Evaluation of flue gas desulfurization gypsum as a low-cost precipitant for phosphorus removal from anaerobic digestion effluent filtrate

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Abstract: Land application of anaerobic digestion (AD) effluent as a fertilizer is desirable for nutrient recycling, but often supplies excess phosphorus (P), which contributes to surface water eutrophication. Reducing the P content in AD effluent filtrate using calcium (Ca) treatment prior to land application is a potential strategy for improving effluent disposal and meeting the discharge standard. This study took flue gas desulphurization (FGD) gypsum, a by-product of coal-fired power plants, as a low-cost Ca source, and combined with traditional phosphorus removal agents to achieve high phosphorus removal efficiency with less chemical cost. As the results showed, FGD gypsum dosages of 20 mmol/L Ca (3.44 g/L) and 40 mmol/L Ca (6.89 g/L) removed up to 97.1% of soluble P (initially 102.8 mg/L) within 60-90 minutes. Combining FGD gypsum treatment with traditional chemical treatments using calcium hydroxide [$Ca(OH)_2$] or ferric chloride ($FeCl_3$) could achieve >99% P removal with reduced chemical costs. This study demonstrated that FGD gypsum is an efficient calcium-based precipitant for phosphorus removal, offering a cost-effective and sustainable approach to enhance wastewater treatment practices and meet discharge standards in wastewater management.

Keywords: flue gas desulfurization gypsum, anaerobic digestion effluent, precipitation, phosphorus removal, eutrophication
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1 Introduction

Anaerobic digestion (AD) is an important waste-to-energy technology that converts organic wastes into biogas and a nutrient-rich liquid effluent. AD effluent is an effective organic fertilizer that can be disposed of via land application to crops. However, land application of AD effluent often supplies phosphorus in excess of crop needs and soil absorptive capacity[1], especially the dissolved reactive phosphorus (P), which has high runoff potential. Thus, the export of excess P from agricultural areas might lead to a wide range of adverse eco-environmental problems, such as eutrophication, biodiversity reduction, disruption of P cycle, and degradation of ecosystem functions. Thus, land application of AD effluent is often highly regulated in order to reduce nutrient runoff and mitigate the associated water quality problems. A key strategy to address this is to remove phosphorus from AD effluent to protect water quality and improve effluent disposability.

Various physical, chemical, and biological treatments can be integrated to remove and recover phosphorus from wastewater. Membrane filtration can remove very high levels of insoluble and soluble phosphorus, but has high capital and operating costs[2]. Biological treatments such as enhanced biological phosphorus removal or algae can be highly effective, but operation is complicated and expensive, and biological systems are prone to process instability[3]. Coagulation with iron or aluminium coagulants is highly effective, but the resulting sludge has minimal reuse value and must be permanently disposed of via incineration and landfilling[4]. Crystallization of struvite ($MgNH_4PO_4 \cdot 6H_2O$) has been successfully applied to various anaerobically digested wastes, but this method requires expensive magnesium inputs and pH adjustment.

Alternatively, one of the simplest methods for removing phosphorus from wastewater is solid-liquid separation followed by treatment with calcium. Solid-liquid separation is first used to remove particulates and organic matter which interfere with precipitation. Then, by adding a calcium source, soluble phosphorus can be precipitated as insoluble calcium phosphates such as hydroxyapatite [HAP; $Ca_5(PO_4)_3OH$] or amorphous calcium

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phosphate [ACP; $Ca_3(PO_4)_2{\cdot}nH_2O$][5,6]. Calcium treatment is an extremely mature approach, but several challenges prevent its application to high strength wastewaters like AD effluent. Various wastewater constituents compete for Ca ions, particularly carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-)[7]. Large, prohibitively costly quantities of precipitant [typically $Ca(OH)_2$] are required to overcome these interferences and achieve effective phosphorus removal. Reducing the precipitant cost is a key strategy for improving process feasibility.

In recent years, some calcium-rich industrial by-product materials, such as waste concrete and oil shale-ash have been utilized as sorbent materials for phosphate removal[8]. This strategy of using calcium-rich industrial by-products is a ‘win-win’ solution to treating waste with waste. Among the calcium-rich by-products, flue gas desulphurization (FGD) gypsum, a waste by-product of the coal industry during the removal of sulphur dioxide (SO_2) from coal combustion exhaust, has great potential to be used as a low-cost source of calcium for phosphorus removal and recovery from AD wastewater. FGD gypsum contains mainly (typically≥95%) calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$)[9]. As a waste material generated in a large quantity, FGD gypsum may be available for low or no cost (excluding transportation) compared to traditional calcium-, aluminum- or iron-based materials used in P removal treatment.

FGD gypsum has shown good potential to remove P, and the spent FGD gypsum has been widely studied as a safe soil amendment to supplement Ca and S as a fertilizer[10-12]. For example, King et al.[11] reduced phosphate loss in Tile-Drained landscapes using FGD gypsum. After the first application of FGD gypsum, the event mean dissolved reactive P and total P concentrations in tile water at the treatment site were significantly reduced by 21% and 10%, respectively, and the dissolved reactive P concentration in surface runoff was significantly reduced by 14%. Researchers also proposed to stabilize liquid fertilizer by FGD gypsum before application to reduce the potential loss of P and reduce the risk of eutrophication[13]. Importantly, despite its origins in coal energy production, extensive studies have shown that FGD gypsum consistently contains suitably low heavy metal concentrations for environmental applications[14].

Previous studies only showed that FGD gypsum, as a soil amendment, could reduce P runoff from low-concentration irrigation discharge. However, to the best knowledge of the authors, few studies have been conducted to use FGD gypsum to treat AD wastewater, especially by using a controlled reactor. Thus, the objectives of this study are to provide an initial evaluation of the suitability and effectiveness of FGD gypsum for P removal and recovery from AD effluent filtrate, design a potential system, optimize the operating parameters, and provide a preliminary economic analysis. The composition of the resulting precipitates was also determined to evaluate their potential recyclability. The effectiveness of FGD gypsum for P removal was also compared to that of traditional chemicals used in P removal treatments [$Ca(OH)_2$ and ferric chloride ($FeCl_3$)]. Combined and sequential chemical treatments were investigated to achieve high P removal efficiency with reduced chemical inputs. This study provides baseline data about the suitability and effectiveness of using FGD gypsum as a precipitant for removing P from AD effluent filtrate.

