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Appraisal and ranking of poly-aluminium chloride, ferric chloride and alum for the treatment of dairy soiled water

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Abstract

Land spreading of dairy soiled water (DSW) may result in pollution of ground and surface waters. Treatment of DSW through sludge-supernatant separation using chemical coagulants is a potential option to reduce the negative environmental impacts of DSW. The aims of this study were to (1) assess the effectiveness of three chemical coagulants – poly-aluminium chloride (PACl), ferric chloride ($FeCl_3$) and alum – in improving effluent quality, and (2) assess the properties of the sludge that is generated as by-product from the process for its suitability for land application. Taking into consideration optimum doses to minimize pollutants (turbidity, chemical oxygen demand (COD), total phosphorus (TP), total nitrogen (TN), and *E. coli*), optimum mixing times and cost, $FeCl_3$ was the best performing coagulant. Generated sludges had higher nutrient content and fewer *E. coli* than raw DSW, and did not display any

evidence of phytotoxicity to the growth of *Lolium perenne* L. using germination tests. The study discussed the results in a sustainable farm management context, and suggested that the effluent (supernatant) from the treatments may be recycled to wash farm yards, saving water. In parallel, the sludge portion can be applied to amend soil properties with no adverse impacts on the grass growth, providing an agronomic value as an organic fertilizer, and reducing the risk of nutrient losses. This management approach could minimize the overall net cost compared to land application of raw DSW.

Keywords: dairy soiled water, coagulation, agricultural wastewater treatment, ecology, soil science, phytotoxicity.

1. Introduction

Global demand for food and agricultural products is increasing rapidly to meet the increase in global population. Sustainable intensification of agriculture is required to meet this demand, while taking into consideration measures to lessen any negative environmental impacts associated with this expansion. In Ireland, dairy farming is a key agricultural and economic sector, as dairy products represent one third of all Irish agri-food exports (Irish Food Board, 2019). The removal of milk quota restrictions, coupled with ambitious agricultural production targets (e.g. Food Wise 2025; Department of Agriculture, Food and Marine, 2015), has resulted in an increase in the size of dairy herds and increased volumes of dairy soiled water (DSW) – the effluent from the milking parlour, collecting yards, roadways, and other hard-standing areas, which consists of a dilute mixture of cow faeces, urine, milk, detergents, and sediment.

Like many other countries, land application is the primary disposal method for DSW in Ireland (Minogue et al., 2015). Dairy soiled water is typically applied to land either through tankers with splash-plates, or using travelling irrigators. Unlike cattle slurry, DSW can be applied to the land throughout the entire year (S.I. No. 605 of 2017). However, the spreading rate is limited to 50,000 L ha^{-1} in any 6-week period or 5 mm hr^{-1} (S.I. No. 605 of 2017). According to Minogue et al. (2011), the nitrogen (N) fertilizer replacement value (NFRV) of DSW is 72 - 90 %, which indicates that DSW should be viewed as an organic fertilizer, as opposed to a waste, and has the capacity to replace inorganic fertilizers and offer cost savings.

However, DSW is potentially a significant source of pollutants and there are risks associated with inappropriate land application, such as contamination of groundwater or deterioration in surface water quality (Knudsen et al., 2006). In addition to potentially negative environmental impacts, the land application of DSW incurs substantial costs for dairy farmers, as legalisation (S.I. No. 605 of 2017) requires that infrastructure (with a storage capacity of 15 days) is required to store DSW before land application. Furthermore, spreading DSW by tankers incurs an additional cost of an estimated € 1.55 m^{-3} (Fenton et al., 2011). These costs, combined with the negative environmental impacts, make land application an unsustainable method of disposal if it is not well-managed.

Treatment and reuse of DSW may be a more sustainable option for farmers, with methods such as integrated constructed wetlands (ICWs) (Scholz et al., 2007; Harrington and Mclness, 2009) and intermittent sand filters (ISFs) (Murnane et al., 2016) proving to be cost-efficient and sustainable. Addition of chemical coagulants such as aluminium and ferric salts to amend DSW properties prior to land application, may also have potentially good phosphorus (P) sequestration potential and reduces the risks of nutrient losses (Fenton et al., 2011; Serrenho et al., 2012), and may also be effective in the abatement of greenhouse gas (GHG) and ammonia (NH_3) emissions (Kavanagh et al., 2019). The chemically treated DSW may be subsequently separated into two streams, supernatant and sludge, following settlement. The supernatant may undergo further treatment in ICWs or ISFs, which will require less surface area for treatment, as the supernatant stream has less organic matter (OM) and P. In addition, the problems of regular ponding of sand filters or wetlands will be reduced substantially, because the supernatant has fewer suspended solids (SS). Similarly, the sludge portion of the treated DSW, which is enriched in nutrients and P-sorbing coagulants, may be applied directly to land with less transportation cost and fewer risks of nutrient losses. Chemical amendments to soil by the land application of metal-rich sludges and waste material do not harm soil quality or the environment. For example, Moore and Edwards (2005) studied the long-term effects of alum-treated litter on aluminium (Al) availability in soils, and found that alum did not negatively affect either the Al concentrations in the soil or Al uptake by forage, and speculated that it would take up to 400 years to increase the level of total Al in the soil by 1%.

The continued expansion of the dairy industry is placing increased pressure on farm infrastructure for the management and storage of DSW that is generated in large volumes. The current disposal method of land spreading is costly, and can result in pollution of receiving waters. Therefore, the objective of this work was to assess the feasibility of using chemical coagulants to minimise OM, nutrients (N and P) and pathogens in DSW, while generating sludge suitable for land application. To meet this objective, this study aimed to (1) assess and compare the efficacy of various chemical coagulants in improving effluent quality parameters (2) identify the optimum coagulant and dose, and suitable contact time of mixing (3) evaluate the properties of the generated sludge for its suitability for land application in terms of nutrient and pathogen content, and its potential toxicity to plants, and (4) evaluate the cost of using these coagulants to achieve greatest effluent quality.

2. Materials and methods

2.1 Sample collection

A bulk sample of 150 L of DSW was collected from Moorepark Dairy farm, Fermoy, Co. Cork, Ireland (52˚09'42.0"N 8˚15'09.7"W). In order to obtain a representative sample, DSW was collected over three days during morning and evening milking events, and comprised water generated by washing the yard and the hard standing area, and cleaning the milking plant. The DSW was stored at 4 ˚C until testing commenced, which was no longer than three days after sample collection. The properties of the collected sample (raw DSW) are shown in Table 1. Raw DSW was regarded as a study control of the experiment.

Table 1 Raw dairy soiled water characteristics (control).

Parameter	Units	Mean ± standard deviation
pH		7.15 ± 0.17
Temperature	˚C	14.40 ± 2.87
Turbidity	NTU	6550 ± 415
Chemical oxygen demand (COD)	mg L^{-1}	10410 ± 866
Total nitrogen (TN)	mg L^{-1}	259.75 ± 11.78
Ammonium (NH_4-N)	mg L^{-1}	161.81 ± 5.50
Total phosphorous (TP)	mg L^{-1}	43.40 ± 1.66
Dissolved reactive phosphorus (DRP)	mg L^{-1}	33.16 ± 2.70
Dry matter (DM)	%	1.0 ± 0.11
E. coli	MPN 100 ml^{-1}	$4.76 \times 10^{7*}$

* Lower 95% confidence interval (CI) = 2.70×10^7 (MPN 100 ml^{-1}), upper 95% confidence interval (CI) = 7.70×10^7 (MPN 100 ml^{-1}).

