


Influence of mixing conditions on coagulant recovery efficiency and quality

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ABSTRACT

In this work, the influence of mixing conditions on aluminium recovery from alum sludge and on the recovered coagulant (RC) quality was investigated using acidic treatment. The response surface methodology with a Face Centred Design was used to evaluate the effects of velocity gradient and mixing time on aluminium recovery efficiency, and on the chemical oxygen demand (COD), total suspended solids (TSS) and total phosphorus contents of the RC. No significant effects of both mixing intensity and mixing time on aluminium recovery efficiency were observed; however, these factors significantly affected the quality of the RC in terms of COD, TSS and total phosphorus. The higher velocity gradient increased COD and TSS and the longer mixing time increased phosphorus and TSS in the RC. Operational conditions velocity gradient = 100 s^{-1} and mixing time = 5 minutes) for aluminium recovery were suggested on economic basis. At these conditions, the RC presented the lowest values of TSS and total phosphorus (100 mg L^{-1} and 7.0 mg P L^{-1} , respectively), and the following other characteristics: $1,001\text{ mg Al L}^{-1}$; 384 mg Fe L^{-1} ; $1100\text{ mg COD L}^{-1}$.

Key words: coagulant recovery, mixing time, response surface methodology, velocity gradient, water treatment sludge

HIGHLIGHTS

- The influence of mixing conditions on coagulant recovery efficiency and quality was investigated.
- Mixing intensity was studied in terms of the velocity gradient.
- Mixing conditions did not influence the aluminium recovery from sludge.
- The use of low velocity gradient and low mixing time results in better quality of the recovered coagulant.

1. INTRODUCTION

While coagulation–flocculation–sedimentation plays a key role in drinking water treatment (DWT) by removing the bulk of impurities from raw water, it produces a large volume of sludge (Keeley *et al.* 2014).

In many developing countries, water treatment sludge (WTS) is disposed into nearby rivers or streams (Ahmad *et al.* 2016a). However, the discharge of WTS affects the water quality of the receiving water body and may lead to accumulation of metals in aquatic organisms (Ahmad *et al.* 2016b). The large volume of WTS produced in water treatment plants (WTPs) requires proper handling and disposal, and may account for a significant part of overall costs of water treatment works (Babatunde & Zhao 2007). Therefore, reducing WTS production, as well as WTS handling costs, is crucial for a cost-effective management. WTS recycling options include building materials production (Gomes *et al.* 2019), coagulant recovery (Parsons & Daniels 1999; Ishikawa *et al.* 2007; Chen *et al.* 2012; Ahmad *et al.* 2021; Dahasahastra *et al.* 2022) and its use as an adsorbent in wastewater treatment (Muisa *et al.* 2020).

Coagulant recovery for use in wastewater treatment is an attractive process, since it reduces both the commercial coagulant demand and waste production (Keeley *et al.* 2016). Several techniques are available for coagulant recovery, such as acidification, basification, ion exchange and membrane separation; acidification is one of the most applied options due to its high efficiency and low cost (Xu *et al.* 2009). It is a simple process comprising acid addition to the sludge, mixing and solids separation. The reaction between aluminium hydroxide – a major constituent of aluminium sludge (Nair & Ahammed 2014) – and sulphuric acid, producing alum, is

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represented in Equation (1):



Hydrochloric acid has also been used for coagulant recovery, however, due to similar efficiencies obtained with sulphuric acid and its higher cost, the latter is usually preferred (AWWA 1991). The use of nitric acid for aluminium recovery has been recently investigated too (Dahasahastra *et al.* 2022), however, its economic feasibility compared to using sulphuric acid is still to be demonstrated.

Coagulant recovery by acidification is not a selective process, i.e., during aluminium solubilization, heavy metals and organic matter are also solubilized (Xu *et al.* 2009). Whereas recovered coagulant (RC) reuse in DWT is not recommended due to the potential contamination of drinking water with heavy metals and trihalo-methanes (THM) generation, this should not be a major problem in wastewater treatment (Nair & Ahammed 2014).

The coagulant recovery process is influenced by both the WTS characteristics and operational parameters. In turn, the WTS characteristics depend on the raw water quality (e.g., turbidity and humic acid concentration), the coagulant type and dosage. At high humic acid concentration in raw water, the WTS surface may be coated with organic matter and impair aluminium resolubilization; with high raw water turbidity, the presence of inert solids could make the contact between aluminium and acid difficult, reducing recovery efficiency (Nair & Ahammed 2017). Also, the WTS solids content may affect both the recovery efficiency and the aluminium concentration in the RC. At high WTS solids concentration, the aluminium concentration in the RC tends to be higher, but the recovery efficiency (%) lower, than with low WTS solids concentration (Nair & Ahammed 2014). High aluminium concentration in the RC is particularly important for RC reuse in wastewater treatment. As high aluminium doses are required for chemical precipitation, if the aluminium concentration in the RC is low, high dosing pump flow rate and a high volumetric dose (litres of RC per litre of wastewater) would be required to meet the desired dose, making the RC reuse less attractive.

