 rps, SAP = 0.5 g/L, standard error = 1.0–7.0% ($n = 3$).

The CupriDyne™ SAP, a superabsorbent polymer, causes bridging, and therefore, requires more mixing time than that required during charge neutralization. If inadequate mixing is provided, the adsorption of the polymer onto the colloidal particles may not occur [24]. Based on the preliminary results of the present study, the optimization of the CupriDyne™ SAP and tablet doses was conducted using rapid mixing at 3.33 rps for 300 s.

3.2. Optimum polymer doses

The first phase of this study considered the use of CupriDyne™ superabsorbent polymer. The determination of optimum conditions was based on maximum TSS removal efficiency during coagulation and flocculation followed by sedimentation. Different dilution factors (1:1, 1:3, and 1:5) of the primary-settled liquid swine manure and different pHs were tested to optimize the TSS removal efficiency. It was found that the dilution of the liquid swine manure had a pronounced effect on the TSS removal efficiency (see Table 1 for details). Studies have shown a decrease of the zeta (ζ) potential (electric potential in the interfacial double layer in colloidal systems) with increasing dilution factors due to the reduction of the repulsion between particles, therefore, the particles tend to collapse [27,28]. Due to the smaller solid concentrations in the diluted supernatant, the removals were higher than those in the non-diluted liquid manure. As displayed in Table 1, the highest TSS removal efficiency was achieved using 0.5 g/L SAP at pH 11 in experiments using diluted supernatant (five-fold dilution). No statistically significant ($p < 0.05$) TSS removals were achieved by reducing the manure pH. In addition, the acid used to reduce the pH reacted with the calcium carbonate ($CaCO_3$) in the manure, thus, releasing CO_2 during the treatment process.

Fig. 3 shows the effect of SAP doses on the TSS removal efficiency. When the experiments were performed using the supernatant without any dilution, the highest TSS removal efficiency (32.8%)

Table 1
Levels of TSS reduction^a at different pHs and dilution factors.

Dilution factor	pH ^b	Initial TSS (mg/L) ^b	TSS reduction (%)
No dilution	4.07 ± 0.11	1238 ± 47	5.9
No dilution	7.38 ± 0.06^c	2300 ± 100	13.8
No dilution	11.12 ± 0.04	4375 ± 427	37.8
1:5	4.09 ± 0.02	285 ± 18	18.0
1:5	7.62 ± 0.12^c	174 ± 15	50.2
1:5	11.01 ± 0.02	313 ± 6	81.6

^a Experimental conditions: SAP dose = 0.5 mg/L, mixing speed = 3.33 rps, mixing time = 300 s.

^b Mean \pm standard deviation, $n = 3$.

^c Natural pH of liquid swine manure.

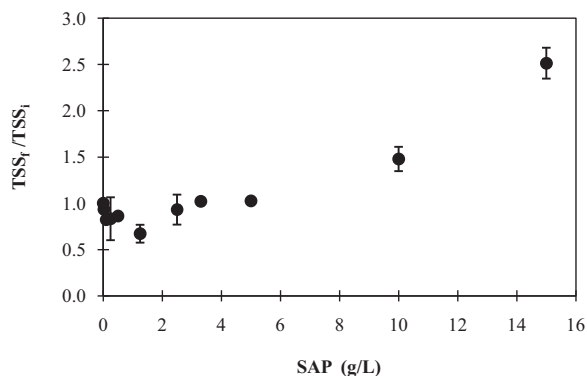


Fig. 3. Effect of SAP doses on TSS removal efficiency. Experimental conditions: TSS_i = 2300 mg/L, pH_i = 7.4, mixing speed = 3.33 rps, mixing time = 300 s, standard error = 1.0–7.0 ($n = 3$). Subscript f denotes the condition after treatment.

was achieved using 1.25 g/L SAP at pH 7.40 ± 0.02 . As shown in Fig. 3, overdosing SAP caused a decrease in the TSS removal efficiency due to re-stabilization. Saturation of available surfaces by adsorbed polymer produces the re-stabilization of the colloid particles [11].

The results indicated that at an optimum SAP dose of 1.25 g/L, the pH was reduced from 7.68 ± 0.05 ($n = 3$) to 7.60 ± 0.09 ($n = 3$) (not statistically significant). In diluted supernatants, the pH changed from 10.90 ± 0.03 ($n = 3$) to 10.79 ± 0.02 ($n = 3$) (not statistically significant). The results also showed that the addition of SAP reduced the BOD₅ and COD of the liquid swine manure. It was found that BOD₅ decreased by 22% and 10% in the supernatant at pH 7 and diluted supernatant at pH 11, respectively.