2 Materials and methods

2.1 Anaerobic digestion effluent filtrate

The AD effluent used in this study was collected from a commercial AD facility that is operated by quasar energy group in Columbus, OH. Prior to collection, the effluent was dewatered using a polymer-assisted belt filter press (Komline-Sanderson, Peapack, NJ, USA). The liquid portion (AD effluent filtrate) from the dewatering was collected for testing. The filtrate was allowed to stabilize and was stored at 4°C to minimize compositional changes over time. Before sampling, filtrate in the storage tank was mixed thoroughly to resuspend particles. A 2 L sample was then collected and allowed to reach room temperature before the start of testing. The characteristics of the AD effluent are summarized in Table 1. The pH was stable for the duration of the storage period (8.57±0.02). The total phosphorus (TP) content was 124.8 mg/L and the total dissolved phosphorus (TDP) was 102.8 mg/L, indicating most of the P (about 82%) was present in the dissolved phase. The presence of mostly dissolved P necessitates the use of chemical removal methods, as opposed to physical separations alone. The total ammonia nitrogen (TAN=592 mg/L) was relatively low for an anaerobically digested wastewater, likely due to volatilization prior to collection. The total alkalinity (TA) was high (TA=2720), which was expected to negatively influence P removal. The chemical oxygen demand (COD) and volatile solids (VS) values indicate high levels of organic matter, and the total solids to total suspended solids (TS/TSS) values indicate high levels of particulate matter. Both may impact P removal efficiency[15].

Table 1 Characteristics of anaerobic digestion effluent filtrate

Characteristic	Unit	Measurement
pH	-	8.57±0.02
Total Solids (TS)	%	0.56±0.10
Total Volatile Solids (TVS)	%	0.12±0.02
Total Suspended Solids (TSS)	mg/L	3320.0±40.0
Chemical Oxygen Demand (COD)	mg/L	2033.0±121.0
Total Alkalinity (TA)	mg/L (as $CaCO_3$)	2720.0±26.0
Total Ammonia Nitrogen (TAN)	mg/L	592.0±9.0
Total Phosphorus (TP)	mg/L	124.8±5.6
Total Dissolved Phosphorus (TDP)	mg/L	102.8±4.6

2.2 Characterization of FGD gypsum and precipitates

The FGD gypsum used in this study came from a coal-fired power plant in Ohio. The water content was determined gravimetrically by first drying the FGD gypsum at 40°C to remove free moisture and then at 250°C to remove the water within the crystal structure (combined water)[16]. Elemental composition was determined using an Agilent 7500 inductively coupled plasma mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Prior to inductively coupled plasma mass spectrometry (ICP-MS) analysis, samples were digested using a Mars Xpress microwave digestion oven (CEM Corp., Matthews, NC, USA). The release of heavy metals from a high dosage of FGD gypsum was tested by placing 2.0 g FGD gypsum in 50 mL deionized (DI) water. Samples were shaken at 150 r/min at 25°C in a temperature-controlled shaker for 24 h. The supernatant was analyzed using ICP-MS (Perkin-Elmer, Waltham, MA, USA) to quantify heavy metals.

2.3 Synthetic wastewater

Synthetic wastewater was used in the test to study the reaction mechanisms with the flexibility to adjust some parameters, such as pH and alkalinity[17,18]. FGD gypsum was added to the synthetic wastewater, which was used for modelling of P removal kinetics. The synthetic wastewater had a pH of 8.60 and contained 100 mg/L PO_4^{3-}-P, 600 mg/L NH^{4+}-N, and carbonate alkalinity of 2000 mg/L as calcium carbonate ($CaCO_3$). Stock solutions of PO_4^{3-}, NH^{4+}, and HCO_3^- were prepared using reagent grade potassium dihydrogen phosphate (KH_2PO_4), ammonium chloride (NH_4Cl), and sodium bicarbonate ($NaHCO_3$) (Sigma-Aldrich), which were stored in sealed containers. After appropriate quantities of PO_4^{3-}, NH_4^+, HCO_3^-, and DI water were mixed, the pH of the wastewater was adjusted dropwise to 8.60 using sodium hydroxide (NaOH). The pH was allowed ample time to stabilize (at least 20 min). Samples were tightly capped to minimize the intrusion of atmospheric carbon dioxide (CO_2). The pH was checked and readjusted just before FGD gypsum was added to ensure proper pH. Tests were done in triplicate.

2.4 Phosphorus removal experiment

The effect of mixing time (0-180 min) on TDP removal using three FGD gypsum dosages (10 mmol/L Ca, 20 mmol/L Ca, 40 mmol/L Ca) was studied to develop a time course of TDP removal.

The effect of mixing time (0-180 min) on TDP removal was investigated using three FGD gypsum dosages (10 mmol/L Ca, 20 mmol/L Ca, 40 mmol/L Ca). FGD gypsum dosages were generally defined in terms of the mmol/L Ca (1 g $CaSO_4{\cdot}2H_2O$= 5.80 mmol/L Ca). This was chosen in order to compare with other calcium reagents in later experiments. The dosages correspond to the following quantities: 10 mmol/L Ca=1.72 g/L; 20 mmol/L Ca=3.44 g/L; 40 mmol/L Ca=6.89 g/L; 80 mmol/L Ca=13.76 g/L. The FGD gypsum samples were manually ground to break up large particles before being used in experiments. For the synthetic wastewater, the pH was adjusted dropwise to 8.60 using 1 mol/L NaOH. Three dosages of FGD gypsum were added and mixed at 360 r/min for 180 min. At different sampling times (0, 15, 30, 40, 50, 60, 90, 120, and 180 min), 5 mL samples were taken for P analysis. For AD effluent filtrate, the same treatment was used, but without pH adjustment. To study phosphorus removal at equilibrium without interferences, a fixed dosage of FGD gypsum (1.0 g) was added to 100 mL of phosphate solution of varying concentrations. P Solutions with concentrations (50, 100, 150, 300 and 500 mg/L) were made using reagent-grade KH_2PO_4. After 24 h, samples were collected, filtered and analyzed for the final total dissolved phosphorus (TDP_{final}). To evaluate the effects of initial pH on TDP removal, 20 mmol/L Ca of FGD gypsum was dosed to AD effluent filtrate that had been adjusted to different pH levels (5.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0). A control at the natural pH (8.57) was included. Briefly, 5 mol/L NaOH was added dropwise to about 450 mL of AD effluent filtrate. The pH was allowed to stabilize (at least 20 min) before 200 mL aliquots were dosed with 20 mmol/L Ca FGD gypsum and mixed for 1 h. The NaOH volumes required were ≤1% of the wastewater volume so the effects of dilution were ignored. Controls included the pH-adjusted wastewater that did not receive FGD gypsum and wastewater that did not receive pH adjustment (pH=8.57). This test was done in duplicate.