Operational parameters impacting coagulant recovery include acid to aluminium ratio, extracting pH and mixing time (AWWA 1991; Fouad *et al.* 2017). As indicated in Equation (1), the theoretical stoichiometric acid requirement based on WTS aluminium content is 1.5 mol H₂SO₄ per mol Al (5.45 kg H₂SO₄ per kg Al). Actually, due to additional acid consumption by, for instance, solubilization of other sludge constituents and reaction with its alkalinity, higher H₂SO₄:Al ratios should be necessary in order to effectively achieve aluminium solubilization. Extracting pH and acid to aluminium ratio are closely related parameters, so that the application of acid from one to two times the stoichiometric demand typically results in a final RC pH range of 1.8–3.0 (AWWA 1991). Nair & Ahammed (2014) observed an increase of recovery efficiency from 62 to 81% with pH decrease from 2.0 to 1.0. However, the amount of sulphuric acid necessary to drop the pH from 2.0 to 1.0 increased five times (compared to the amount added to drop the pH from its initial value to pH = 2.0), as also observed in a previous study by our research group. As decreasing the pH increases recovery efficiency, but also increases acid demand, Nair & Ahammed (2014) optimized the coagulant recovery at pH = 2 taking into account both responses: acid demand and recovery efficiency.

The optimum mixing time for coagulant recovery is WTS-specific. Several authors noticed increasing recovery efficiency with increasing mixing time until a plateau is reached and no further aluminium resolubilization took place; the following optimum values were reported in the literature: 20 min (Cheng *et al.* 2012), 30 min (Nair & Ahammed 2014), 40 min (Fouad *et al.* 2017) and 120 min (Dahasahastra *et al.* 2022). However, only a few studies investigated the influence of mixing intensity on aluminium recovery efficiency. Cheng *et al.* (2012) and Fouad *et al.* (2017) reported similar results of aluminium recovery efficiency for different mixing intensities: recovery increased with increasing mixing speed until a threshold was reached, after which no further aluminium dissolution was observed. However, the mixing intensities in those studies were reported in terms of the impeller rotational speed (revolutions per minute – rpm), whereas mixing intensity is better characterized by velocity gradient (*G*), which is related to the power applied per unit volume of the liquid (Equation (2); Wang *et al.* 2005). In turn, the applied power depends on the design of the mixing equipment, e.g., the impeller characteristics such as size, shape and rotational speed (Equation (3); Rushton 1952). So, even if the same power is applied by different impellers, if the volume of the jars used in different studies are not the same, the resulting mixing intensities will

also be different (Equation (2)):

$$G = \sqrt{\frac{P}{\mu V}} \quad (2)$$

where P is the applied power (N m s^{-1}); μ is the dynamic viscosity (N s m^{-2}) and V is the reactor volume (m^3).

$$P = K_i \rho_w N^3 D_i^5 \quad (3)$$

where K_i is the coefficient depending on impeller type and shape; ρ_w is the water specific mass (kg m^{-3}); N is the rotational speed (rotations per second = rpm/60) and D_i is the impeller diameter (m).

In continuous flow reactors, the choice of the mixing time results in a given reactor volume, while in batch reactors, it determines energy consumption. In addition, the selection of mixers is based on appropriate values of velocity gradient. However, to the best of our knowledge, there are no studies in the literature on the influence of the velocity gradient on coagulant recovery. In the present work, the influence of mixing conditions, in terms of velocity gradient and mixing time, on aluminium recovery from alum sludge, consequently on the RC quality, was investigated using the response surface methodology (RSM). The hypothesis of this work was that there would be an optimum combination of mixing time and mixing intensity, leading to maximizing coagulant recovery efficiency and the resulting coagulant quality. The results presented herein will be applied to investigate the use of the RC in tertiary treatment of piggy wastewater for phosphorus removal.

Finally, the economic feasibility of recovering coagulants is complex and depends on various factors, related to sludge treatment, and disposal costs, to the coagulant recovery process itself, as well as to the intended use of the RC. When the RC is to be used in DWT, further purification following acidification would be required, which has been proven to not be economic feasible (Keeley *et al.* 2012). On the other hand, Keeley *et al.* (2016) showed that RC use for phosphorus removal in wastewater treatment is economically feasible, resulting in almost 50% savings compared to using fresh coagulant, with acid price accounting for most of overall costs.

2. MATERIALS AND METHODS

2.1. Sludge source and characterization

The sludge used in the experiments was taken from the water treatment plant (WTP) of the University of Viçosa (UFV), located in Viçosa, state of Minas Gerais, Brazil. The WTP is a conventional one, encompassing coagulation, using alum as a coagulant, flocculation, sedimentation, filtration and disinfection. Raw water is collected downstream two reservoirs in series, resulting in low water turbidity values for most of the year. WTS was collected from the WTP settler and stored in 80 L containers. Before the coagulant recovery tests, the sludge was characterized in terms of pH, total organic carbon (TOC), solids concentration and metals (aluminium and iron).