Although SAP was added to remove TSS, it also caused a decrease in the TP, TKN, and NH₃. Removal efficiencies of 5%, 14% and 11% for TP, TKN, and NH₃, respectively, were recorded after the addition of 1.25 g/L SAP in the supernatant at pH 7. A decrease of 36% for TP and 22% for TKN were found after the SAP addition in the diluted supernatant at pH 11.

3.3. Optimum free iodine doses

The optimum doses of CupriDyne™ tablets as free iodine were determined based on the maximum TOC and NH₃ removal efficiencies. As shown in Fig. 4, the NH₃ concentration dropped from 1486 ± 79 mg/L to 304 ± 8 mg/L using 40 mg/L of free iodine. When using diluted supernatant at pH 11, 80 mg/L of free iodine was required to reduce the NH₃ concentration from 325 ± 12 mg/L to 163 ± 15 mg/L. SAP and free iodine had limited effect on the

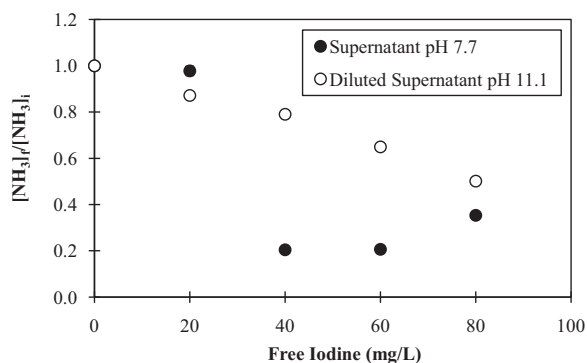


Fig. 4. Effect of free iodine on ammonia concentration. Experimental conditions non-diluted supernatant: NH_{3i} = 1486 mg/L, pH_i = 7.7, SAP = 1.25 g/L. Experimental conditions diluted supernatant: dilution factor = 1:5, NH_{3i} = 325 mg/L, pH_i = 11.1, SAP = 0.5 g/L, standards error = 0.0006–0.01 ($n = 3$).

TP removal efficiency, especially in non-diluted supernatant (see Table 2). Higher TP removal efficiencies were achieved using diluted supernatant (five-fold dilution), achieving 68% removal efficiency.

The TOC level was also reduced by the addition of free iodine. The TOC was reduced by 67% in experiments using non-diluted supernatant at 1.25 g/L SAP. A 50% TOC reduction was observed using 80 mg/L of free iodine in experiments using diluted supernatants. The application of the SAP and free iodine led to the reduction of the BOD₅ and COD levels by up to 55% under different experimental conditions.

A TSS removal efficiency of 44% was achieved using SAP (1.25 g/L) followed by free iodine (40 mg/L) in experiments using supernatant without any dilution. Higher TSS reductions (percentage) were found to be statistically significant in experiments using diluted supernatant at SAP dose of 0.5 g/L and 80 mg/L free iodine, achieving a 91% TSS removal efficiency. Ndegwa et al. [8] reported that concentrations of 1500 mg/L of FeCl₃ and alum led to the improvement in the separation of solids from slurries by 66 to 76% and 96%, respectively. Walker and Kelley [29] found the optimum PAM concentration in the range of 62–750 mg/L, requiring 750 mg/L PAM to reduce 78% of the initial TSS (162 mg/L). Walker and Kelley also reported a decrease of the COD levels in the range of 15–27% using 375–750 mg/L of PAM.