2.5 Kinetics and Sorption isotherm of phosphorus removal

The kinetics for TDP removal was modelled using the first order, second order, and pseudo-second order kinetic models. In addition, the Langmuir and Freundlich isotherms were investigated to fit the experimental adsorption isotherms.

The first order dynamics formula is as follows:

$$\ln\frac{C_t}{C_o} = -k_1 t \tag{1}$$

where, C_t is the phosphorus concentration at any time, mg/L; C_o is the phosphorus concentration at the initial moment, mg/L.

The second order dynamics equation is as follows:

$$\frac{1}{C_t} = \frac{1}{C_O} + k_2 t \tag{2}$$

where, k_2 is the rate constant of sorption.

The pseudo-second order equation is below[19-21].

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{t}{q_e} \tag{3}$$

where, q_t is amount of solute sorbed on the surface of the sorbent at any time, mg/g; q_e is the amount of adsorption at equilibrium, mg/g; k_{p2} is the rate constant of sorption.

The Freundlich model can be expressed as follows:

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{4}$$

where, C_e is the average residual phosphorus concentration at equilibrium, mg/L; n is the Freundlich isotherm fitting coefficient; K_F is the fitting constant of Freundlich isotherm.

The form of the Langmuir model can be expressed below:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \tag{5}$$

where, q_m is the amount of maximum adsorption, mg/g; k_L is the Langmuir isotherm equilibrium constant.

2.6 FGD gypsum-$Ca(OH)_2$/$FeCl_3$ treatment

In this test, other traditional precipitates were added after FGD gypsum treatment to evaluate the effect of a combined treatment. AD effluent filtrate was used for this test. Different blends of FGD gypsum to $Ca(OH)_2$ were added to 200 mL AD effluent filtrate and mixed for 2 h. The Ca blends were based on the Ca (mmol/L) contributed by each material. The following blends of FGD gypsum to $Ca(OH)_2$ were used: 0/80, 20/60, 40/40, 60/20, 80/0. The TDP removal at each blend was compared to the TDP removal using single precipitants (80/0 and 0/80 FGD gypsum to $Ca(OH)_2$). Optimization of this treatment involved further testing of 10/40, 20/40, and 0/60 blends of FGD gypsum to $Ca(OH)_2$. The pH was also recorded after treatment.

A sequential FGD gypsum-$FeCl_3$ treatment was also evaluated to determine whether pretreating AD effluent with FGD gypsum filtrate could reduce the required consumption of $FeCl_3$ to reach a 99% P removal. First, 3.4 g/L (20 mmol/L Ca) FGD gypsum was mixed in 200 mL AD effluent filtrate for 2 h. Following this, the samples were allowed to settle for 30 min. Then, 145 mL of supernatant was transferred to a 250 mL flask without disturbing the precipitates. Next, 5 mL $FeCl_3$ solution (≥98% anhydrous $FeCl_3$; Sigma-Aldrich) was added to achieve the desired $FeCl_3$ concentration (0.5, 1.0, 1.5, 2.0 g/L). Samples were shaken in a mechanical shaker for 10 min at 175 r/min. After shaking, samples were removed from the shaker and allowed to settle completely for 20 min[22]. The supernatant was collected and filtered for TDP analysis. The controls were samples that received the same iron dosage (0.5-2.0 g/L) without calcium pretreatment to compare TDP removal efficiency and chemical inputs.

2.7 P analysis

Phosphorus determination was done using APHA Standard Methods 4500-P Sec. B4 (sulfuric-nitric acid digestion) and 4500-P Sec. E (ascorbic acid method for orthophosphate determination). The acid digestion step converts all forms of P in the sample to orthophosphate, which can be quantified via ascorbic acid colorimetry. For TP analysis, samples were not filtered. For TDP analysis, samples were filtered through a 0.45 µm membrane as per the standard methods. TDP (which includes the digestion step) was chosen as the primary measurement instead of dissolved reactive P (no digestion step). This was because various inorganic and organic P compounds can interfere with the detection of orthophosphate in this colorimetry method[23]. Because the AD wastewater typically contains many of these interfering P species, a digestion step was used to reduce possible interferences. For H_2SO_4-HNO_3 digestion, 0.3-1.0 mL of sulfuric-nitric acid mixture (5 parts concentrated H_2SO_4 and 1 part concentrated HNO_3) was added to ≤2.0 mL sample in acid hydrolysis tubes. Volume was made up to 3 mL with DI water. Samples were autoclaved (Yamato SM310 autoclave, Japan) for 30 min at 121°C. Following digestion, samples were allowed to cool and then neutralized with 5 mol/L NaOH. Following digestion, samples were diluted appropriately to within the detectable range (0.10-1.2 mg/L P) for ascorbic acid colorimetry. Acid-washed glassware was reserved for use in these experiments.

2.8 Structural analysis

To characterize the precipitates produced after FGD gypsum treatment, FGD gypsum (20 or 40 mmol/L Ca) was added to 200 mL of synthetic wastewater (prepared as previously described) and AD effluent filtrate, then mixed them at 360 r/m for 180 min. After mixing, the precipitates were settled for 30 min. The supernatant was siphoned off using a pipette and the precipitates were washed out and collected on wax paper. The samples were dried at 40°C overnight. Dry samples were stored in a desiccator (SP Scienceware, Wayne, NJ, USA) until analysis. Fourier transform infrared spectroscopy (FTIR) was done using a Perkin-Elmer Fourier transform infrared spectrometer (Perkin-Elmer, Waltham, MA, USA) to characterize the functional groups.