2.2. Recovery experiments

Coagulant recovery tests were conducted using 0.4 N sulphuric acid, with the sludge solids content previously adjusted to 2.0% ($20,000 \text{ mg L}^{-1}$). The concentration of sulphuric acid and the volumes of acid (0.75 L) and WTS (1.25 L at 2.0%) used resulted in a 4.63 kg $\text{H}_2\text{SO}_4/\text{kg Al}$ ratio (1.3 mol $\text{H}_2\text{SO}_4/\text{mol Al}$) and $\text{pH} \approx 2.0$. The recovery tests were conducted in a Jar Test equipment, varying the velocity gradient (G) from 100 to 200 s^{-1} (86–170 rpm) and mixing time (t) from 5 to 20 min. For solids separation, a settling time of 40 min was used. These experimental conditions and ranges of values were chosen based on the literature (AWWA 1991; Cheng *et al.* 2012; Nair & Ahammed 2014). In all recovery experiments, the temperature was kept between 22 and 23 °C.

The traditional approach of experimental designs for optimizing water and wastewater treatment processes is testing one factor at a time, which is costly, time-consuming and unable to estimate the interaction effects between factors. On the other hand, the RSM is an efficient and economical statistical design that requires a smaller number of experiments to be carried out and allows the estimates of the main and interaction effects of factors. RSM is becoming increasingly used to optimize water and wastewater treatment, and coagulant recovery processes (Nair & Ahammed 2014, 2015; Ahmad *et al.* 2021; Dahasahastra *et al.* 2022).

The combinations of factors G and t were determined based on a face centred design (FCD), completely randomized with four replicates at the central point. In total, nine treatments were tested and 12 trials were carried out in order to determine the best mixing conditions for coagulant recovery. The FCD was chosen because (i) it allows the evaluation of the main effects for each factor, as well as interaction effects; (ii) it does not require a large number of runs; (iii) the use of replicates at the central point allows internal estimation of error and (iv) it is possible to evaluate the model adequacy, including lack of fit (Montgomery 2013).

2.3. Quality of the recovered coagulant

At the end of the recovery experiments, the quality of the RC was evaluated in terms of total suspended solids (TSS), COD, total phosphorus and metals. Considering the aluminium concentrations in the WTS sample and the soluble aluminium concentration in the RC, the percentage of aluminium recovered in each experiment was calculated using Equation (4):

$$\text{Recovered aluminium (\%)} = \frac{\text{Soluble aluminium in the recovered coagulant (mg Al)}}{\text{Aluminium content of the dry WTS (mg Al)}} \times 100\% \quad (4)$$

2.4. Analytical methods

All analyses were carried out according to the Standard Methods for the Examination of Water and Wastewater (APHA AWWA WEF 2017). For the pH analyses, a pHmeter Digimed DM-2P, calibrated daily, was used. pH analyses were conducted immediately after sludge collection and after the coagulant recovery tests, as recommended by the SM 4500-H⁺ B. Solids concentration in the WTS and in the RC were determined by gravimetry (SM 2540 B). According to the Standard Methods for Examination of Water and Wastewater, the method 2540G is the most suitable one for total solids analysis of solid and semi-solid samples. However, due to the large volume of sludge required, it cracked into quite large pieces during drying in the water bath, and did not dry properly. Such problem was overcome with method 2540B, which was successfully used, giving results with relative percent differences between duplicates < 10% and the solid masses were in the range of 25–200 mg, as required by the method. WTS samples were analysed for total, fixed and volatile solids, whereas RC was analysed for TSS only. For TSS analyses, samples were previously filtered through a glass fibre filter (pore size = 1.2 µm), and in order to determine the fixed solids fraction samples were calcined at 550 °C. COD analyses of the RC samples were conducted by closed reflux and colorimetry (SM 5220 D). TOC analyses were carried out on two samples of RC and three samples of WTS, in a Shimadzu TOC SSM 5000 equipment. Total phosphorus in RC and WTS was determined by the stannous chloride method (SM 4500-P D), after digestion with concentrated nitric acid and sulphuric acid. Metals (aluminium and iron) were analysed by flame atomic absorption spectrometry (FAAS). WTS samples were oven-dried at 105 °C and sieved in a 200 mesh (0.075 mm) sieve, for further digestion according to the EPA 3050B method (USEPA 1996), which is carried out using concentrated nitric acid, hydrogen peroxide and concentrated hydrochloric acid. To avoid damage to the flame spectrometer nebulizer, the digested WTS samples were filtered with a quantitative paper filter. Such a strong digestion method allows determining environmentally available elements, but does not achieve full digestion of the sample. Preparation of RC samples for metal analyses was carried out according to the EPA 3010A method (USEPA 1992), a strong digestion technique using concentrated nitric acid and subsequent reflux with hydrochloric acid. It is considered the most suitable method for aqueous samples containing suspended solids (USEPA 1992), such as the RC.