The use of the CupriDyne™ tablets generates free iodine, which is an effective, simple, and cost efficient method of disinfection [15]. Iodine is commonly used in the aquiculture sector [30,31]. As shown in Table 2, the addition of SAP (Phase 1) caused a decrease in the total and fecal coliforms' levels (detection limits of 1 CFU per 100 mL) since the SAP itself yields 20 mg/L of free iodine. By adding the CupriDyne™ tablets, the total coliforms decreased from $(1.0 \pm 1.1) \times 10^5$ to $(8.9 \pm 0.7) \times 10^4$ CFU/100 mL. For the diluted supernatant, no total and fecal coliforms were detected after treatment with 80 mg/L free iodine. The free iodine was enough to inactivate the pathogenic microorganisms. Iodine has been found to be very effective against bacteria, with lower germicidal action against protozoan cysts [32]. In contrast to chlorine which is very sensitive to pH changes, the equilibrium concentrations of the predominant iodine species (iodide, iodate, triiodide) are not influenced by the pH [33]. Vanotti et al. [34] used a series of treatment processes to remove pathogens from the liquid swine manure, using solid–liquid separation (polymer addition), followed by biological nitrogen removal using nitrification and denitrification and lime precipitation for phosphorous removal. The results of Vanotti's study showed reduction values between 0.5 and 1 log₁₀ for *Salmonella* and microbial indicators after solid–liquid separation. In the current study, a 0.1 log₁₀ for total coliform reduction and 0.7 log₁₀ for fecal coliform reduction were found using 40 mg/L of free iodine. By using diluted supernatant (five-fold dilution), 3.8 log₁₀ and 3.2 log₁₀ for total and fecal coliform reduction, respectively, were found using 80 mg/L of free iodine. These results show that the free iodine is more effective in diluted liquid swine manure.

3.4. Gaseous emissions

Emission of gases such as NH₃ and CO₂ are potential problems associated with manure production, storage, and management [35]. The levels of NH₃, H₂S, and CO₂ gases were measured before and after treatment. The results indicated that NH₃ gas decreased by 37% after treatment using free iodine at 40 mg/L (see Fig. 5). The initial H₂S levels (25.5 ± 0.4 mg/L, $n = 3$) decreased below the detection limit (0.1 mg/L) and the levels of CO₂ decreased from 1100 ± 120 mg/L to 680 ± 36 mg/L ($n = 3$) after treatment using 40 mg/L of free iodine. For the diluted supernatants (five-fold dilution), the NH₃ gas decreased by 24% using 0.5 g/L SAP and by 77% using 80 mg/L of free iodine. In addition, H₂S and CO₂ were not detected in the diluted samples. It was also found that the NH₃

Table 2
Characteristics of the liquid swine manure before and after treatment^a.

Parameter	Supernatant ^b			Diluted supernatant (1:5) ^b		
	Raw wastewater	After Phase 1	After Phase 2	Raw wastewater	After Phase 1	After Phase 2
TSS (mg/L)	1237 ± 24	840 ± 37	690 ± 28	540 ± 9	110 ± 14	51 ± 8
pH	7.68 ± 0.05	7.60 ± 0.09	7.57 ± 0.06	10.90 ± 0.03	10.79 ± 0.02	10.68 ± 0.03
Turbidity (NTU)	459 ± 9	370 ± 5	172 ± 6	211 ± 2	202 ± 4	100 ± 10
Conductivity (mS/cm)	15.7 ± 0.1	15.1 ± 0.1	12.5 ± 0.06	6.3 ± 0.1	5.6 ± 0.02	3.5 ± 0.1
TOC (mg/LC)	1858 ± 80	1732 ± 357	580 ± 56	599 ± 10	509 ± 13	118 ± 9
TP (mg/L)	310 ± 4	296 ± 12	286 ± 4	217 ± 1	138 ± 2	69 ± 1
TKN (mg/L)	2344 ± 326	2012 ± 325	1698 ± 207	727 ± 87	561 ± 92	253 ± 82
NH ₃ (mg/LN)	1662 ± 81	1486 ± 79	304 ± 8	329 ± 12	325 ± 2	163 ± 15
COD (mg/L)	10,888 ± 399	8459 ± 313	7025 ± 95	2114 ± 476	1755 ± 240	1469 ± 225
BOD ₅ (mg/L)	6345 ± 456	4950 ± 245	2835 ± 210	2430 ± 542	2205 ± 235	1380 ± 139
Total coliforms (CFU/100 mL)	(1.2 ± 0.1) × 10 ⁶	(1.0 ± 1.1) × 10 ⁵	(8.9 ± 0.7) × 10 ⁴	(9.2 ± 0.1) × 10 ³	(6.2 ± 0.01) × 10 ³	ND ^c
Fecal coliforms (CFU/100 mL)	(1.1 ± 0.03) × 10 ⁵	(9.3 ± 0.9) × 10 ³	(2.1 ± 0.5) × 10 ³	(2.9 ± 0.05) × 10 ³	(1.6 ± 0.3) × 10 ³	ND
Inhibition of <i>Vibrio fischeri</i> (%)	94.0 ± 0.2	92.8 ± 0.3	92.1 ± 0.6	65.5 ± 3.0	64.7 ± 2.1	90.9 ± 1.2

^a Phase 1: addition of SAP to the liquid swine manure; Phase 2: addition of free iodine under optimum SAP doses.