3 Result and discussion

3.1 Characterization of FGD gypsum

Key compositional characteristics of FGD gypsum are listed in Table 2. The Ca content was used to estimate gypsum purity. The calcium content of pure $CaSO_4·2H_2O$ is 23.2% of the total mass. This sample contained 22.1% Ca or 221 mg/g Ca. In addition, the free moisture of the material was 0.22% and the combined water content was 19.94% (solid content was 80.06%). For 100% pure $CaSO_4·2H_2O$, 79.1% solids and 20.9% combined water would be expected. Based on the Ca content and combined water content, the FGD gypsum purity was estimated to be around 95%. The impurities include the other elements that were detected in appreciable amounts, such as ferrum (Fe), aluminum (Al), and magnesium (Mg). Each of these species may also contribute to P removal by forming various Fe-P, Al-P, or Mg-P compounds[5]. The quantities of these elements were orders of magnitude lower than Ca, indicating that Ca is the main precipitant.

Table 2 Characterization of FGD gypsum.

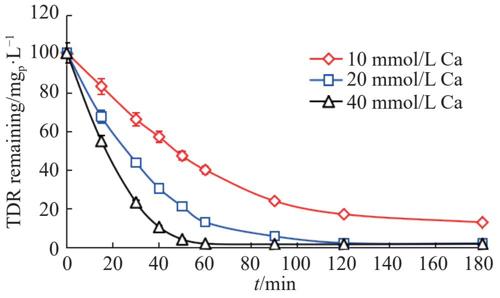
Composition			
Combined water	19.94%		
Free water	0.22%		
Solid content	80.06%		
Estimated purity	95.00%		
Elements/mg·kg^{-1}			
Ca	221 000.00	As	<4.00
Na	1000.00	Cd	<0.05
Fe	3900.00	Cr	<3.00
Al	2000.00	Pb	<0.80
Mg	3200.00	Se	<5.00
P	100.00	Hg	<0.10
K	360.00	Mo	<0.40

FGD gypsum itself contains some heavy metals, and there may be a safety problem of heavy metals flowing into the ecosystem during utilization[24]. Although many studies have shown that the application of heavy metals in FGD gypsum has almost no negative impact on the environment, the harm of heavy metals should still be fully considered and studied. All of the tested heavy metals, including arsenic (As), cadmium (Cd), chromium (Cr), plumbum (Pb), selenium (Se), hydrargyrum (Hg), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), etc., in the leachate were below the detectable range for ICP-MS (around 10-60 μg/L for these elements) and well below biosolids regulations.

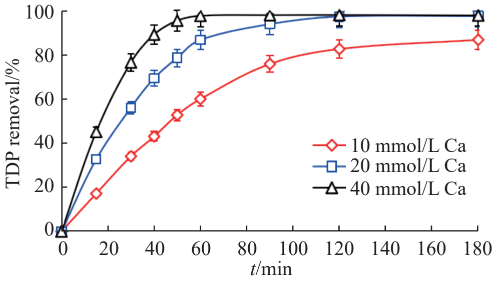
3.2 P removal using FGD gypsum in synthetic wastewater

3.2.1 Kinetics of phosphate removal in synthetic wastewater

At the FGD gypsum dosages of 10, 20, and 40 mmol/L Ca, 86.8%, 97.6%, and 97.9% of TDP was removed in synthetic wastewater, respectively, within the 180-min test period (Figure 1a and 1b). At the lowest dosage, 13.21 mg/L P remained in solution after 180 min. The final TDP remaining in solution at 20 mmol/L Ca (2.36 mg/L P) and 40 mmol/L Ca (2.09 mg/L P) were not significantly different (p<0.05). The FGD gypsum appeared to reach equilibrium at the higher dosages, but did not reduce TDP below 2 mg/L finally. The 20 mmol/L Ca dosage took 120 min to reach the highest level of removal (97.6%). The 40 mmol/L Ca dosage exhibited the highest removal, reaching maximum removal in 60 min. Higher calcium dosages can improve P removal in several ways. First, the presence of higher Ca concentrations increases the supersaturation of the solution with respect to calcium phosphate. Supersaturation is the thermodynamic driving force for the formation of precipitates; higher supersaturation typically results in higher removal rates[25]. Also, the presence of undissolved FGD gypsum could provide surface area for the nucleation of calcium phosphate crystals (i.e. seeding). The presence of seeding surfaces decreases the activation energy required for crystallization to occur, resulting in higher removal rates[17,26].



a. Time course for TDP removal in synthetic wastewater at different FGD gypsum dosages

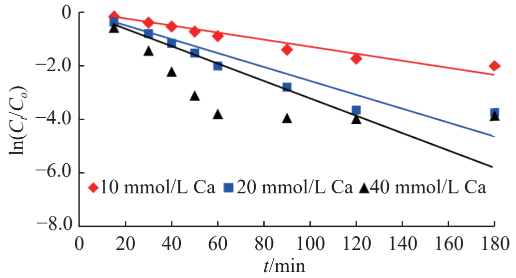


b. Kinetics of TDP removal in synthetic wastewater using FGD gypsum

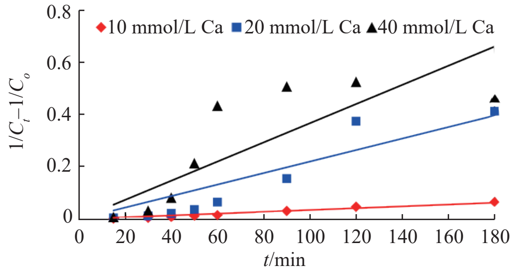
Figure 1 Process of TDP removal from synthetic wastewater