2.5. Statistical analyses

A response surface was fitted to the results of aluminium recovery efficiency, TSS, COD and phosphorus. The significance of each model's terms was assessed by the Student's t -test, with $\alpha = 5\%$, with the respective variables in the coded form. For converting the model factors from the original scale to the coded one, the following equation was used:

$$x_{\text{cod}} = \frac{X_i - X_0}{X_{+1} - X_0} \quad (5)$$

where x_{cod} is the value of variable X on the coded scale; X_i is the value of variable X in the original scale; $i = -1$

(lower limit), 0 (central point) and +1 (upper limit); X_{+1} is the upper limit of the range of values of variable X on the original scale and X_0 is the central point of the range of values of variable X on the original scale.

The model fitting was performed using coded design variables ($-1 \leq x_{\text{cod}} \leq 1$), i.e., the model coefficients were estimated with the same precision, as all of them are dimensionless and measure the effect of changing each design factor over a one-unit interval (same step width and interval). It is important to evaluate the model fitting with the coded design variables, since the model should have a reasonably consistent and stable variance of the predicted response at points of interest (Montgomery 2013). For each response variable initially analysed, a complete second-order model was fitted (Equation (6)):

$$y = \beta_0 + \beta_1 g_{\text{cod}} + \beta_2 t_{\text{cod}} + \beta_{11} g_{\text{cod}}^2 + \beta_{22} t_{\text{cod}}^2 + \beta_{12} g_{\text{cod}} t_{\text{cod}} + \varepsilon \quad (6)$$

where g_{cod} is the velocity gradient on the coded scale; t_{cod} is the mixing time on the coded scale and ε is the experimental error.

Subsequently, the non-significant terms (β_{ij}) were progressively removed from the models following the hierarchy principle (Montgomery 2013). The final model (containing only the significant terms) was evaluated using analysis of variance (ANOVA); the lack of fit of each model was evaluated by Fisher's F test. The ANOVA assumption of normally distributed residuals was verified using the Kolmogorov–Smirnov test (KS_{test}). All these tests were performed at 5% significance. The statistical analyses were carried out using the software R version 3.2.1 and the rsm package; the contour plots were obtained with the 'graphics' package.

3. RESULTS AND DISCUSSION

3.1. Sludge characteristics

The characteristics of the raw WTS used for coagulant recovery experiments are shown in Table 1. As above mentioned, the WTS solids concentration was adjusted to 2.0% (20,000 mg L⁻¹) before the recovery experiments were carried out.

Table 1 | Characteristics of the raw WTS

Characteristic	Value*
Solids concentration (mg L ⁻¹)	29,821 ± 917
Volatile solids fraction (%)**	32 ± 1.9
TOC (mg L ⁻¹)	2,462 ± 155
Aluminium (mg L ⁻¹)	3,822 ± 98
Iron (mg L ⁻¹)	2,204 ± 126
Phosphorus (mg L ⁻¹)	42.6 ± 1.9
pH	7.0 ± 0.1

*Mean ± standard deviation; $n = 12$.

** (Volatile solids/total solids) × 100%.

The characteristics of the raw WTS did not show large variability. Due to the long storage time in the WTP settler (269 days), the concentration of solids was high (3.0%), and about a third of the total solids content were volatile solids. The TOC was also quite high, indicating a high organic matter content in the WTS. Supposedly, the aluminium concentration found in the sludge is mainly due to aluminium added to the raw water as a coagulant, whereas the iron and phosphorus came from the raw water itself. This is because the method used for the sludge digestion allows the quantification of fractions that are environmentally available only, i.e., it does not include the aluminium or iron of the silicate structure of the solids present in the raw water.

3.2. Recovered coagulant characteristics

The design matrix used in the coagulant recovery experiments and the results of TSS, COD, phosphorus and aluminium concentrations found in the RC are shown in Table 2.

Table 2 | Design matrix for coagulant recovery from alum sludge and characteristics of the recovered coagulant

Experiment	Gradient (s ⁻¹)*	Time (min)*	TSS (mg L ⁻¹)	COD (mg L ⁻¹)	Phosphorus (mg L ⁻¹)	Aluminium (% recovered)
1	100 (-1)	5 (-1)	109	1,100	6.7	63.9
2	100 (-1)	20 (1)	170	1,118	7.1	64.7
3	200 (1)	5 (-1)	225	1,124	7.1	65.1
4	200 (1)	20 (1)	354	1,218	8.0	59.9
5	100 (-1)	12.5 (0)	126	1,036	7.5	62.1
6	200 (1)	12.5 (0)	286	1,163	7.7	62.9
7	150 (0)	5 (-1)	114	1,061	7.0	58.1
8	150 (0)	20 (1)	238	1,041	7.8	64.3
9	150 (0)	12.5 (0)	168	1,027	6.9	68.5
10	150 (0)	12.5 (0)	182	1,094	7.2	59.5
11	150 (0)	12.5 (0)	182	1,082	7.5	66.6
12	150 (0)	12.5 (0)	184	998	7.7	58.6

*Values within parentheses represent the coded values of the variables in FCD.