^b Mean ± standard deviation, n = 3.

^c ND: not detected.

emissions at pH 11 were three times higher than those from the supernatants at pH 7. It has been found that increasing pH increases NH₃ (pKa = 9.2) emissions but decreases H₂S emissions [36].

Several strategies have been used to reduce the gaseous emissions from animal feeding facilities, including dietary manipulation, precipitation, chemical degradation and biodegradation. Predicala et al. [37] reported the removal of H₂S in the headspace gas from swine manure using 80 mM NO₂⁻ or 2 mM molybdate. Lee et al. [38] reported the removal of NH₃ and H₂S from swine manure at levels of 88 and 79%, respectively, using aqueous keratin hydrolysate foam combined with microorganisms and chemical additives.

3.5. Concentration of main ions

Table 3 displays the concentrations of major ions in the samples before and after treatment under the optimum SAP and free iodine doses. A decrease of the major ions was found in all trials, except for the sulphate (SO₄²⁻) concentrations. Because free iodine is generated by the chemical reaction of CuSO₄ and KI, an increase in the levels of SO₄²⁻ ions in the treated water was expected, mainly in the form of potassium sulphate (K₂SO₄).

The levels of S²⁻ ions in the liquid swine manure were found to decrease after the addition of SAP and free iodine, achieving removal efficiencies up to 86%. Lower S²⁻ removals (55%) were observed in the diluted supernatants at pH 11. An increase of the

sodium (Na⁺) ions was observed at pH 11 in diluted supernatants because of the pH adjustment using NaOH.

3.6. Sludge depth

The SAP added to the jar test was a dry granular material able to absorb and retain water and suspended solids present in the supernatant. The flocs formed after the SAP addition had a gel appearance. The TSS removal was caused by the adsorption of the colloidal manure particles on the formed gel. The depth of sludge formed was lower than 20 mm per litre of liquid swine manure under different experimental conditions. After the addition of the CupriDyneTM tablets, the sludge depth increased to 18 mm and 30 mm per L of supernatant, for the supernatant at pH 7 and diluted supernatant at pH 11, respectively. Control experiments were performed using alum at 1600 mg/L. A 79% TSS removal efficiency and 375 mm of sludge per L of treated supernatant were found after the alum treatment. The large sludge production is one of the most significant disadvantages of alum relative to PAM [11] or CupriDyneTM technology.

3.7. Toxicity analysis

The Microtox[®] bioassay was used to test the toxicity of the untreated and treated samples. The liquid swine manure was found to be toxic to the *Vibrio fischeri*, therefore, to estimate the inhibitory concentrations (IC), the 6% Microtox[®] basic test was used. In

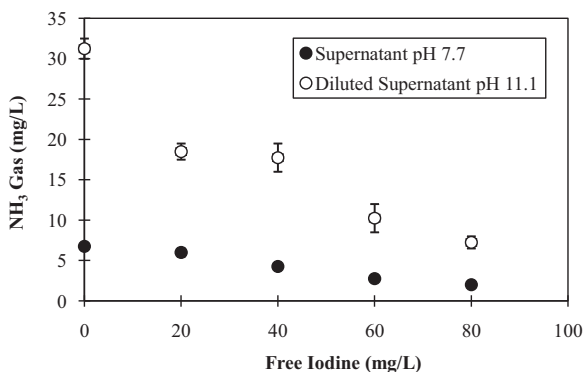


Fig. 5. Effect of free iodine on ammonia gas emissions. Experimental conditions of non-diluted supernatant: NH_{3i} = 6.8 mg/L, pH_i = 7.7, SAP = 1.25 g/L. Experimental conditions diluted supernatant: dilution factor = 1:5, NH_{3i} = 31.3 mg/L, pH_i = 11.1, SAP = 0.5 g/L, standards error = 0.25–1.75 mg/L (n = 3).