3.2.2 Kinetic models of TDP removal in synthetic wastewater

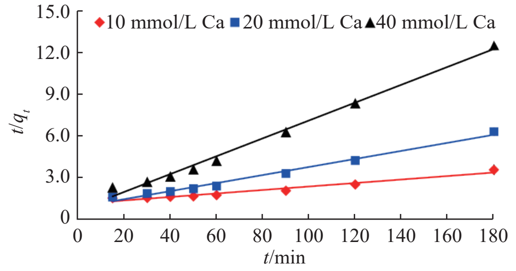
First order, second order, and pseudo-second order kinetic models were applied to further investigate the nature of removal and possible removal mechanisms. Figure 2 displays the fit of the curves to the data and Table 3 contains the model coefficients. Over 180 min, the first order model describes DRP (dissolved reactive phosphorus) removal moderately well for 10 mmol/L Ca (R^2=0.925) but not well for 20 mmol/L Ca (R^2=0.852). However, the correlation coefficients for both 10 mmol/L Ca (R^2=0.993; k_1'=0.015) and 20 mmol/L Ca (R^2=0.993; k_2'=0.031) are high over 120 min. Apparently, the first order model describes the data well until maximum removal is achieved around 120 min. Several studies have shown similar results, where adsorption data fit well to first or second order models initially, but not over longer periods[21,27]. Also, over 120 min, the rate constant k at 20 mmol/L Ca (k_2'=0.0231) was almost exactly twice the rate constant at 10 mmol/L Ca (k_1'=0.015). Doubling the dosage in this case doubled the reaction rate according to the first order model. At 40 mmol/L Ca, the first order curve was non-linear and did not exhibit significant fit (p>0.05).



a. First order model of phosphorus removal kinetics



b. Second order model of phosphorus removal kinetics



c. Pseudo-second order model of phosphorus removal kinetics

Figure 2 Modeling of phosphorus removal kinetics

Table 3 Coefficients relating to kinetic models for DRP removal

		FGD gypsum dosage					
		10 mmol/L Ca		20 mmol/L Ca		40 mmol/L Ca	
Model	Plot	Coefficients	R^2	Coefficients	R^2	Coefficients	R^2
First order	$\ln(C_t/C_o)$ vs t	k_1=0.0131	0.925	k_1=0.0258	0.852	*	*
Second order	$1/C_t$-$1/C_o$ vs t	k_2=0.0003	0.946	k_2=0.0022	0.834	k_2=0.0037	0.611
Pseudo second order	t/q_t vs t	k_{p2}=0.000 16 q_e=79.36	0.953	k_{p2}=0.000 70 q_e=34.36	0.985	k_{p2}=0.002 68 q_e=15.50	0.991

Note: Coefficients are for models applied to entire test period (180 min); Units: q_e, (mg/g); * denotes that model fit was not significant (p<0.05).

The second order model exhibited good fit at 10 mmol/L Ca (R^2=0.944). However, based on the model constraints, the intercept of the trendline must be zero. When the 10 mmol/L Ca data were not constrained to zero, the intercept term in the experimental model was statistically significant (p<0.05). This suggests that the data do not actually fit the second order model, despite the fairly high correlation coefficient (R^2=0.944). The second order model exhibited statistically significant but poor fit at 20 mmol/L Ca (R^2=0.834) and 40 mmol/L Ca (R^2=0.611).

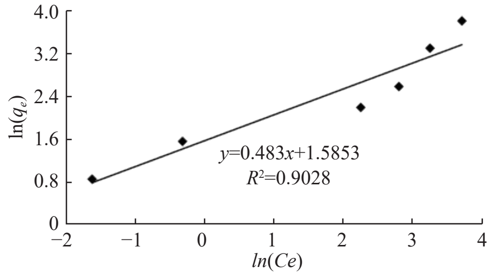
For each dosage, the pseudo-second order model described the data well over the entire 180 min. At 10 mmol/L Ca (R^2=0.953), 20 mmol/L Ca (R^2=0.985), and 40 mmol/L Ca (R^2=0.991), the correlation coefficients were high. Compared to first or second order models, the pseudo-second order model has been shown in numerous cases to fit best over longer periods of time, while other models may only apply initially[21,27,28]. The pseudo-second order model differs from the other models in that it is based on adsorption capacity (q= P/sorbent, mg/g) instead of phosphate concentration in solution (C, mg/L)[27]. This model is more specific to adsorption whereas the others are general models for chemical reactions. The good fit in each case for the whole test period suggests that initially, adsorption is a key removal mechanism during phosphorus removal with FGD gypsum. At equilibrium, the moderate fit of the Freundlich model (R^2=0.902) suggested that adsorption did not describe phosphorus removal completely. Apparently, adsorption is a key removal mechanism initially, but precipitation also occurs as the reaction system equilibrates.

The pseudo-second order model tended to overestimate the maximum phosphorus adsorption capacity (q_e) compared to the data. At 40 mmol/L Ca, the experimental q_e was 14.38 mg/g while the model q_e was 15.50 mg/g, the model was overestimated by 7.2%. At 20 mmol/L Ca the overestimation was 16.7% and at 10 mmol/L Ca the overestimation was 35.8%. This suggests that the pseudo-second order model was most applicable when larger quantities of undissolved gypsum are present and adsorption is more likely to occur. It is possible that a longer reaction time would be needed for the 10 mmol/L Ca dosage to reach equilibrium.

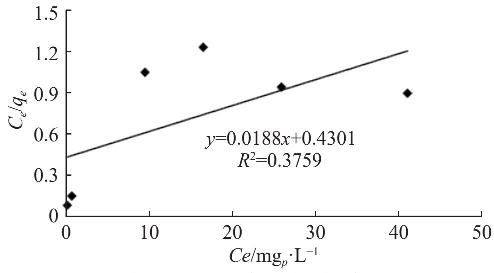
3.2.3 Adsorption isotherm fitting of TDP removal in synthetic wastewater

The fit of the Freundlich isotherm was significant (R^2=0.902) (Figure 3a). The assumption of Freundlich model is that the surface of adsorbent is heterogeneous, the adsorption is a multi-layer adsorption system and the total amount of adsorption is the cumulative adsorption of all surface sites. In the Freundlich model, the closer the $1/n$ value is to zero, the more heterogeneous the surface of the adsorbent is, and the $1/n$ value of 0.483 indicates a heterogeneous surface. In addition, the n value between 1 and 10 is considered favorable to absorption.