3.3. Influence of mixing conditions on the recovered coagulant quality

3.3.1. Aluminium

Mixing time and velocity gradient did not have a significant effect on aluminium recovery ($p_{\text{value model}} = 0.83$) and iron solubilization ($p_{\text{value model}} = 0.18$), which mean values were 62.5 and 41.9%, respectively. The average concentration of aluminium and iron in the RC were 1,001 and 384 mg L⁻¹, respectively. The relatively low percentage of aluminium recovery could be explained by three main reasons: (i) the high WTS solids concentration; (ii) the H₂SO₄/Al ratio, slightly lower than the theoretical stoichiometric demand and (iii) sludge aging during the sludge storage time in the WTP settler. Nair & Ahammed (2014) reported 62.7% aluminium recovery from alum sludge under optimized conditions (mixing time = 30 min; pH = 2.0; solids concentration of 0.5%). They observed lower recovery efficiency with higher solids concentration; however, if the goal is to obtain high concentration of aluminium (in mg L⁻¹) in the RC, higher concentration of solids may suit better. It should be noted that metal concentration in the coagulant affects its effectiveness as well as operational aspects related to product dosage. In this work, the sludge had a solids concentration of 2.0% and the RC presented an aluminium concentration of at least 1,000 mg L⁻¹, even if the recovery efficiency was not so high. Nevertheless, the aluminium concentration obtained in this study was higher than that reported by Nair & Ahammed (2014) (685 mg L⁻¹), with similar recovery efficiencies in both studies, despite the higher concentration of solids and shorter mixing times used here.

The H₂SO₄/Al ratio initially planned was an attempt to meet the stoichiometric demand (1.5 mol H₂SO₄/mol Al or 5.45 kg H₂SO₄/kg Al – Equation (1)) of sulphuric acid based on the aluminium content of the WTS, as well as to result in an RC with pH close to 2.0. However, in practice, a ratio of 1.3 mol H₂SO₄/mol Al or 4.63 kg H₂SO₄/kg Al was used, which resulted in a final pH of 2.2. Considering the stoichiometric demand of sulphuric acid, with the H₂SO₄/Al ratio actually applied it would be possible to recover a maximum of 85% of the aluminium from the WTS. In addition, other demands for acid may have taken place (for example, for solubilization of other metals, reaction with alkalinity), therefore interfering in the aluminium recovery efficiency.

Following the addition of alum to water, amorphous aluminium hydroxide flocs are almost instantaneously formed, but its progressive crystallization reduces solids reactivity (Duffy & van Loon 1994) and floc's solubility (Snoeyink & Jenkins 1980). Due to the long sludge storage time in the settler (269 days), it is expected that aging and solids crystallization took place, but this could only be confirmed by X-ray diffraction analysis, which was not carried out in this study. In addition, the presence of organic matter and inert solids in the sludge (Table 1) may have hindered the contact between acid and the aluminium in the sludge (Nair & Ahammed 2017). Hence, low coagulant recovery efficiencies (%) were obtained in the present work.

Regarding mixing intensity, the objective of this work was to suggest guideline values of velocity gradient for the design of reactors for coagulant recovery, given that in the available literature the results (from bench

scale experiments) are reported in rpm, which are not easily extrapolated to full-scale reactors. Cheng *et al.* (2012) evaluated the effect of different mixing intensities (20–120 rpm) on the recovery of aluminium from sludge in a 0.5 L reactor, and found that recovery increased with increasing rotational speed up to 80 rpm, using a mixing time of 20 min. In Egypt, Ayoub & Abdelfattah (2016) noted little increase (from 36.5 to 38.2%) in aluminium recovery (pH = 1.36) from WTS of a full-scale WTP by increasing the mixing rotational speed from 90 to 150 rpm, while increasing from 150 to 200 rpm had no further effect. Similarly, Fouad *et al.* (2017) reported that aluminium recovery from WTS of a full-scale WTP (in El-Sheikh Zayed, Egypt) increased from 38 to 50% when changing rotational speed from 20 to 80 rpm, but no further gain was noted from 80 to 100 rpm.