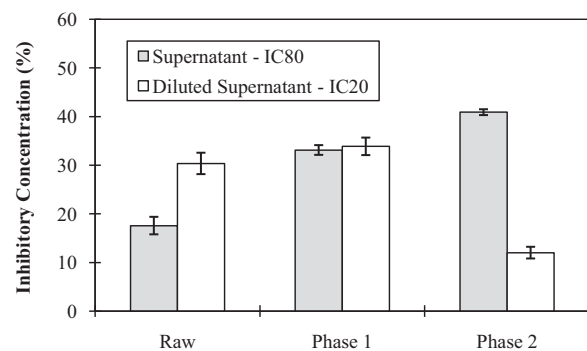


Fig. 6. Inhibition concentration (IC) using 6% Microtox[®] basic test. Experimental conditions non-diluted supernatant: pH_i = 7.7, SAP = 1.25 g/L. Experimental conditions diluted supernatant: dilution factor = 1:5, pH_i = 11.1, SAP = 0.5 g/L, standards error = 1.0–2.2% (n = 3).

Table 3
Concentration of main ions before and after treatment^a.

Ion (mg/L)	Supernatant ^b			Diluted supernatant (1:5) ^b		
	Raw waste	After Phase 1	After Phase 2	Raw waste	After Phase 1	After Phase 2
Anions						
Chloride	760.8 ± 85.5	611.8 ± 98.4	486.6 ± 55.6	192.1 ± 53.0	189.8 ± 54.8	100.3 ± 20.8
Nitrite	9.1 ± 0.1	6.7 ± 0.3	4.5 ± 0.1	1.5 ± 0.4	1.4 ± 0.3	0.7 ± 0.1
Bromide	6.9 ± 0.4	2.2 ± 0.5	0.1 ± 0.01	1.1 ± 0.01	0.9 ± 0.02	0.3 ± 0.05
Nitrate	7.0 ± 0.8	5.2 ± 0.2	3.1 ± 0.4	0.9 ± 0.06	0.4 ± 0.02	0.3 ± 0.03
Phosphate	111.5 ± 13.7	105.4 ± 11.4	79.7 ± 12.8	17.3 ± 1.6	15.2 ± 2.4	9.5 ± 0.5
Sulphate	7.1 ± 0.4	38.3 ± 1.2	54.3 ± 2.8	27.6 ± 3.5	32.3 ± 3.5	108.7 ± 5.8
Sulphide	21.1 ± 4.2	7.3 ± 0.5	3.0 ± 0.3	0.7 ± 0.5	0.6 ± 0.01	0.3 ± 0.03
Cations						
Sodium	484.6 ± 22.3	398.1 ± 25.8	322.6 ± 11.6	1241.3 ± 87.8	1226.5 ± 56.3	674.0 ± 43.9
Potassium	1003.7 ± 14.9	965.7 ± 12.9	782.9 ± 20.9	204.3 ± 20.6	197.5 ± 37.9	160.5 ± 19.0
Magnesium	12.56 ± 0.9	11.57 ± 0.3	9.21 ± 0.1	35.61 ± 0.9	7.49 ± 0.6	5.62 ± 0.5
Calcium	155.7 ± 15.1	122.8 ± 11.9	72.0 ± 9.8	18.7 ± 0.8	16.9 ± 0.6	11.0 ± 0.6

^a Phase 1: addition of SAP to the liquid swine manure; Phase 2: addition of free iodine under optimum SAP doses.

^b Mean ± standard deviation, $n = 3$. Experiments performed using different raw manure samples.

Table 4
Leaching of major ions after 48 h^a.

Trace element (mg/L)	Supernatant pH 7		Diluted supernatant (1:5) pH 11	
	Sludge after Phase 2 ^b	% of leaching after 48 h	Sludge after Phase 2 ^b	% of leaching after 48 h
Chloride	274.3 ± 34	24.4	91.8 ± 20.6	12.0
Nitrite	4.6 ± 0.3	0.0	0.8 ± 0.05	1.5
Bromide	6.7 ± 0.5	0.3	0.9 ± 0.06	ND ^c
Nitrate	3.8 ± 0.6	1.0	0.6 ± 0.04	0.8
Phosphate	31.8 ± 10.6	49.7	7.8 ± 0.6	131.9
Sodium	162.0 ± 14.2	18.4	567.3 ± 56.6	16.0
Ammonium	529.5 ± 24.8	5.1	106.9 ± 21.2	0.5
Potassium	220.8 ± 18.0	21.4	43.8 ± 9.8	40.4
Magnesium	3.4 ± 0.3	14.0	30.0 ± 3.6	1.7
Calcium	83.7 ± 2.6	5.3	7.8 ± 0.4	31.8

^a Phase 1: addition of SAP to the liquid swine manure; Phase 2: addition of free iodine under optimum SAP doses.