2.2 Experimental set up

Three coagulants that are commonly used in water and wastewater treatment were examined in the study – poly-aluminium chloride (PACl) (18% Al_2O_3), ferric chloride ($FeCl_3$) (40% w/w) and aluminium sulphate ($Al_2 (SO_4)_3$) (8% Al_2O_3). All coagulants were in liquid form to ensure full mixing with the DSW. One litre of raw DSW was placed in separate glass jars, which were subsequently treated with one of the three chemical coagulants (Table S1) at different stoichiometric rates of addition (Table 2). Dosages were selected to achieve the maximum possible removal efficiencies of water quality parameters by the coagulants.

Table 2 Addition rates of coagulants expressed in different stoichiometric forms.

Coagulant	Stoichiometric parameter	Dose			
		ml L^{-1}	mg L^{-1}	g kg^{-1} dry matter	g g^{-1} P
PACl	Al	1	125	12.5	2.88
	Al	2	250	25.0	5.76
	Al	3	375	37.5	8.64
$FeCl_3$	Fe	1	235	23.5	5.41
	Fe	2	470	47.0	10.83
	Fe	3	705	70.5	16.24
$Al_2(SO_4)_3$	Al	2	112	11.2	2.58
	Al	3	168	16.8	3.87
	Al	5	280	28.0	6.45

Cylindrical stir bars with a size 50 x 8 mm (ThermoFisher Scientific, USA) were placed at the base of each container and rotated at a velocity gradient (G) of 650 s^{-1}, for defined mixing times (5, 10 or 15 min), using digital magnetic stir plates (RT Touch Series, ThermoFisher Scientific, USA). Following mixing, the treated DSW was allowed to settle for three hours. Each experimental condition was replicated three times (n=3). The fully-factorial design resulted in a total of 81 individual batch tests.

2.3 Analytical method

Following the settling phase, 250 ml of supernatant was decanted from the treated DSW, and analysed for pH, temperature, turbidity, chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), dissolved reactive phosphorus (DRP), ammonium (NH_4-N), dry matter (DM), and *E. coli*. Temperature and pH were measured using an HQ40d Multi Meter (HACH, USA), and turbidity was measured using a portable turbidity meter (Orion AQUAfast AQ3010, ThermoFisher Scientific, USA) and expressed as Nephelometric Turbidity Units (NTU). Samples for COD were preserved at -20 ˚C until analysis and samples for TN, TP, NH_4-N and DRP were preserved at 4 ˚C until analysis. COD was measured using the dichromate method. Total nitrogen and TP were measured using the Persulphate Oxidative Digestion method, and DRP and NH_4-N were analysed spectrophotometrically, following filtration through 0.45 µm filters, using a nutrient analyser (Aquakem 600A/ Konelab 60, Thermo Clinical Labsystems, Vantaa, Finland). For detection and enumeration of *E. coli* (analysed as an indicator for the presence of pathogenic microorganisms), samples were stored at 4 ˚C for a maximum of 48 h before analysis using the Colilert-24 method, as per the manufacturer's guidelines (IDEXX Laboratories, Westbrook, Maine, US). Dry matter content was measured by drying samples at 105 ˚C for 24 h. All water quality parameters were tested in accordance with the standard methods (APHA, 2005).

The removal efficiency of each parameter per treatment was calculated using:

$$Removal\ efficiency\ (R)\% = \frac{C_{Raw\ DSW} - C_{Supernatant}}{C_{Raw\ DSW}} \qquad (1)$$

Where $C_{Raw\ DSW}$ is the influent concentration (mg L^{-1}) of a specific water quality parameter before treatment and $C_{supernatant}$ is its effluent concentration (mg L^{-1}) after treatment.

2.4 Sludge properties

The sludges (n=9, 3 coagulants x 3 doses) were collected at the end of the mixing experiment and stored at 4 ˚C. Sludge was characterized by DM content, pH, *E. coli* and nutrient content, and germination index (GI) (to examine the toxicity of certain composts after amendment to soil). Theoretical sludge volumes were calculated using a mass balance equation:

$$DM_{Raw\ DSW} * V_{Raw\ DSW} + DM_{Coagulant} * V_{Dose} = DM_{Sludge} * V_{Sludge} + DM_{Supernatant} * V_{Supernatant} \quad (2)$$

Where V denotes the volume (L) and DM is the dry matter (%).

The TN and TP content of sludge were also calculated using mass balance equations (Eqn. 3 and Eqn. 4). The equations assumed the removal mechanism of nutrients through coagulants is by precipitation/sedimentation only.

$$TP_{Raw\ DSW} * V_{Raw\ DSW} = TP_{Sludge} * V_{Sludge} + TP_{Supernatant} * V_{Supernatant} \quad (3)$$

$$TN_{Raw\ DSW} * V_{Raw\ DSW} = TN_{Sludge} * V_{Sludge} + TN_{Supernatant} * V_{Supernatant} \quad (4)$$

2.5 Phytotoxicity test- germination index

Seed germination and root elongation tests were carried out as described by Troy et al. (2012). The tests (n=3 replicates) were performed by mixing 300 g of soil with 100 g (wet weight) of corresponding treatment, i.e. the PACl, $FeCl_3$, and alum sludges and control (distilled water), giving a w/w ratio of 75:25, respectively. The soil was collected from Moorepark, Fermoy, Co. Cork, Ireland (52˚09'47.7"N 8˚15'08.8"W), and sieved through a 2 mm mesh. The soil pH was

7.3, and had available P, potassium (K) and magnesium (Mg) of 26.6, 141, and 75 mg/l, respectively. The soil texture was clay loam, and consisted of 41 % sand (2.00 - 0.063 mm), 30 % silt (0.063 - 0.002 mm), and 29 % clay (< 0.002 mm). Ten seeds of *Lolium perenne* L. (variety: Astonenergy) were placed in square plastic petri dishes (120 × 15 mm), inclined at 80-90° to the horizontal plane, with seeds in the bottom side, each containing 133 g of the prepared mixture. In total, there were 30 petri dishes, which included three controls of distilled water. The petri dishes were germinated at 25.5 ± 0.5 ˚C in darkness, to facilitate the growth of seeds. The numbers of seeds germinated were counted and the lengths of the roots were measured after 2, 4 and 5 days. Germination was defined as a primary root of ≥ 5 mm and the measurements were performed when at least 65 % of the control seeds germinated and developed roots that were at least 20 mm long (USEPA, 1996). Seedling performance was assessed using the relative seed germination (RSG) (Eqn. 5) after Zucconi et al. (1981).

$$\text{Relative seed germination (RSG)(\%)} = \frac{\text{number of seeds germinated in treated soil}}{\text{number of seeds germinated in control soil}} \times 100 \qquad (5)$$

The relative root growth (RRG) (Eqn. 6), after Zucconi et al. (1981), compares the % root growth of seeds of amended soil with different treatments to the % root growth of seeds present in the control soil.

$$\text{Relative root growth (RRG)(\%)} = \frac{\text{mean root length in treated soil}}{\text{mean root length in control soil}} \times 100 \qquad (6)$$

The GI test (Eqn. 7), after Tiquia et al. (1996), gives an overall percentage based on the RSG and RRG calculated.

$$\text{Germination index (GI)(\%)} = \frac{\text{RSG x RRG}}{100} \qquad (7)$$

2.6 Statistical Analysis

Statistical analyses were carried out using SAS 9.4 (SAS Institute Inc., USA). Statistical differences in water quality parameters between the different coagulants, doses, and mixing times were tested using a generalized linear mixed modelling procedure (PROC GLIMMIX). The model was designed as a three-factor factorial experiment (3*3*3) with three replications, consisting of three categorical independent variables (coagulant, dose, mixing time). The main effects of each factor, along with interaction effects, were investigated by the model against each water quality parameter, which was set as a continuous dependent variable in the model. A reduced model was then run where non-significant higher order interactions were dropped. In addition, the model was extended to include multiple pairwise comparisons on main effects, as well as interactions using LSMEANS statement and adjusted by Post-hoc Tukey's procedure or Dunnett's procedure, whenever comparisons were made to the study control (raw DSW).