At low mixing intensities, the thickness of the diffusion layer is reduced with increasing velocity gradient until the thickness of the diffusion layer is minimized and no longer the aluminium dissolution is controlled by film diffusion (Cheng *et al.* 2012). In the present study, mixing intensity had no significant effect on coagulant recovery. It is possible that the range tested here (100–200 s⁻¹) was beyond the velocity gradient value resulting from the 80 rpm used by Cheng *et al.* (2012) and Fouad *et al.* (2017), therefore, exerting no influence on aluminium recovery. With respect to mixing time, the American Water Works Association (AWWA) recommends that tests should be conducted to find the optimal mixing time for each specific WTS, suggesting, though, that values between 10 and 20 min tend to be suitable for most WTS. In addition, there are reports of up to 80% recovery with 5 min mixing time in laboratory tests and 10 min in full-scale reactors (AWWA 1991). Xu *et al.* (2009) obtained aluminium recovery efficiency of 80% with 30 min of mixing, with 70% having taken place in the first 10 min. Cheng *et al.* (2012) also observed an increase in aluminium recovery with increasing mixing time up to 20 min. Nair & Ahammed (2014) concluded that mixing time (between 10 and 30 min) influenced coagulant recovery more or less intensely depending on pH and solids concentration; in any case, aluminium recovery increased with increasing mixing times. Ayoub & Abdelfattah (2016) evaluated the influence of mixing time between 15 and 90 min on aluminium recovery from the WTS above mentioned (pH = 2.0; mixing rotational speed = 150 rpm). No influence of mixing time was observed between 15 and 45 min and between 60 and 90 min, but it slightly increased, from 9.75 to 11.48%, with 45 and 60 min, respectively; therefore, the authors selected the optimum mixing time as 60 min. Fouad *et al.* (2017), evaluating the influence of mixing times from 10 to 50 min, found similar results: little influence between 10 and 30 min and between 40 and 50 min, aluminium recovery increase from ≈60 to ≈80% between 30 and 40 min, and no further increase beyond 40 min. Although the range of mixing time values tested in the present study (5–20 min) is similar to those used in the above-mentioned studies, no influence of mixing time on aluminium recovery was observed here. Probably, aluminium dissolution was kinetically limited between 5 and 20 min of reaction. Usually, recovery efficiency increases with increasing mixing time during the first minutes, becoming fairly constant after extraction becomes kinetically limited (AWWA 1991). According to the AWWA (1991), after some time of acid extraction, aluminium dissolution becomes kinetically limited because the remaining aluminium in the sludge is more difficult to extract. As aluminium dissolution proceeds, the sludge core shrinks and there is an accumulation of inert particles (as clay minerals, containing SiO₂ and Al₂O₃) forming an inert layer. This barrier impairs the diffusion of acid into the core and also the diffusion of the solubilized aluminium to the solution, limiting the coagulant recovery efficiency (Cheng *et al.* 2012).

A summary of the results from the presented studies about mixing conditions for coagulant recovery is given in Table 3. Although optimum mixing conditions could not be identified in the present study, this is the only work where a recommendation of mixing intensity was given in terms of velocity gradient (which, on the other hand, makes it difficult a comparison with the other results), and where the significance of the results were statistically tested, including the interaction between mixing intensity and mixing time.

Since neither velocity gradient nor mixing time significantly influenced aluminium recovery efficiency, the lowest values of velocity gradient (100 s⁻¹) and mixing time (5 min) tested here were assumed as the 'best conditions', in as much as low mixing intensity means less energy consumption and short mixing time results in more compact reactors. However, it is likely that similar recovery could be obtained using even shorter mixing time (<5 min) and lower mixing intensity (<100 s⁻¹), which should be confirmed in future experiments. Nonetheless, it is worth noticing that although velocity gradient and mixing time did not influence aluminium recovery, both of them affected the quality of the RC in terms of TSS, COD and phosphorus.

Table 3 | Studies about mixing conditions for coagulant recovery

Research	Mixing intensity range tested	Mixing time range tested (min)	Recommended mixing intensity	Recommended mixing time (min)	Aluminium recovery (%)
Xu <i>et al.</i> (2009)	170 rpm	10–150	–	30	84
Cheng <i>et al.</i> (2012)	20–120 rpm	5–60	80 rpm	20	>80
Nair & Ahammed (2014)	100 rpm	10–30	–	30	63
Ayoub & Abdelfattah (2016)	90–200 rpm	15–90	150 rpm	60	≈40
Fouad <i>et al.</i> (2017)	20–100 rpm	10–50	80 rpm	40	82
This study	100–200 s ⁻¹	5–20	100 s ⁻¹	5	63

3.3.2. Total suspended solids (TSS)

The TSS content of the RC varied significantly depending on the combinations of velocity gradient (G) and mixing time (t). Table 4 shows the Student's t -test results for the model coefficients and the ANOVA for the final model. The final model obtained is presented in Equation (7) and in Figure 1:

Table 4 | Results of ANOVA and Student's t -test for TSS

Source	DF	SS	MS	F_{calc}	p_{value}
Model	5	56,276	11,255.2	119.3	$6.40 \times 10^{-6*}$
g_{cod} (velocity gradient)	1	–	–	–	$1.24 \times 10^{-6*}$
t_{cod} (mixing time)	1	–	–	–	$1.17 \times 10^{-5*}$
g_{cod}^2	1	–	–	–	0.00105*
t_{cod}^2	1	–	–	–	0.660
$g_{\text{cod}}t_{\text{cod}}$	1	–	–	–	0.0128*
LOF	3	402	133.9	2.45	0.241
Pure error	3	164	54.7	–	–
Residuals	6	566	94.3	–	–

*Significant at 5%; p_{value} ($K_{\text{S}_{\text{test}}}$) = 0.432; DF, degrees of freedom; SS, sum of squares; MS, mean square.

$$\text{SST} = 247.25 + 0.0131G^2 - 2.96G + 0.0489t^2 - 1.04t + 0.0453Gt \quad (7)$$

$$R^2 = 0.99; R_{\text{adj}}^2 = 0.98$$

In spite of the resulting quadratic model and the interaction effect between velocity gradient and time being significant, the model interpretation is quite simple: within the range of values tested, an increase in the suspended solids content was observed either with the increase in velocity gradient or mixing time, or both. Suspended solids ranged from 100 to 350 mg L⁻¹. The coefficient of determination (R^2) indicates how much of the variability of a response variable is explained by the model, and should be close to 1.0. As R^2 always increase with increasing number of model factors (significant or not), the use of the adjusted coefficient of determination (R_{adj}^2) is preferred, since it also reflects the number of factors included in the model (Montgomery 2013). The high values of R^2 and R_{adj}^2 indicate that the TSS concentration is strongly influenced by the variation of the velocity gradient and/or mixing time.