^b Mean ± standard deviation, $n = 3$.

^c ND: not detected.

the 6% basic test, the luminescent bacterium is exposed to a range of concentrations of the material being tested, up to a concentration of 6% (vol). The results indicated that the percentage of inhibition of the luminescent bacteria decreased with increased free iodine concentrations. At pH 7 and using 40 mg/L of free iodine, the level of inhibition was 92%. The percentage of inhibition in the diluted samples increased with increasing iodine concentrations. Control tests were performed using free iodine dissolved in ultrapure water. These tests showed that free iodine had inhibition effects on the *Vibrio fischeri*. Free iodine residue in the diluted samples may inhibit the luminescent bacteria, showing an increment of inhibition levels.

As illustrated in Fig. 6, the IC_{80} for the non-diluted supernatant increased after treatment, indicating a reduction of the toxicity of the samples after treatment. The IC_{20} of the diluted samples decreased after treatment mainly because of the residual iodine concentration.

3.8. Leaching results

Because of the potential contamination due to nutrient leaching after sludge disposal, this study evaluated the possible leaching of nutrients and major ions from the sludge generated after treatment. Table 4 shows the levels of ions in the sludge after SAP and iodine additions. After treatment, the sludge contained high levels of chloride (Cl^-), Na^+ , and ammonium (NH_4^+) ions. Fig. 7 shows the levels of the TOC in the ultrapure water after several hours of contact with the sludge. The results indicate an increment in the TOC in the ultrapure water. In addition, NO_2^- , NO_3^- , and NH_3 were detected at very low concentrations or not detected in the ultrapure

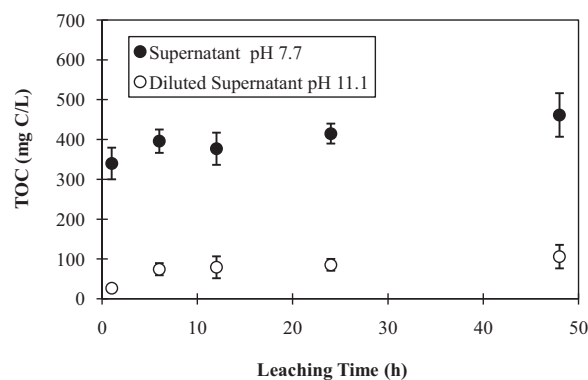


Fig. 7. Level of TOC in the ultrapure water after contact with the manure sludge following the physico-chemical treatment. Experimental conditions non-diluted supernatant: $pH_1 = 7.7$, $SAP = 1.25$ g/L. Experimental conditions diluted supernatant: dilution factor = 1:5, $pH_1 = 11.1$, $SAP = 0.5$ g/L, standards error = 6.9–39.0 mg/L ($n = 3$).

water after 48 h. The results of this study indicate that Cl^- , PO_4^{3-} , Na^+ , potassium (K^+), and magnesium (Mg^{2+}) could be released into the environment from deposited manure sludge generated from physicochemical treatment of liquid swine manure.

4. Conclusions

Separation of suspended solids and nutrients from liquid swine manure is a critical step in the management of animal manure. In this study, liquid swine manure was treated by physical–chemical treatment, including coagulation and flocculation, followed by sed-

imentation and oxidation at a bench scale level. CupriDyne™ superabsorbent polymer and CupriDyne™ tablets were used as coagulant and disinfectant agents, respectively, applied at different phases. A reduction of 44% in TSS was achieved after application of 1.25 g/L SAP followed by 40 mg/L of free iodine. Meanwhile, 91% of the initial TSS was removed using 0.5 g/L SAP and 80 mg/L of free iodine in experiments using diluted supernatant (five-fold dilution) at pH 11. Reduction of TP, BOD, COD and total coliforms were also noted after treatment. Reduced sludge production was found after the physico-chemical treatment. From the leaching tests, PO₄³⁻ and Cl⁻ ions were found in the ultrapure water after 48 h. Potential contamination due to leaching of NH₃, NO₂⁻ and NO₃⁻ was found to be statistically insignificant. The results obtained suggest that the CupriDyne™ technology may be a very effective alternative to existing liquid manure handling methods in terms of nutrient, TSS, and total coliform reductions. Tests at a large-scale level need to be performed to confirm the treatment efficacy.