Statistical differences in sludge properties (between different sludges) were analysed by a one-way analysis of variance (ANOVA). Pairwise comparisons were carried out using Post-hoc Tukey's procedure or Dunnett's procedure, whenever comparisons were made to the study control (raw DSW). Statistical differences in germination indices between different treated soils (including the control soil) were tested separately for day 4 and day 5 using a one-way analysis of variance (ANOVA). Pairwise comparisons between individual treatments (including the control soil) were carried out separately for day 4 and day 5 using Post-hoc Tukey's procedure following each ANOVA. Following this, the model was extended to a two-way analysis of variance (ANOVA) to study the main effect of day and interaction of day*treatment on germination indices. PROC UNIVARIATE was used in the models to validate the assumptions of variances homogeneity and normality of data. In the case of unequal variances, the data were log transformed before statistical analysis was conducted and reverse transformed into geometric means for reporting. SAS was used for computing and testing correlation coefficients between different water quality parameters using PROC CORR.

2.7. Cost-benefit analysis

The treatment cost was calculated based on the estimated cost of coagulants, delivery, and mixing. Additional costs are required after coagulant treatment to dispose of the sludge produced (spreading costs € 1.55 m^{-3}; Fenton et al., 2011). However, savings may be obtained by recycling the supernatant to wash the farm yard (water costs € 1.87 m^{-3}; Irish Water, 2019). These costs are calculated in Eqns. 8 to 11.

$$Total\ cost\ (€\ m^{-3}\ DSW) = Treatment\ cost\ (€\ m^{-3}\ DSW) + Sludge\ handling\ cost\ (€\ m^{-3} DSW) \tag{8}$$

$$Sludge\ handling\ cost\ (€\ m^{-3} DSW) = Sludge\ volume\ (\%) * 1.55\ (€\ m^{-3}\ DSW) \tag{9}$$

$$Overall\ net\ cost\ (€\ m^{-3} DSW) = Total\ cost\ (€\ m^{-3} DSW) - Benefit\ cost\ (€\ m^{-3} DSW) \tag{10}$$

$$Benefit\ cost\ (€\ m^{-3} DSW) = Supernatant\ volume\ (\%) * 1.87\ (€\ m^{-3}\ DSW) \tag{11}$$

The percentages of sludge and supernatant may differ at field scale. Nevertheless, the total cost was calculated for a dairy farm consisting of 100 cows for one year based on the results of the batch tests, assuming a production rate of 10,000 L of DSW per cow per year (Minogue et al., 2015). Furthermore, the predictive model of cost estimation did not account for the cost that will be incurred by the post-treatment step to polish the effluent, and did not consider the benefit cost that could be recovered by the sludge in replacing synthetic fertilizers and assisting grass growth. Overall, the feasibility of coagulants was determined based on the cost of implementation, effectiveness, and the volume of sludge generated.

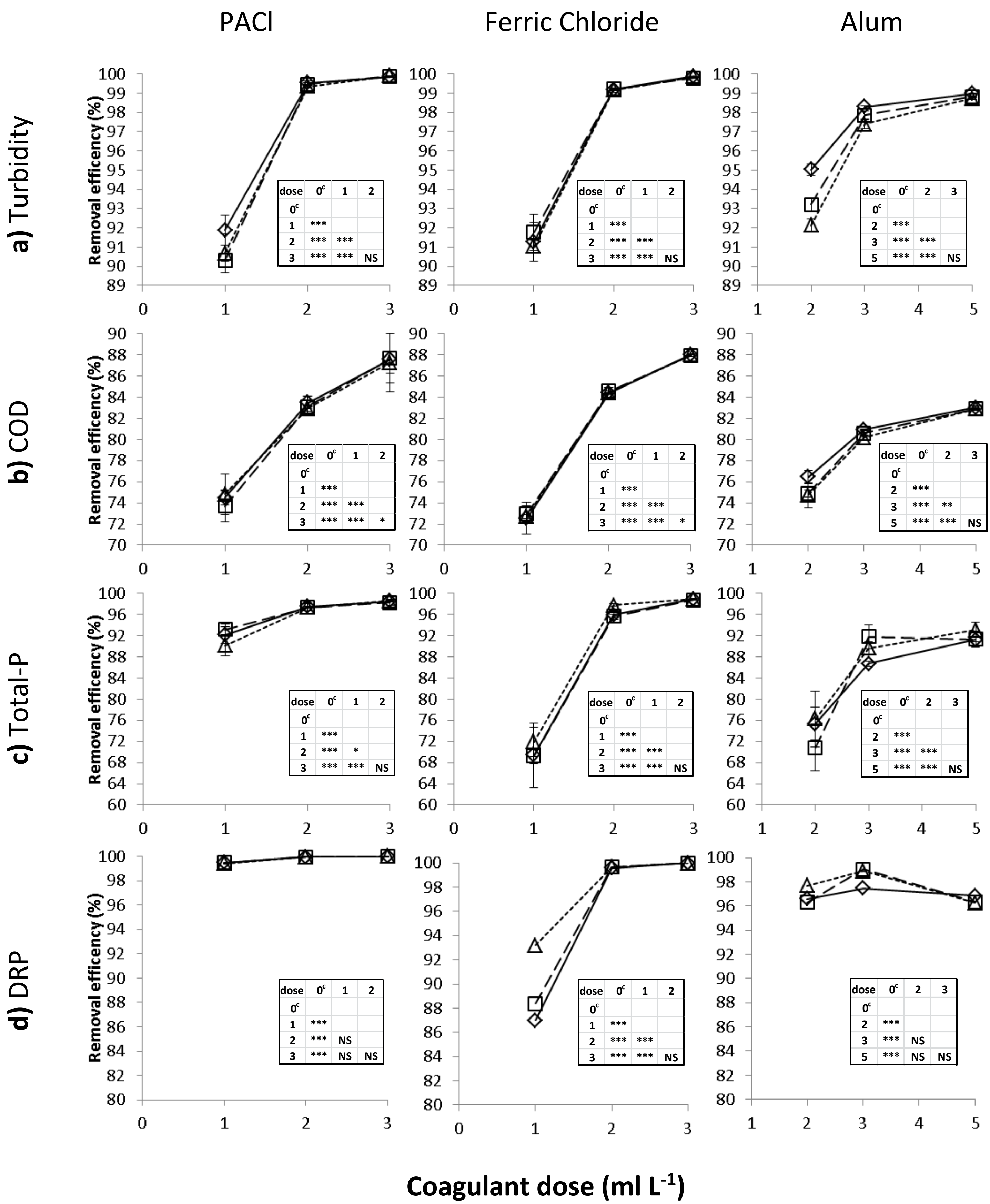
3. Results and Discussion

3.1 Effect of coagulants on the removal of water quality parameters

3.1.1. Turbidity and organic matter removal

Turbidity was reduced significantly ($P < 0.0001$) from 6550 NTU in the raw DSW to a minimum of 6, 10, and 67 NTU for PACl, $FeCl_3$ and alum, respectively, at their highest doses (representing a reduction ≥ 99% in turbidity) (Figure 1-a). There were no statistical differences between coagulants ($P = 0.9836$). Cameron and Di (2019) obtained similar removals using poly-ferric sulphate coagulant to treat DSW at optimum dosage of 214 mg Fe L^{-1}.