The Langmuir model can be used to estimate the maximum phosphorus adsorbing capacity of a material (Figure 3b). This model is based on several key assumptions: it assumes that adsorption occurs in a single layer, the surface is homogeneous, and the adsorption sites have equal sorption capacities[29]. The Langmuir model did not exhibit significant fit to the data (Figure 3b). This may be due to the fact that the heterogeneous composition of FGD gypsum invalidates the hypothesis of identical adsorption sites. Penn et al.[30] also identified precipitation as a major mechanism of phosphorus removal with FGD gypsum. Precipitation cannot be adequately modeled using adsorption isotherms. This likely explains the moderate to poor fit of the isotherms tested here.



a. Freundlich adsorption isotherms

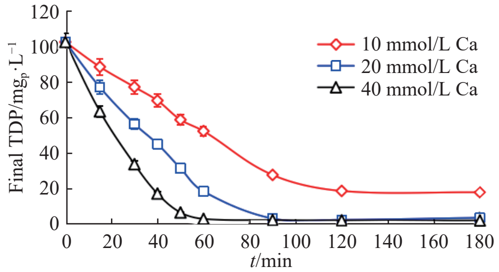


b. Langmuir adsorption isotherms

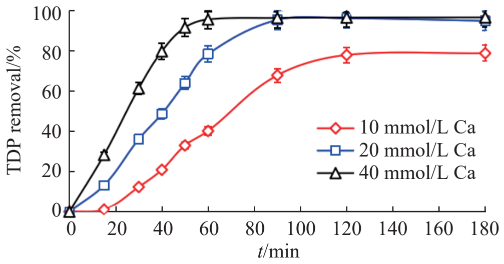
Figure 3 Evaluation of different adsorption isotherm

3.3 P removal using FGD gypsum in AD effluent filtrate

At the three dosages tested (10 mmol/L Ca, 20 mmol/L Ca, 40 mmol/L Ca), removal of 79.2%-97.1% TDP was observed within the 180 min test period (Figure 4a and 4b). The final TDP remaining in solution after 180 min mixing with 10 mmol/L Ca was 18.3 mg/L (79.2% removal). At 20 mmol/L Ca, 96.6% TDP removal was achieved in 90 min, and at 40 mmol/L Ca, 97.1% TDP removal was achieved in 60 min. The TDP_{final} at the higher dosages was between 2-3 mg/L. There was no significant difference (p<0.05) in TDP removal for the two higher dosages between 90-180 min. Subsequent experiments demonstrated that higher FGD gypsum dosages did not increase TDP removal efficiency to over 97%. The color lightened but remained murky and opaque even after prolonged settling.



a. Time course for TDP removal in AD effluent filtrate at different FGD gypsum dosages



b. Kinetics of TDP removal in AD effluent filtrate using FGD gypsum

Figure 4 Process of TDP removal from AD effluent filtrate

These results were very consistent with similar test in synthetic wastewater, this again may indicate that adsorption plays an important part in the removal of soluble P at high dosages, whereas precipitation may be more likely at low dosages. At the lower dosage (10 mmol/L Ca), the gypsum would be expected to solubilize well, suggesting that removal at this dosage would primarily occur by precipitation. At the higher dosages (20 mmol/L Ca and 40 mmol/L Ca), P removal and removal rate increased in the presence of undissolved gypsum, which likely acted as a seed material[17,26].

3.4 Effect of initial pH on TDP removal

The initial pH had a very significant effect on P removal, and different precipitation products will be generated at different pH. Selecting an appropriate initial pH can greatly improve the TDP removal efficiency. The effects of initial pH on TDP removal at a fixed time/dosage (20 mmol/L Ca, 60-min mixing) are shown in Figure 5. The TDP removal at all treatment levels was significantly different (p<0.05) except for pH 8.0 and 10.0. The final pH values for solution with initial pH of 5.0, 7.0, 8.0, 8.57, 9.0, 10.0, 11.0, and 12.0 were 5.3, 7.3, 7.7, 8.2, 8.4, 9.8, 10.8, and 11.8, respectively. The results indicated that the solubility of calcium phosphates decreases greatly with increasing pH (thus favoring precipitation/nucleation), which was observed here. As expected, TDP removal was very low at pH 5.0. This is because calcium phosphates are highly soluble under acidic conditions.

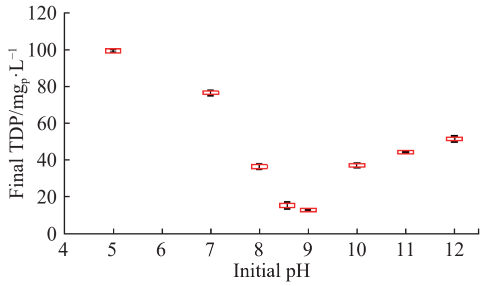


Figure 5 Effect of initial pH on TDP removal using 20 mmol/L Ca of FGD gypsum

The optimal pH range observed was 8.5-9.0, with about 87% P removed at pH 9.0. Higher pH values (>9.0) did not continue to enhance TDP removal. With the increase of pH, the phosphoric acid and calcium ions formed by precipitant will gradually transform in the order of calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$], calcium hydrogen phosphate ($CaHPO_4$), and calcium phosphate [$Ca_3(PO_4)_2$]. It is known that pH values in the range of 10-12 are theoretically most favorable for the formation of highly stable calcium phosphates, such as hydroxyapatite (HAP)[25,29]. However, these compounds have slow formation kinetics. The conditions in this experiment may have been more favorable for the formation of amorphous calcium phosphates (ACP, $Ca_3(PO_4)_2 \cdot nH_2O$), which are less thermodynamically stable but have faster formation rate. Also, higher pH also favors the competing reaction between calcium and carbonate, which can reduce the amount of calcium in solution, thereby reducing P removal efficiency[30,31].

3.5 Structural and compositional characteristics of precipitates

FTIR was used to characterize the functional groups present in precipitates formed in different FGD gypsum treatments. The FTIR spectra are shown in Figure 6. Several PO_4-derived bands are observed. The bands around 875 cm^{-1} are likely derived from HPO_4^{2-}, while bands around 470 cm^{-1}, 560 cm^{-1}, 1020 cm^{-1} are likely PO_4^{3-}-derived[32]. These peaks are absent in the initial FGD gypsum, proving that P was incorporated into the precipitate structure.