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References

- [1] S. Sakar, K. Yetilmezsoy, E. Kocak, Anaerobic digestion technology in poultry and livestock waste treatment—a literature review, *Waste Manage. Res.* 27 (2009) 3–18.
- [2] M. Girard, J. Nikiema, R. Brzezinski, G. Buelna, M. Heitz, A review of the environmental pollution originating from the piggery industry and of the available mitigation technologies: towards the simultaneous biofiltration of swine slurry and methane, *Can. J. Civ. Eng.* 36 (2009) 1946–1957.
- [3] M.R. McLaughlin, J.P. Brooks, A. Adeli, Characterization of selected nutrients and bacteria from anaerobic swine manure lagoons on sow, nursery, and finisher farms in the Mid-South USA, *J. Environ. Qual.* 38 (2009) 2422–2430.
- [4] M.H. Chantigny, J.D. MacDonald, C. Beaupré, P. Rochette, D.A. Angers, D. Massé, L.E. Parent, Ammonia volatilization following surface application of raw and treated liquid swine manure, *Nutr. Cycl. Agroecosyst.* 85 (2009) 275–286.
- [5] J.A. Oleszkiewicz, Changes in hog manure in a flow-through anaerobic storage tank, *Environ. Technol.* 21 (2000) 597–600.
- [6] C.M. Williams, Development of environmentally superior technologies in the US and policy, *Bioresour. Technol.* 100 (2009) 5512–5518.
- [7] M. Hjorth, K.V. Christensen, M.L. Christensen, S.G. Sommer, Solid–liquid separation of animal slurry in theory and practice. A review, *Agron. Sustain. Dev.* 30 (2010) 153–180.
- [8] P.M. Ndegwa, J. Zhu, A. Luo, Effects of solid levels and chemical additives on removal of solids and phosphorus in swine manure, *J. Environ. Eng.* 127 (2001) 1111–1115.
- [9] K. Zhu, M. Gamal El-Din, A.K. Moawad, D. Bromley, Physical and chemical processes for removing suspended solids and phosphorus from liquid swine manure, *Environ. Technol.* 25 (2004) 1177–1187.
- [10] D.M. Sievers, M. Jenner, M. Hanna, Treatment of dilute manure wastewaters by chemical coagulation, *Trans. ASAE* 37 (1994) 597–601.
- [11] M.B. Vanotti, P.G. Hunt, Solids and nutrient removal from flushed swine manure using polyacrylamides, *Trans. ASAE* 42 (1999) 1833–1840.
- [12] M.C. García, A.A. Szogi, M.B. Vanotti, J.P. Chastain, P.D. Millner, Enhanced solid–liquid separation of dairy manure with natural flocculants, *Bioresour. Technol.* 100 (2009) 5417–5423.
- [13] G.A. Sincero, A.P. Sincero, *Physical–Chemical Treatment of Water and Wastewater*, IWA Publishing, CRC Press, Boca Raton, Florida, 2003.
- [14] J.C. Crittenden, R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, *Water Treatment Principles and Design*, second ed., John Wiley & Sons Inc., Hoboken, New Jersey, 2005.
- [15] S. Punyani, P. Narayana, H. Singh, P. Vasudevan, Iodine based water disinfection: a review, *J. Sci. Ind. Res.* 65 (2006) 116–120.
- [16] APHA, *Standard Methods for the Examination of Water and Wastewater*, twenty-first ed., American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, 2005.
- [17] V.L.K. Jennings, M.H. Rayner-Brandes, D.J. Bird, Assessing chemical toxicity with the bioluminescent photobacterium (*Vibrio fischeri*): a comparison of three commercial systems, *Water Res.* 35 (2001) 3448–3456.
- [18] S.S. Parvez, C. Venkataraman, S. Mukherji, A review on advantages of implementing luminescence inhibition test (*Vibrio fischeri*) for acute toxicity prediction of chemicals, *Environ. Int.* 32 (2006) 265–268.
- [19] J.P. Chastain, M.B. Vanotti, M.M. Wingfield, Effectiveness of liquid–solid separation for treatment of flushed dairy manure: a case study, *Appl. Eng. Agric.* 17 (2001) 343–354.