Chemical oxygen demand was reduced significantly ($P < 0.0001$) from 10410 mg L^{-1} in the raw DSW to a minimum of 1283, 1245, and 1767 mg L^{-1} for PACl, $FeCl_3$ and alum, respectively, at their highest doses (Figure 1-b). These effluent concentrations were almost 10 times higher than the limit of 125 mg L^{-1} set by the EU Urban Water Discharge Regulations (91/271/EEC; EEC, 1991). Both PACl and $FeCl_3$ achieved a maximum removal of 88 % and performed significantly better than alum ($P < 0.05$), which achieved a maximum removal of 83 %. The removal of COD achieved by alum in this study was higher than that obtained by Hamoda and Al-Awadi (1996), who reported a removal of 55 % for DSW treated with alum at optimum dosage of 200 mg L^{-1} alum. The removal efficiencies of COD achieved in this study were higher than those achieved by other methods of DSW treatment. For example, Ruane et al. (2011) and Murnane et al. (2016) achieved COD removal efficiencies of 66 % and 78 %, respectively, using woodchip filters.


PACl
Ferric Chloride
Alum
a) Turbidity
b) COD
c) Total-P
d) DRP
Removal efficency (%)
Coagulant dose (ml L-1)
dose 0c 1 2
dose 0c 2 3
NS

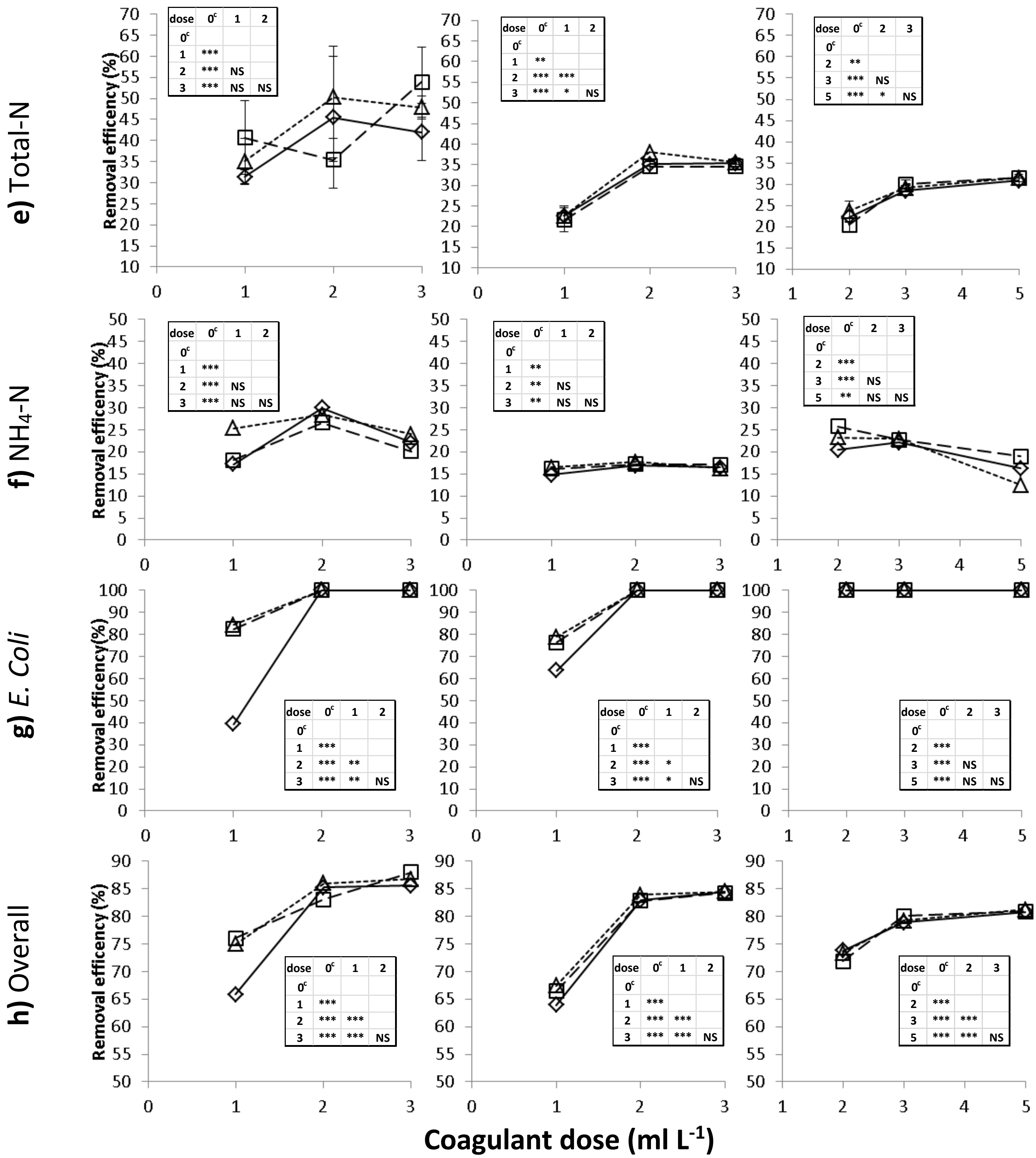


Figure 1 Removal efficiency of turbidity, chemical oxygen demand (COD), total phosphorus (TP) , dissolved reactive phosphorus (DRP), total nitrogen (TN) , NH_4-N, and *E. coli* from DSW after additions of coagulants at different dosage rates and different mixing periods: 5 min mixing (—◇—), 10 min mixing (—□ –), 15 min mixing (---△---). Overall efficiency is an average of Turbidity, COD, TN, TP, and *E. coli*. Statistically significant differences between different doses as well as comparison to control (0^c) for each coagulant are shown at $p < 0.001$ as ***; $p < 0.01$ as **; $p < 0.05$ as * and no significant difference as NS.

There was a strong linear relationship between turbidity and COD (R= 0.98), which suggests the removal of COD was due to the removal of turbidity/SS (results not displayed). The remaining COD in the supernatant/effluent was likely in dissolved form, which can be only removed through the oxidation process (Henze et al., 2008).

3.1.2. Phosphorus removal

Total P was reduced significantly ($P < 0.0001$) from 43 mg L^{-1} in the raw DSW to a minimum of 0.62, 0.48, and 3 mg L^{-1} for PACl, $FeCl_3$ and alum, respectively, at their highest doses. Both PACl and $FeCl_3$ achieved corresponding maximum removals of 99 %, and performed significantly better than alum ($P < 0.001$), which achieved a maximum removal of 93 % (Figure 1-c). The concentration of TP in PACl and $FeCl_3$-treated DSW was below the EU Directive concentration of 2 mg L^{-1} (91/271/EEC; EEC, 1991). There was a strong linear relationship between TP and DRP (R = 0.97) (results not displayed). Therefore, the removal efficiency of DRP by the coagulants had similar trends to TP (Figure 1-d).

The results of TP and DRP were comparable to those achieved by Fenton et al. (2011), who achieved P effluent concentrations less than 1 mg L^{-1} using $FeCl_3$ and alum at corresponding stoichiometric rates of 200 g Fe g^{-1} P and 8.8 g Al g^{-1} P for DSW treatment. The results were also consistent with those of Cameron and Di (2019), who achieved a removal of 99 % for both TP and DRP using poly-ferric sulphate coagulant at an optimum dosage of 214 mg Fe L^{-1}. Other methods of DSW treatment couldn't achieve these targets, and produced poor P removals. For example, Ruane et al. (2011) and Murnane et al. (2016) achieved P removal efficiencies of only 31 % and 50 %, respectively, using woodchip filters. Healy and O' Flynn (2011) surveyed the performance of seven constructed wetlands treating DSW on Irish farms, and reported an average P removal efficiency of only 80 %.