The spectra do not exactly fit the pattern for the most common calcium phosphates, but show some similarities. In the 40 mmol/L

Ca precipitates, the broad PO_4-derived bands around 473 cm^{-1}, 558 cm^{-1}, and 870 cm^{-1} may be associated with ACP[33]. The PO_4-derived bands around 558 cm^{-1}, and 1024 cm^{-1} may be associated with HAP ($Ca_5(PO_4)_3OH$) and the PO_4-derived band at 870 cm^{-1} may be associated with dicalcium phosphate dihydrate (DCPD; $CaHPO_4 \cdot 2H_2O$)[15,34,35]. The amorphous structure prevented clear identification of calcium phosphates but the incorporation of phosphate into the solid was confirmed.

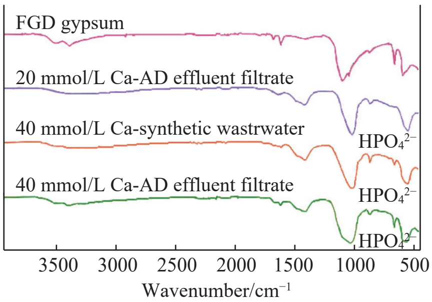


Figure 6 FTIR spectra for precipitates in synthetic wastewater and AD effluent filtrate

The precipitates in AD filtrate and synthetic wastewater were very similar at 40 mmol/L Ca. The synthetic wastewater contained only soluble orthophosphate, while the AD effluent filtrate may contain various forms of P. This may suggest that in the real wastewater, orthophosphate was the primary reactant, despite the various possible forms of P. It should be noted that the removal of particles by coarse/fine filtration was necessary to obtain the precipitates for analysis. Otherwise, the precipitates will be dispersed in the organic-rich sludge and cannot be analyzed.

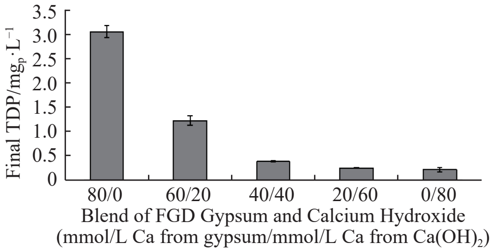
The P content of the initial gypsum was very low (0.10 g/kg). The P content in the sediment formed at 20 mmol/L Ca and 40 mmol/L Ca dosages were 52.0±4.6 mg/kg and 22.3±0.5 mg/kg, respectively. Calcium phosphates must have a P content of 13%-17% [30%-40% phosphorus pentoxide (P_2O_5)] in order to be viable feedstocks for fertilizer production[36,37]. With less than 6% by dry weight, this product is likely not to be used as a raw material for fertilizer production. So, recycling the product directly as a soil amendment is more feasible. However, Grubb et al.[38] determined that P-saturated FGD gypsum is not an effective P fertilizer. Thus, increase the P content by multiple recycles or identifying the best reuse application for the P-saturated gypsum requires further study.

3.6 Combined FGD gypsum-$Ca(OH)_2$ treatment

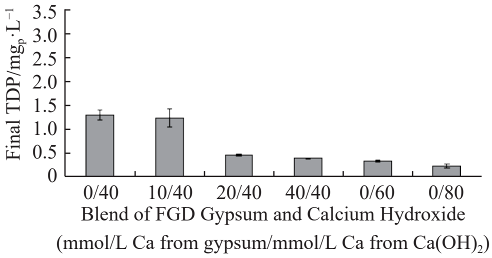
In order to improve P removal efficiency and potentially reduce traditional precipitates inputs, different blends of FGD gypsum and $Ca(OH)_2$ were added simultaneously to 200 mL filtrate (2 h mixing; 360 r/min). In the blends reported here, the FGD gypsum quantity (mmol/L Ca) is listed first and $Ca(OH)_2$ quantity (mmol/L Ca) second.

From left to right in Figure 7a, the amount of FGD gypsum is decreasing while $Ca(OH)_2$ is increasing. The 40/40 and 20/60 blends were not significantly different from 80 mmol/L Ca of $Ca(OH)_2$ alone. The effectiveness of the 40/40 blend demonstrated that $Ca(OH)_2$ consumption could be reduced by up to 50% by blending with FGD gypsum. The final pH at 40/40 was 10.61 and at 20/60 was 12.11. The 40/40 blend was favorable due to reduced $Ca(OH)_2$ usage and lower final pH.

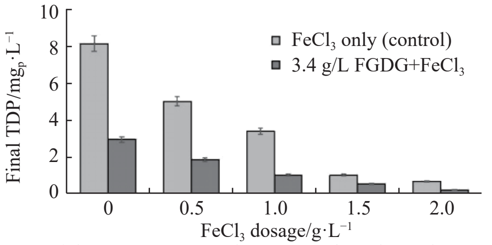
Based on Figure 7a, at least 40 mmol/L Ca from $Ca(OH)_2$ was necessary to reach the target removal. It was hypothesized FGD gypsum dosages could be reduced while still achieving P<1 mg/L. Additional blends of 10/40 and 20/40 were evaluated to test this (Figure 7b). The 10/40 blend did not significantly improve TDP removal compared to 0/40 [$Ca(OH)_2$ only]. However, the 20/40 blend reduced TDP to below 0.5 mg/L while reducing FGD gypsum usage by 50% compared to 40/40. Compared to the control of 0/60, the 20/40 blend reduced $Ca(OH)_2$ usage by 33%. The final pH at 20/40 was 10.35, which is more favorable compared to pH>12 at 0/60 and 0/80. Based on the ratios tested here, the 20/40 blend was the best in terms of TDP removal, reagent usage, and final pH. A rigorous optimization would likely further reduce chemical inputs.