Increasing the mixing time or the velocity gradient favours the breakage of solids present in the sludge and its dispersion in the solution, hence, increasing the TSS concentration in the final RC.

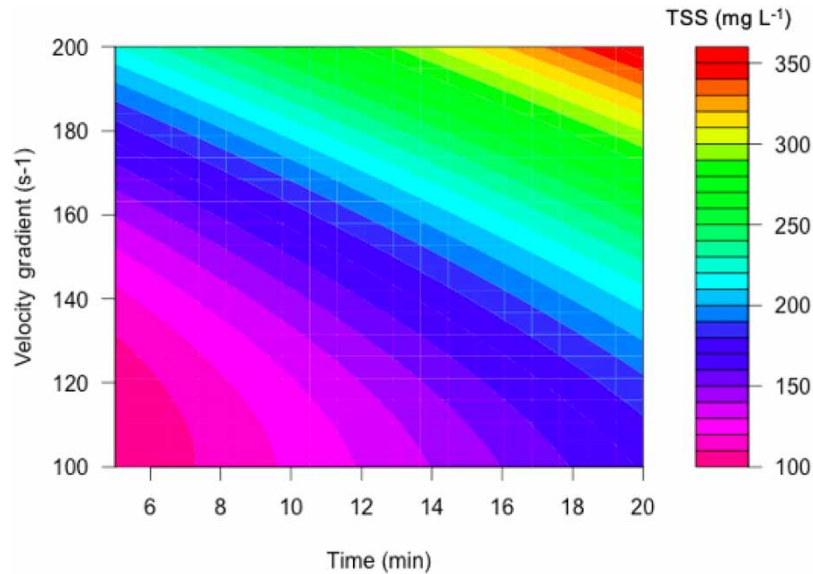


Figure 1 | Estimates of total suspended solids (TSS) as a function of mixing time and velocity gradient.

3.3.3. Chemical oxygen demand (COD) and phosphorus

The COD content of the RC varied significantly with velocity gradient (G). On the other hand, only mixing time (t) presented a significant effect on total phosphorus in the RC. Tables 5 and 6 show the Student's t -test results for the model coefficients and the ANOVA for the final model, for COD and phosphorus, respectively. The model obtained for COD is presented by Equation (8) and Figure 2 and by Equation (9) and Figure 3, for phosphorus:

$$\text{DQO} = 1622.3 + 0.03G^2 - 8.48G \quad (8)$$

$$R^2 = 0.65; \quad R_{\text{adj}}^2 = 0.57$$

Table 5 | Results of ANOVA and Student's t -test for COD

Source	DF	SS	MS	F_{calc}	P_{value}
Model	2	28,596	14,298	8.19	0.00940*
g_{cod} (velocity gradient)	1	–	–	–	0.0366*
g_{cod}^2	1	–	–	–	0.0105*
LOF	6	8,392	1,398.2	0.57	0.743
Pure error	3	7,312.8	2,437.6	–	–
Residuals	9	15,702	1,745	–	–

*Significant at 5%; $p_{\text{value}} (K_{\text{S}_{\text{test}}}) = 0.9371$; DF, degrees of freedom; SS, sum of squares; MS, mean square.

Table 6 | Results of ANOVA and Student's t -test for phosphorus

Source	DF	SS	MS	F_{calc}	P_{value}
Model	1	0.735	0.735	6.84	0.0258*
t_{cod} (mixing time)	1	–	–	–	0.0258*
LOF	7	0.645	0.922	0.75	0.661
Pure error	3	0.368	0.123	–	–
Residuals	10	1.02	0.114	–	–

*Significant at 5%; $p_{\text{value}} (K_{\text{S}_{\text{test}}}) = 0.6721$; DF, degrees of freedom; SS, sum of squares; MS, mean square.

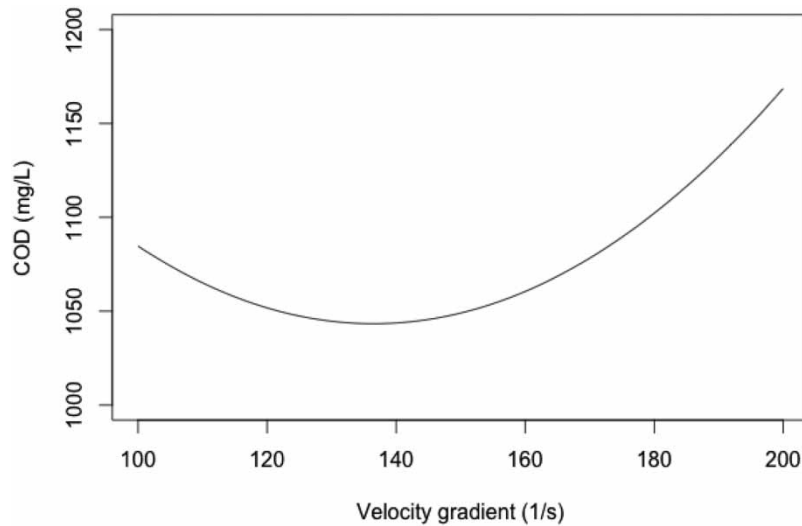


Figure 2 | Estimates of chemical oxygen demand (COD) as a function of velocity gradient.