3.1.3. Nitrogen removal

Total nitrogen was reduced significantly ($P < 0.0001$) from 260 mg L^{-1} in the raw DSW to a minimum of 120, 167, and 178 mg L^{-1} for PACl, $FeCl_3$ and alum, respectively, at their highest doses. These were all above the EU Directive concentration of 15 mg L^{-1} (91/271/EEC; EEC, 1991). There were no significant differences between the $FeCl_3$ and alum in the removal of TN ($P=0.1275$), and both achieved a maximum removal of about 35 % (Figure 1-e). PACl performed significantly better than $FeCl_3$ ($P<0.001$) and alum ($P<0.0001$), and achieved a maximum removal of 54 % (Figure 1-e). The remaining N in the effluent/supernatant mainly comprised NH_4-N (about 80-90 %), which suggests that the removal of particulate matter/SS was the main mechanism of coagulants in the removal of N. At optimal performance of the coagulants, NH_4-N concentrations were 115, 135, and 125 mg L^{-1}, respectively, for PACl, $FeCl_3$ and alum, with respective removals of only 30, 15 and 25 % (Figure 1-f).

The coagulants used in the current study produced poor N removals compared to SS and TP removals. Similar to the current study, Cameron and Di (2019) reported a maximum TN removal of 57 %, with a corresponding effluent concentration of 87 mg L^{-1} using poly-ferric sulphate coagulant to treat DSW at optimum dosage of 214 mg Fe L^{-1}. Hamoda and Al-Awadi (1996) achieved NH_4-N removal of only 10% at an optimum dosage of 200 mg L^{-1} alum. The residual N can be only removed either through nitrification/de-nitrification processes or through NH_4-N volatilization at high pH (Henze et al., 2008). Novel bimetallic catalytic methods "metal-on-metal", such as indium-decorated palladium and gold-on-palladium, were proven to be efficient in nitrogen reduction (Guo et al., 2018; Li et al., 2019). However, these methods can't be applied at farm-scale because they require technical knowledge and are sophisticated. Rather, simple methods such as ICWs and ISFs can be introduced as a post-treatment step to polish the remaining N in the effluent.

3.1.4. *E. coli* removal

The coagulants reduced *E. coli* significantly (P < 0.0001) from 4.76×10^7 MPN/100 ml in the raw DSW to a minimum of 63, < 2.2, and 153 MPN/100 ml, respectively, for PACl, $FeCl_3$ and alum at their highest doses. Ferric chloride was more effective than PACl and alum in removing *E. coli* logarithmically (P<0.0001), achieving a complete removal of *E. coli* to below detection limits of the assay (about 7.5 log removal). The removal mechanism of *E. coli* was not likely due to sedimentation/precipitation, because the sludge had lower *E. coli* concentrations than the raw DSW, which indicates there was an overall reduction in *E. coli* as a result of the coagulant, likely to be in the form of dead or damaged cells. This could be due to the acidic nature of coagulants which acted as a toxicant or disinfectant, killing bacteria cells at low pH, or rendering them "viable, but non-culturable" (Xu et al., 1982). This is supported by the current study, as $FeCl_3$ had the lowest pH among all the coagulants (Figure 2-a), which corresponds with the highest removal efficiency of *E. coli* (Figure 2-b). There was a significant linear relationship between decreasing pH and logarithmic removal of *E. coli* (P<0.0001); however, it varied with the type of coagulant (Figure 2-b). For instance, PACl has the capacity to remove 5 log units of *E. coli* per unit reduction of pH, which is 5 times higher than the rate of alum. Similarly, Conner and Kotrola (1995) studied the growth and survival of *E. coli* (Type: O157:H7) under acidic conditions, and found the survival of *E. coli* is pH dependent, but the pH threshold in which *E. coli* survive is varied with the type of acidulant. For example, at 25 $^{\circ}C$, *E. coli* can survive up to pH 5 in mandelic and acetic acids, while it can survive up to pH 4 in tartaric acid.

Considering the high removal of *E. coli* achieved in this study, the effluent can be recycled to wash farm yards and hard standing areas, without imposing health risks to farmers and animals.

This approach could save water use by up to 70%, with external water only being needed only to wash the milking plant, which requires high quality and standard water.

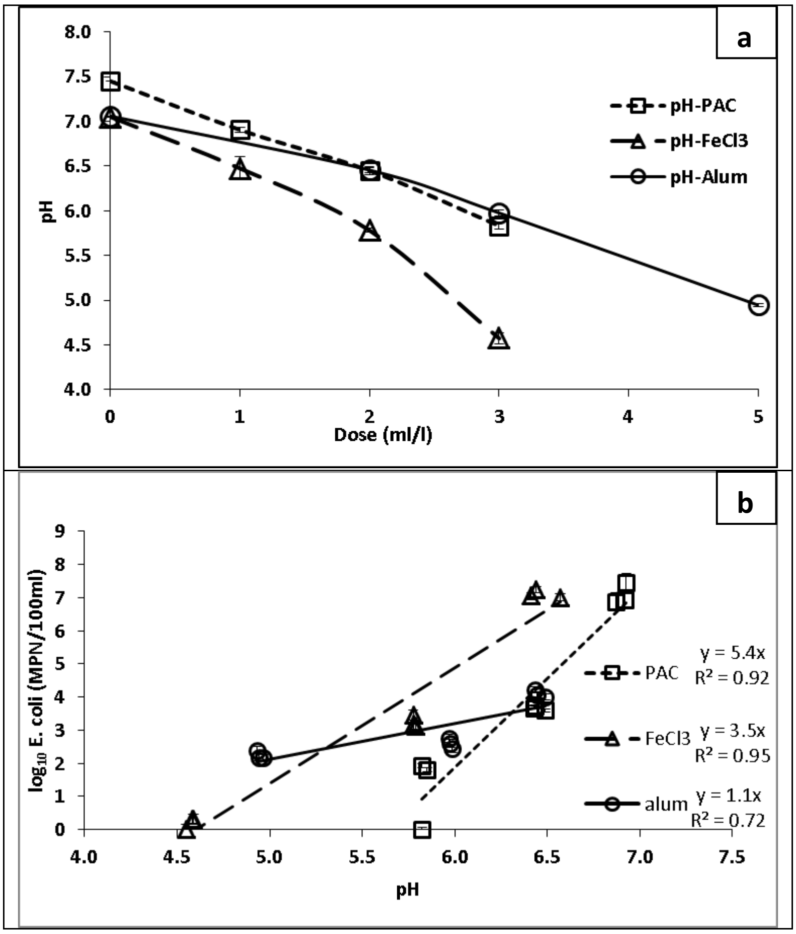


Figure 2 (a) Relationship between doses of coagulants and pH reduction (b) Relationship between pH and logarithmic reduction of *E. coli*

3.2 Effect of mixing regime and dosage on the removal of water quality parameters

With the exception of the turbidity parameter, when alum was added to the DSW, there were no significant differences between mixing periods (5, 10, 15 min) in the removal of water quality parameters ($P \simeq 1$, for most of the comparisons) (Figure 1). The lower the mixing time the better the removal of turbidity by alum. However, the effect of mixing time on the removal of turbidity reduced as doses increased because at higher doses of alum, the mechanism of particle destabilization by alum is sweep coagulation/co-precipitation, while at lower doses, the main mechanism of particle destabilization is adsorption/charge neutralization (Benjamin and Lawler, 2013), which is more sensitive to mixing time (Amirtharajah and Mills, 1982). Therefore, a 5-min mixing period is likely the optimum mixing time. Mixing at a time lower than 5 min will make the settled sludge unstable/fragile and prone to floating, creating a crust sludge layer at the surface due to the build-up of gases which aren't stripped out in the short mixing time (observed in preliminary tests that were run with mixing times< 5 min).