a. TDP removal at different FGD gypsum-$Ca(OH)_2$ ratios (initial test)



b. TDP removal at different FGD gypsum-$Ca(OH)_2$ ratios (test with reduced inputs)



c. Sequential FGD gypsum-$FeCl_3$ treatment for enhanced TDP removal

Figure 7 FGD gypsum treatment in combination with conventional chemicals

3.7 Sequential FGD gypsum-$FeCl_3$ treatment

FGD gypsum (20 mmol/L Ca=3.44 g/L) was used as a pretreatment prior to $FeCl_3$ treatment to reduce coagulant consumption. The TDP removal with the sequential gypsum-iron treatment was compared to controls that received only $FeCl_3$ (Figure 7c). At 0.5 g/L $FeCl_3$, the iron-only treatment only achieved around 60% TDP removal (TDP_{final}=5.03 mg/L). Compared to the FGD gypsum-only treatment (TDP_{final}=2.98 mg/L), the sequential treatment with 0.5 g/L $FeCl_3$ (TDP_{final}=1.89 mg/L) improved TDP removal by 36% compared to the FGD gypsum-only treatment, this improvement was not significant (p>0.05). The sequential treatment with 1.0 g/L $FeCl_3$ (TDP_{final}=1.06 mg/L) was significantly better (p<0.05) than the control and close to the target of P<1 mg/L. Furthermore, the sequential treatment with 1.0 g/L $FeCl_3$ achieved the same level of treatment as 1.5 g/L $FeCl_3$ alone; the sequential treatment therefore, reduced $FeCl_3$ requirements by 33%, which could represent considerable cost savings. The final pH in the iron treated samples were between 5.0 and 7.0.

There were no significant differences between the final TDP levels in any of the sequential treatments or controls at iron dosages ≥1.5 g/L $FeCl_3$. However, the sequential treatment with 1.5 g/L

$FeCl_3$ achieved the target of P<1 mg/L significantly, whereas the control not. At 2.0 g/L of $FeCl_3$, the iron-only treatment (TDP_{final}= 0.73 mg/L), was not significantly less than 1.0 mg/L P target . The sequential treatment at 2.0 g/L $FeCl_3$ achieved very low TDP levels (TDP_{final}=0.27 mg/L). In summary, the sequential treatment at both 1.5 and 2.0 g/L $FeCl_3$ reduced the dose of $FeCl_3$ required, which could reduce final TDP to a level significantly below 1.0 mg/L P. In addition, Fe-Ca-P phase is prepared by Fe-Ca complex, which gives full play to the advantages of Fe-P phase and Ca-P phase, and has broad application prospects in P removal and recycling[39].

3.8 Preliminary comparison of chemical input costs

FGD gypsum is a waste material from coal processing and could potentially be obtained for a low cost for use in AD effluent filtrate treatment. A preliminary economic analysis of different P removal treatments was performed. It is assumed that FGD gypsum is obtained free of charge, the cost price of $Ca(OH)_2$ is about $140/t and the cost price of $FeCl_3$ is about $400/t. First, the chemical inputs required to achieve TDP removal similar to that of the FGD gypsum-only treatment (97%-98%) were compared. Assuming that the wastewater treatment capacity is 1×10^6 L and the transportation cost is ignored, it is obvious that when FGD gypsum (80/0) is used alone, the economic cost for materials was the lowest at $0. For similar treatment, the cost of the $Ca(OH)_2$-only treatment was $414, and the cost of the $FeCl_3$-only treatment was $400. While FGD gypsum is the least costly, it required the largest amount of reagent (3.44 t) and may have higher logistical costs. The $FeCl_3$-only treatment was the most effective in reagent use, achieving 97% TDP removal at the lowest test dose (1.0 t). Notably, the cost of $FeCl_3$ treatment was lower than for $Ca(OH)_2$, despite the fact that $FeCl_3$ is more expensive per ton.

Treatments that could achieve very low final TDP values (<1.0 mg/L) were also compared. Using 60 mmol/L Ca (4.44 g/L) $Ca(OH)_2$ alone, 4.44 t of $Ca(OH)_2$ at a cost of $622 are required to reach the research objective (>99% TDP removal). The cost of equivalent treatment with the combined calcium treatment [3.44 g/L gypsum+2.96 g/L $Ca(OH)_2$] was $414, 33% cheaper than the $Ca(OH)_2$ only treatment. Similarly, the sequential gypsum-$FeCl_3$ treatment reduced the cost by 25 percent but increased the reagent count by 2.5 times compared to the treatment with $FeCl_3$ alone. The combined calcium treatment was the cheapest of these options. Under the condition of ensuring good P removal efficiency, the use of FGD gypsum in advance can effectively reduce the cost of P removal (Table 4).

Table 4 Chemical input costs

Treatment	Max TDP removal	Required chemical dosage/$g\cdot L^{-1}$	Total reagent quantity/t	Chemical input cost/$
FGD gypsum only	97%	3.44 g/L FGD gypsum	3.44	0
$Ca(OH)_2$ only	98%	2.96 g/L $Ca(OH)_2$	2.96	414
$FeCl_3$ only	97%	1.0 g/L $FeCl_3$	1.00	400
$Ca(OH)_2$ only	>99%*	4.44 g/L $Ca(OH)_2$	4.44	622
Combined calcium treatment	>99%*	3.44 g/L gypsum+ 2.96 g/L $Ca(OH)_2$	6.40	414
$FeCl_3$ only	>99%*	2.0 g/L $FeCl_3$	2.00	800
Sequential gypsum-iron treatment	>99%*	3.44 g/L gypsum+ 1.5 g/L $FeCl_3$	4.94	600

*Can reduce TDP to below 1.0 $mg\cdot L^{-1}$.

Considering the transportation cost in practical application, the amount of FGD gypsum is larger and the transportation cost is higher than that of other chemicals due to its higher relative impurity and lower P removal efficiency. However, if a FGD gypsum source is readily available, the economic cost for materials can still be reduced compared with using $Ca(OH)_2$ or $FeCl_3$ alone.

4 Conclusions

FGD gypsum was demonstrated as an effective precipitant for the removal and recovery of soluble phosphorus from a high-strength wastewater (such as AD effluent filtrate). FGD gypsum dosages of 20 mmol/L Ca and 40 mmol/L Ca removed up to 97.1% of soluble P within 60-90 min. The main components of the precipitate were undissolved gypsum, $CaCO_3$, ACP and HAP. The initial pH had a very strong influence on TDP removal efficiency, with the optimal range occurring at pH 8.5-9.0. Combining FGD gypsum treatment with traditional precipitates such as $Ca(OH)_2$ or $FeCl_3$ can both enhance the removal of TDP from wastewater and reduce the consumption of expensive traditional reagents. A primary focus of future research should be the design and scale-up of FGD gypsum treatment systems, and its effectiveness on varied wastewater streams such as manure or municipal wastewater.

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