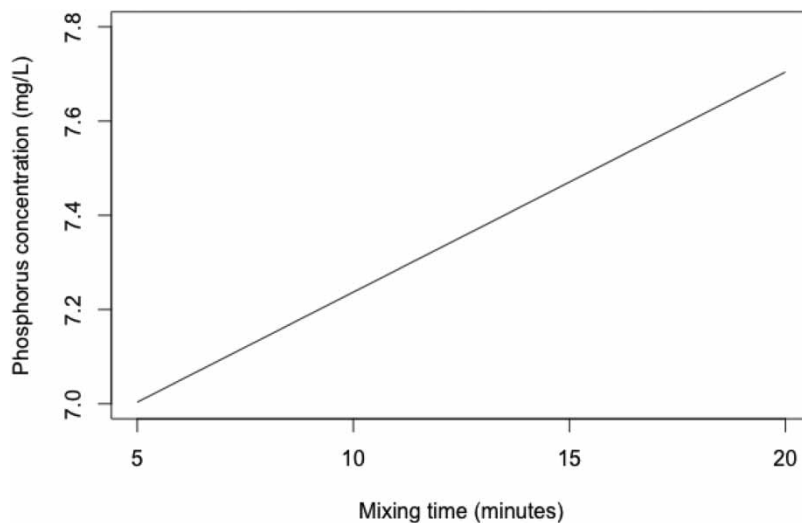


Figure 3 | Estimates of phosphorus concentration as a function of mixing time.

$$P = 6.77 + 0.047T \quad (9)$$

$$R^2 = 0.41; R_{adj}^2 = 0.35$$

For both COD and phosphorus models, the R_{adj}^2 values (0.57 and 0.35, respectively) were lower than that for TSS. This means that the variations of COD and phosphorus contents of the RC are less explained by variations in the model factors, and may have been influenced by other uncontrolled factors too. In any case, as the ranges of values of COD (1,040–1,170 mg L⁻¹) and total phosphorus (7.0–7.8 mg P L⁻¹) in the RC were quite narrow, it was indeed expected that both these variables would have little influence on the RC quality. RC samples were further analysed for TOC, showing values as high as 306 mg C L⁻¹, confirming thus that the RC had a high organic matter content.

3.4. Recovered coagulant quality at the chosen mixing conditions

The results obtained here aimed at being applied to evaluate the use of the RC for phosphorus removal in tertiary treatment of piggery wastewater. Given that most of the organic matter and TSS was removed by secondary

treatment, and the main objective of the tertiary treatment is to remove phosphorus, it is desirable that the RC has low values of COD, TSS and phosphorus. Two samples of the RC were analysed for total and soluble COD and phosphorus, and the results showed that nearly 100% of both COD and phosphorus were soluble, i.e., it will not be removed from the RC solely by physical mechanisms as sedimentation in wastewater treatment plants.

It is noteworthy that the 'best mixing conditions' for aluminium recovery suggested above (the lowest values of velocity gradient = 100 s^{-1} and mixing time = 5 min), provided the lowest values of TSS and total phosphorus in the RC too. Further, under these mixing conditions, the COD of the RC was only 50 mg L^{-1} higher than the minimum COD value obtained in the recovery experiments. Therefore, it is concluded that the conditions defined for the production of the RC at lower costs (in terms of aluminium recovery) also resulted in a better product quality.

4. CONCLUSIONS

The hypothesis that there would be an optimum combination of mixing time and mixing intensity for maximizing coagulant recovery efficiency and the resulting coagulant quality was not confirmed. Within the ranges of values tested here, neither mixing time nor velocity gradient, or the interaction between these two variables, had a significant effect on aluminium recovery. Nevertheless, mixing conditions did influence the RC quality in terms of COD, TSS and total phosphorus, with low velocity gradient and short mixing time resulting in better quality of the RC. Even with the lowest values tested ($G = 100 \text{ s}^{-1}$ and $t = 5 \text{ min}$), the aluminium content in the RC ($1,000 \text{ mg L}^{-1}$) was shown to be high enough to be used for phosphorus removal from piggery wastewater (the ultimate objective of this work).

Finally, we acknowledge that the use of this particular sludge, with a long storage time, may have influenced the results, the same applying to the range of values of velocity gradient and mixing time tested here. Thus, we recommend further investigation using sludge with a shorter storage time, as well as a wider range of mixing conditions.

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DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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