Generally, the removal of all water quality parameters increased as coagulant dosage increased. There is usually an optimum point/dose in which the removals of water quality parameters start to level off without further improvements. Statistical analysis indicated that the medium dose (2 ml L^{-1} for PACl and $FeCl_3$, 3 ml L^{-1} for alum) was the optimum dose (insets of Figure 1).

3.3 Sludge properties

Sludge properties are shown in Table S2. Dry matter of sludges were significantly ($P<0.0001$) increased 2.5 to 3 times more than raw DSW. There were no differences in DM content between $FeCl_3$ and alum sludges ($P=0.95$), and both had DMs higher than PACl sludge ($P<0.05$). Considering this substantial increase in DM, the generated sludge would be regarded as slurry under Irish legislation (S.I. No. 605 of 2017), were it to be disposed of to land. This would also mean that a significant increase in the infrastructure would be required to store generated sludge if it were defined as slurry – 16 to 22 week storage capacities are required for slurry versus 15 d storage capacity for DSW (S.I. No. 605 of 2017). The sludges had pH similar to the supernatants. Sludges of the highest doses had low pH, especially for $FeCl_3$ and alum, which could hinder grass growth if applied to grassland, as the optimum pH for grass growth is 6.3 (Wall and Plunkett, 2016). As a result of pH reduction, *E. coli* was reduced significantly ($P<0.0001$) from the initial concentration of raw DSW of 4.76×10^7 MPN 100 ml^{-1} to a minimum of 3.70×10^3, 1.70×10^4, and 5.34×10^4 MPN 100 ml^{-1} for PACl, $FeCl_3$, and alum sludges, respectively, at the highest doses. These concentrations are within the limits set by the WHO guidelines (WHO, 2006) for the safe use of wastewater, excreta and grey-water for agricultural purposes. Therefore, selecting the appropriate dose is a trade-off between the reducing the level of *E. coli*, and keeping the soil at optimum pH.

Nutrient concentrations of sludges were significantly higher ($P<0.0001$) than the initial concentration in the raw DSW. There were no statistical differences in TN and TP between different sludges ($P=0.6758$) and ($P=0.0870$), respectively. The TP of the sludges was three times higher than the raw DSW and the TN was two times higher than raw DSW. Consequently, the TN: TP ratio had dropped from 6:1 in the raw DSW to between 3:1 and 4:1 in sludges. The typical N: P for grassland requirements is 14:1 at a stocking rate of 170 kg ha^{-1} organic N (Coulter et al., 2002), which means that application rates determined according to pasture N requirements may result in excess P application. However, due to the formation of ferric/Al-phosphate chemical bonds, there will be a reduction in the solubility and mobility of P, thus reducing the risk of P transfer to water via runoff and/or drainage (Fenton et al., 2011; McDowell and Nash, 2012). Assuming an average sludge production of 30% for all treatments, a typical Irish dairy farm stocked at 2 cows ha^{-1} could therefore supply approximately 3-4 and 1 kg ha^{-1} of total N and P, respectively, annually across the farm to meet some of the nutrient requirements for herbage production and potentially replace some of the synthetic fertilizer use. However, the availability of these nutrients was likely not in a form suitable for uptake by plants (González Jiménez et al., 2019). Lime can be applied periodically to facilitate the release of these nutrients. Additions of lime may be determined based on the nutrient requirement by plants, and should be applied incrementally over time to minimise losses to surface and groundwater. Besides stimulating nutrient release and improving soil fertility, lime may also assist in reducing the adverse impacts of excessive chemical loading that can put the topsoil quality at a risk of being barren. Lime is a good conditioner that can adjust the soil pH, and reduce the acidity of soil caused by sludge applications, therefore reducing the availability of metals (Al^{+3}/ Fe^{+3}).

3.4 Phytotoxicity test- germination index

There was no seed germination at day 2 (Figure 3), and germination started after 3 days. The mean root length in the control soil exceeded 20 mm at day 4, with an average elongation of 23 ± 4 mm and with a corresponding average number of germinated seeds of 7.7 ± 1.2 seeds out of 10 seeds. While on day 5, the elongation and number of germinated seeds in the control soil were 44 ± 7 mm and 8.3 ± 1.2 seeds, respectively (Figure S1). With the exception of the sludges of the lowest doses on day 4, all sludges had GIs less than control (Figure 4). Increasing the dose of coagulants reduced the GIs of the sludges (Figure 4), which was likely due to pH reduction in the soil. Too much acidity causes root plant injury by H^+, and also increases Al^{+3} availability, which is toxic to plant roots (Wall et al., 2015). The level of GI that indicates toxicity has been debated in the literature. For example, Zucconi et al. (1981) identified a GI between 50-80 %, whereas Tiquia et al. (1996) and Jodice (1989) identified GIs of 80% and 50-70 %, respectively. According to these defined levels, all the sludges in this study were not toxic at a level of 50 %, while some of them were toxic at a level of 80 % GI (Figure 4).

However, there was no statistical difference in GI between all treatments, including control, as the main effect of treatment on GI was not significant at the 5 % level (P= 0.6527) and (P= 0.6356), respectively, for days 4 and 5. In addition, pairwise comparisons found no differences in GI between any two treatments, including comparisons to control ($P\simeq1$, for most of the comparisons). There was no difference in GIs between day 4 and day 5 (P= 0.5571), and the test was identical in day 5 as in day 4, as the interaction between effect of day and treatments is not significant at the 5 % level (P=1, day*treatment). The high variability within each treatment (Figure 4) might be a reason for not detecting differences between treatments. Another ecotoxicological test, the so-called “choice test” (Udovic and Lestan, 2010), should be done to support the hypothesis of no differences between treated soils.