- [20] Y.C. Gao, P.H. Liao, K.V. Lo, Chemical treatment of swine wastewater, *J. Environ. Sci. Health A* 28 (1993) 795–807.
- [21] T.D. Reynolds, P.A. Richards, *Unit Operations and Processes in Environmental Engineering*, second ed., PWS Publishing Company, Boston, 1996.
- [22] M. Choudhary, L.D. Bailey, C.A. Grant, Review of the use of swine manure in crop production: effects on yield and composition and on soil and water quality, *Waste Manage. Res.* 14 (1996) 581–595.
- [23] E. Meers, D.P.L. Rousseau, E. Lesage, E. Demeersseman, F.M. Tack, Physico-chemical P removal from the liquid fraction of pig manure as an intermediary step in manure processing, *Water Air Soil Poll.* 169 (2006) 317–330.
- [24] G. Tchobanoglous, F.L. Burton, D.H. Stensel, *Wastewater Engineering: Treatment, Disposal, and Reuse*, fourth ed., McGraw-Hill, New York, 2003.
- [25] D.M. Sievers, Rapid mixing influences on chemical coagulation of manures, *Biol. Wastes* 28 (1989) 103–114.
- [26] American Water Works Association (AWWA), in: R.D. Letterman (Ed.), *Water Quality and Treatment. A Handbook of Community Water Supplies*. American Water Works Association, fifth edition, McGraw-Hill Inc, New York, 1999.
- [27] R. Sivamohan, J.M. Cases, Dependence of shear-flocculation on surface coverage and zeta potential, *Int. J. Miner. Process.* 28 (1990) 161–172.
- [28] C.L. de Vasconcelos, K.T. de Moura, W.A. Morais, T.N.C. Dantas, M.R. Pereira, J.L.C. Fonseca, Dispersing phase viscometry and zeta potential in alumina dispersions, *Colloid Polym. Sci.* 283 (2005) 413–420.
- [29] P. Walker, T. Kelley, Solids, organic load and nutrient concentration reductions in swine waste slurry using a polyacrylamide (PAM)-aided solids flocculation treatment, *Bioresour. Technol.* 90 (2003) 151–158.
- [30] M.K. Manisseri, K.M. Spann, R.J.G. Leste, Iodine as a disinfectant against Monodon Baculovirus (MBV), *Asian Fish. Sci.* 12 (1999) 105–111.
- [31] E.J. Wagner, R.E. Arndt, E.J. Billman, A. Forest, W. Cadender, Comparison of the efficacy of iodine, formalin, salt, and hydrogen peroxide for control of external bacteria on rainbow trout eggs, *N. Am. J. Aquacul.* 70 (2008) 118–127.
- [32] H. Backer, J. Hollowell, Use of iodine for water disinfection: iodine toxicity and maximum recommended dose, *Environ. Health Perspect.* 108 (2000) 679–684.
- [33] W. Gottardi, Iodine and disinfection: theoretical study on model of action, efficiency, stability and analytical aspects in the aqueous systems, *Arch. Pharm. Pharm. Med. Chem.* 332 (1999) 151–157.
- [34] M.B. Vanotti, P.D. Millner, P.G. Hunt, A.Q. Ellison, Removal of pathogen and indicator microorganism from liquid swine manure in multi-step biological and chemical treatment, *Bioresour. Technol.* 96 (2005) 209–214.
- [35] A.C. VanderZaag, R.J. Gordon, R.C. Jamieson, D.L. Burton, G.W. Stratton, Effects of winter storage conditions and subsequent agitation on gaseous emissions from liquid dairy manure, *Can. J. Soil Sci.* 90 (2010) 229–239.
- [36] D.F. McCrory, P.J. Hobbs, Additives to reduce ammonia and odour emissions from livestock wastes: a review, *J. Environ. Qual.* 30 (2001) 345–355.
- [37] B. Predicala, M. Nemat, S. Stade, C. Laguë, Control of H₂S emissions from swine manure using Na-nitrite and Na-molybdate, *J. Hazard. Mater.* 154 (2008) 300–309.
- [38] S.R. Lee, J.K. Han, Y.J. Choi, K. Nam, Reduction of ammonia and hydrogen sulphide emissions from swine manure using aqueous foams amended with microorganism and chemical additives, *Clean* 35 (2007) 230–234.