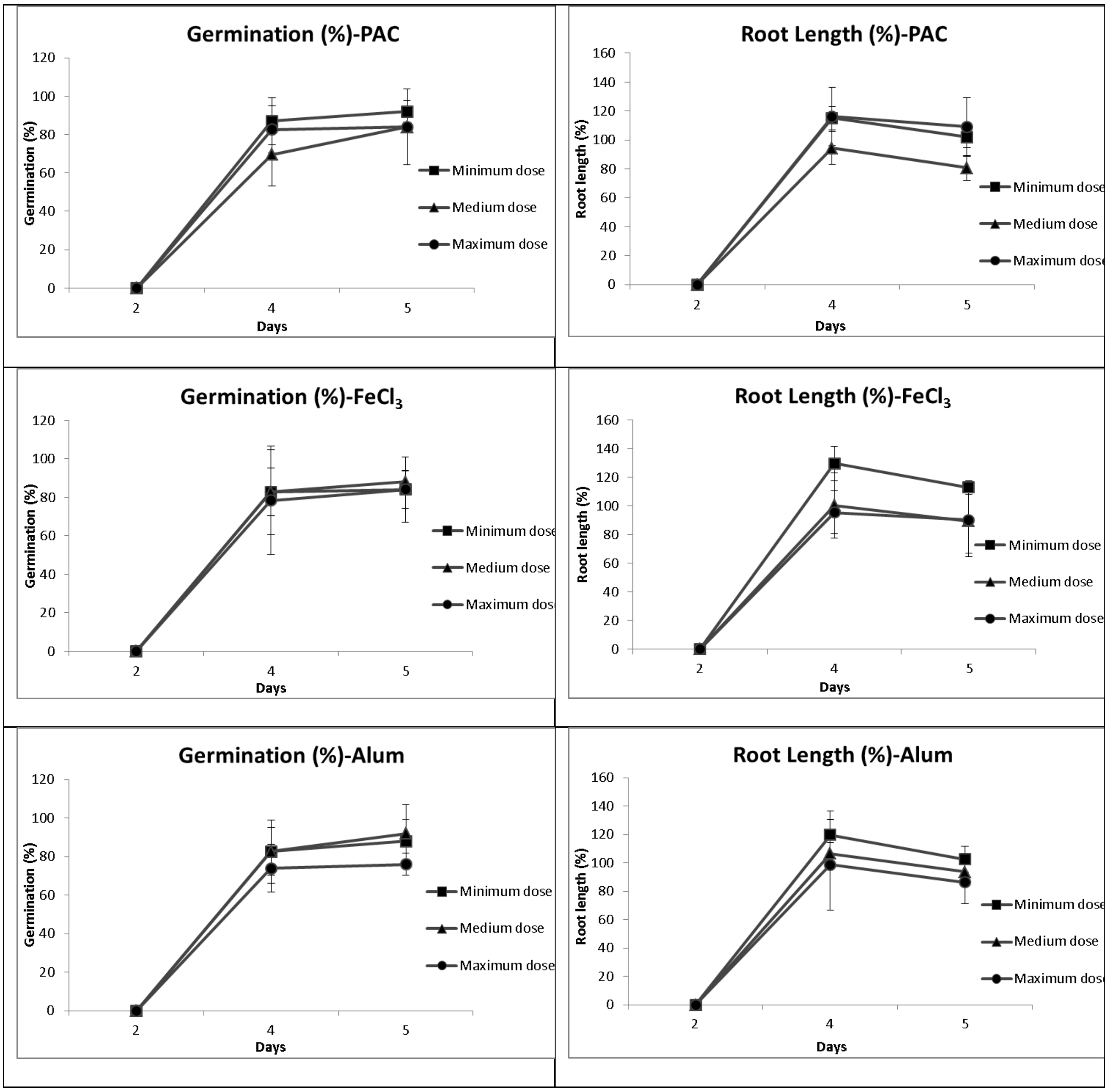


Figure 3 Relative root growth (RRG) and relative seed germination (RSG)

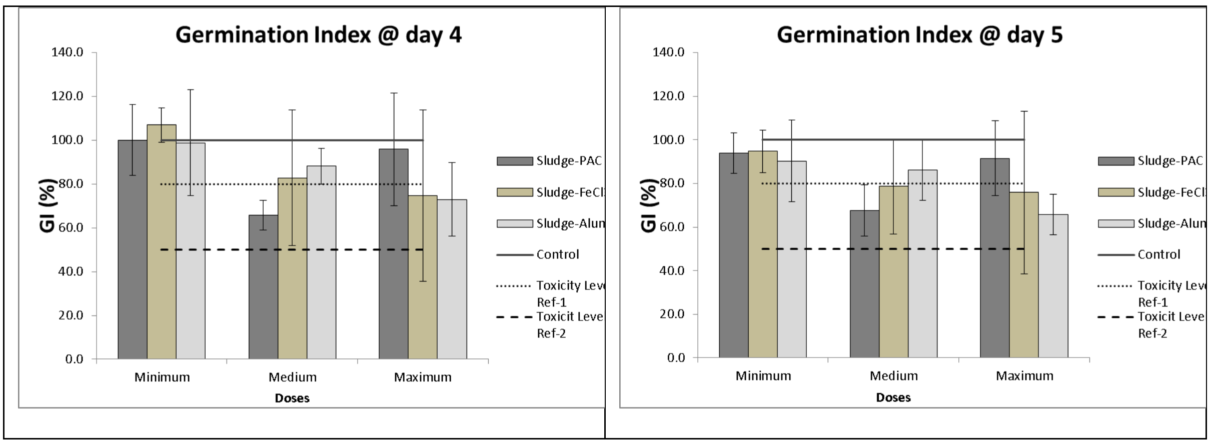


Figure 4 Germination Indices (GI) at day 4 and day 5. Ref-1: low toxicity level. Ref-2: high toxicity level

3.5 Cost analysis and effluent management options

The coagulants were ranked in terms of their feasibility, taking into account their cost, sludge volumes, as well as their performance (Table 3). Starting with the most desirable, the coagulants were ranked as follows: $FeCl_3$, alum, and PACl. The best average removal of all measured water quality parameters was achieved by PACl (85%), which costs € 1.57 m^{-3} of DSW. Sludge handling through spreading by tankers was estimated at € 0.40 m^{-3} for $FeCl_3$. Thus, the total cost of treatment by $FeCl_3$ (including sludge disposal) was estimated to be € 1.97 m^{-3}. Supernatant could be recycled to wash the yard as it was free of *E. coli*, saving 75% of water use, and hence recover € 1.4 m^{-3}. This would minimize the overall net cost of treatment, including sludge handling, to € 0.57 m^{-3} as opposed to € 1.55 m^{-3} for land application of DSW. However, recycling the supernatant many times could increase the concentration of COD and TN in the recycle water, which could pose environmental risks. Therefore, a further polishing step of supernatant through ICWs or ISFs could be an advantage. The land requirement and construction cost of ICWs/ISFs for the treatment of supernatant will be eight times cheaper than ICWs or ISFs designed to treat raw DSW, due to the high reduction in OM/COD achieved by coagulants in this study. In addition, maintenance costs, caused by regular clogging of ICWs or ISFs, will be reduced substantially for the supernatant, as it has fewer SS. Wetlands have the capacity to minimize the remaining OM and NH_4-N by 98% and 88%, respectively (Healy and O’ Flynn, 2011). Introducing ISFs as a tertiary treatment step after coagulant treatment could also reduce the OM by 97% (Mohamed et al., 2017), and could also reduce the TN by 83 % using recirculation mode of flow to stimulate nitrification/de-nitrification processes (Healy et al., 2004)

Table 3 Showing coagulants in order of feasibility score, breakdown of costs[a], cost of treatment m^{-3} DSW, average removal efficiency, sludge volume, sludge handling and total cost m^{-3} DSW, cost for 100 cow farm, saving cost and overall net cost m^{-3} DSW

Coagulant	Feasibility score	Addition rate	Cost[b] of coagulant	Cost	Mixing[c]	Treatment cost	Removal efficiency[d]	Treatment cost efficiency[e]	Sludge volume[f]	Sludge handling cost[g]	Total cost	100 dairy cows farm[h]	Treated effluent volume[i]	Recovery saving cost[j]	Overall net cost
		ml L^{-1}	€ m^{-3}	€ m^{-3}	€ m^{-3}	€ m^{-3}	%	€$_{cent}$ m^{-3} %$^{-1}$	%	€ m^{-3}	€ m^{-3}	€ farm^{-1}	%	€ m^{-3}	€ m^{-3}
Control		0	0	0	0	0	0	0	100	1.55	1.55	1550	0[NR]	0	1.55
Ferric chloride	1	1	520	0.52	0.01	0.53	64	0.83 (2)	26	0.40	0.93	930	74*	–	–
		2		1.04	0.01	1.05	83	1.27 (5)	29	0.45	1.50	1,500	71**	–	–
		3		1.56	0.01	1.57	85	1.86 (8)	26	0.40	1.97	1,970	74***	1.40	0.57
Alum	2	2	245	0.49	0.01	0.50	74	0.68 (1)	24	0.37	0.87	870	76*	–	–
		3		0.74	0.01	0.75	79	0.94 (3)	27	0.42	1.17	1170	73**	–	–
		5		1.23	0.01	1.24	81	1.53 (6)	31	0.48	1.72	1720	69***	1.30	0.42
PACl	3	1	675	0.68	0.01	0.69	66	1.05 (4)	35	0.54	1.23	1230	65*	–	–
		2		1.35	0.01	1.36	85	1.60 (7)	35	0.54	1.9	1,900	65**	–	–
		3		2.03	0.01	2.04	85	2.40 (9)	36	0.56	2.6	2,600	64***	1.20	1.4

a) Calculations based on a typical Irish dairy farm with 100 cows for one year; b) cost was estimated using prices of commercial products available on the market. Cost includes delivery of material and addition of material to DSW in storage tank; c) cost was estimated for 5 minutes mixing period (optimum mixing time). The input power to achieve adequate mixing similar to that in the lab is 0.64 watt per litre of DSW, and the electricity rate is EUR17 cent per unit of electricity-kWh (ESB, 2019); d) to represent the overall performance of coagulant, removal efficiency was calculated as average of all water quality parameters (turbidity, COD, TN, TP, and *E.coli*) for 5 min mixing period experiments only; e) Ranking score by the cheapest treatment per unit removal efficiency (%) is shown in brackets; f) % of sludge volume estimated based on Eqn. 2; g) Additional costs are required post-coagulant treatment to dispose of the sludge produced – spreading costs € 1.55 m^{-3} (Fenton et al., 2011) h) calculations based on 10,000 litres of DSW is produced per cow per year (Minogue et al., 2015); i) Recommendations on the effluent to be recycled for washing the farm yards was judged based on the final effluent quality, in particular *E.coli* content, and rated as following: not recommended as NR, poor as *, fair as ** and good as ***; j) saving costs were only calculated for high rating effluents, and estimated based on water cost of € 1.87 m^{-3} (Irish Water, 2019)

4. Conclusion

The chemical coagulants were able to minimise OM, nutrients (N and P) and pathogens considerably in DSW, leading to significant improvements in water quality parameters of the supernatant, while obtaining sludge with properties more suitable for land application than raw DSW. The supernatant may need to undergo a further treatment step, so that it can be recycled safely to wash the farm yards. Similarly, the sludge portion of the treated DSW, which is enriched in nutrients and P-sorbing coagulants, may be applied directly to land with lower transportation costs and fewer risks of nutrient losses. This management approach could reduce the overall net cost substantially compared to land application of DSW. Future research should focus on the NFRV of the generated sludge and on post-treatment methods such ICWs or ISFs to polish the effluent from the treated DSW.

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Supplementary documents

Table S1 Technical specifications and properties of coagulants

Coagulant / Parameter	PACl	$FeCl_3$	Alum
Chemical Formula	$Al(OH)_a Cl_{3-a}$ with a>1.05	$FeCl_3$, 40 %	$Al_2(SO4)_3.n\ H_2O$
CAS Number	1327-41-9	7705-08-0	10043-01-3
EC Number	215-477-2	231-729-4	233-135-0
Appearance	Colourless to yellow	Brown Fluid	Colourless clear liquid
Specific Gravity	1.37 ± 0.02 @ 15°C	1.7 @ 15°C	1.317 ± 0.007 @ 15°C
pH value	2-4	1-2	_
Free acid			<1.0 % w/w H_2SO_4
Content	17.0 ± 0.5% w/w Alumina (Al_2O_3)	40 % w/w $FeCl_3$	8.00 ± 0.24 % w/w Alumina (Al_2O_3)
Aluminium Content	52.49 ± 1.6 g/kg of Product		42.35 ± 1.27 g/kg of Product
Insoluble matter	< 10 g/kg of Al	_	<23 g/kg Al
Solubility	Fully miscible in water	Fully miscible in water	
Relatively Basicity	0.68 ± 0.32		_
Chemical classification	Acidic Solution	Acidic Solution	Acidic Solution
Crystallization Point	_		- 7°C @ 42.4 g/kg
Boiling point	_	280°C	_
Melting point	_	-10°C	_
Vapour pressure	_	23 hPa@ 20°C	_
Conform to Standards	I.S EN 883:2005	_	I.S EN878:2016
Arsenic (As)	<1.73 mg/L	<= 3 mg/l	<0.78 mg/L
Cadmium (Cd)	<0.25 mg/L	<= 2.15 mg/l	<0.17 mg/L
Chromium (Cr)	<3.70 mg/L	<=100 mg/l	<1.39 mg/L
Mercury (Hg)	<0.49 mg/L	<= 0.2 mg/l	<0.11 mg/L
Nickel (Ni)	<2.47 mg/L	<=71.5 mg/l	<1.12 mg/L
Lead (Pb)	<2.47 mg/L	<=18.6 mg/l	<0.56 mg/L
Antimony (Sb)	<1.23 mg/L	<= 3 mg/l	<0.56 mg/L
Selenium (Se)	<1.23 mg/L	<= 3 mg/l	<0.56 mg/L
Manganese (Mn)	_	< 800 mg/l	_
Copper (Cu)	_	28 mg/l	_
Iron	_		<8.05 mg/L

Table S2 Sludge properties expressed as dry matter content, sludge volume, pH, *E. coli* and nutrient content.

Sludge properties	Dry matter (%) $^{+}$			Sludge volume (%) $^{+}$			pH ^{N}			*E. coli* (MPN 100 ml^{-1}) $^{+++}$		
	PACl***	$FeCl_3^{***}$	Alum***	PACl***	$FeCl_3^{***}$	Alum***	PACl^{NS}	$FeCl_3^{*}$	Alum*	PACl***	$FeCl_3^{***}$	Alum***
Minimum dose	2.30	2.90	3.10	31	26	24	6.74	6.55	6.40	7.65×10^{6}	2.91×10^{7}	3.10×10^{5}
Medium dose	2.60	2.90	2.90	35	29	27	6.27	6.03	6.01	2.16×10^{6}	4.50×10^{6}	4.37×10^{4}
Maximum dose	2.6	3.20	2.80	35	26	31	5.98	4.80	5.01	3.70×10^{3}	1.70×10^{4}	5.34×10^{4}
Nutrient content	**Total P (mg L^{-1}) ^{N}**			**Total N (mg L^{-1}) ^{N}**			**Total P (g kg^{-1} DM) ^{N}**			**Total N (g kg^{-1} DM) $^{++}$**		
	PACl***	$FeCl_3^{***}$	Alum***	PACl***	$FeCl_3^{***}$	Alum***	PACl^{NS}	$FeCl_3^{NS}$	Alum^{NS}	PACl**	$FeCl_3^{***}$	Alum***
Minimum dose	116	127	147	430	419	444	5.10	4.40	4.70	18.70	14.40	14.30
Medium dose	124	144	147	475	484	462	4.80	5.00	5.10	18.30	16.70	15.90
Maximum dose	120	163	130	483	514	436	4.60	5.10	4.60	18.60	16.10	15.60

Statistically significant differences between raw DSW and each sludge type are shown for each parameter in the top of the coagulant names at $p < 0.001$ as ***; $p < 0.01$ as **; $p < 0.05$ as *, and no significant difference as NS. Statistically significant differences between sludges (main effect) are shown in the top of the parameters names at $p < 0.001$ as +++; $p < 0.01$ as ++; $p < 0.05$ as +, and no significant difference as N.

Figure S1 Images of seeds germination at day 5: (one photo was captured for each replicate)