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Evaluation of titanium tetrachloride and polytitanium tetrachloride to remove phosphorus from wastewater

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ABSTRACT

Coagulation of titanium tetrachloride ($TiCl_4$) and polytitanium tetrachloride (PTC) was studied at various conditions in treating wastewater that contained phosphorus (P). Jar-test experiments were performed at various chemical doses (0.02–0.49 mM), alkalinities ($50 \le A_T \le 150$ mg $CaCO_3$/L of $NaHCO_3$), pH levels (3.0–8.5), and OH/Ti ratio ($0.3 \le B \le 3.0$) to determine the conditions at which P (2 mg/L) removal was most efficient. The $TiCl_4$ concentration ([$TiCl_4$]) required to achieve 98–99% P removal was 0.25 mM at 50 mg $CaCO_3$/L, 0.31 mM at 100 mg $CaCO_3$/L, and 0.49 mM at 150 mg $CaCO_3$/L. Response surface analysis predicted that P removal would reach 100% at controlled pH = 3.5 with minimum [$TiCl_4$] = 0.21 mM. PTC removed P most effectively at $B = 0.3$, and the optimal dose at $B = 0.3$ was 0.27 mM. Laboratory results and a pilot experiment will help to optimize use of Ti-based coagulants to remediate wastewater that contains P.

1. Introduction

Municipal and industrial wastewaters often have high concentrations of compounds that contain phosphorus (P). If these wastewaters are not treated to remove P, nutrient enrichment of both groundwater and surface waters may occur; these processes degrade water quality and cause eutrophication of surface water bodies. For this reason, many countries have adopted strict discharge limits of P in wastewaters [1].

Many methods to meet effluent standards entail supplementing the biological system with a chemical precipitating process [1]. P can be reduced to very low levels by adding metal salts [2], which combine with P to form insoluble or biologically-inert products. Metal salts based on aluminum (Al), are widely used as coagulants in wastewater treatment [3]. Alum is effective to treat a wide range of water types at relatively low cost [4]. However, overuse of alum to treat water may lead to an increase of Al concentration, which has been associated with increased likelihood of Alzheimer's disease in humans on long-term exposure [5]. Furthermore, sludge is often used as fertilizer; high concentration of Al can be phytotoxic, so the dose of Al-based precipitants must be controlled [1]. To overcome these problems, titanium (Ti) salts have been evaluated as coagulants [6].

Coagulants based on Ti salts are relatively new. For use in wastewater treatment they have a number of positive attributes [7,8], including a high degree of organic-matter removal, and low residual content of Ti ions [8]. Ti and its compounds have so little toxicity that they are rarely included in water quality guidelines [9,10]. Thus, titanium tetrachloride ($TiCl_4$) is a promising alternative to conventional coagulants [10].

Coagulation occurs by charge neutralization of negatively-charged colloids, and by incorporation of impurities in an amorphous hydroxide precipitate [3]. The relative importance of these mechanisms depends on factors such as pH, alkalinity (A_T), and coagulant dosage [1,11,12]. Coagulation pH is one of the most important factors that will affect the coagulant species [13]. The final pH (pH_F) is more meaningful than the initial pH (pH_I) for coagulation [12]. The amount of Al salts required for detoxification increases linearly with increase in A_T [4,14]. Thunderstorms and rapid snowmelt can decrease A_T, and thereby hinder the ability of conventional coagulation process to meet treatment goals [14].

Recently, Ti-based salts have been investigated as an alternative coagulant for organic matter [6,9,10,15,16]. However, to our knowledge, the only previous quantification of the efficacy of Ti-based salts on P removal compared the efficacy of $TiCl_4$ and $Ti(SO_4)_2$ coagulation for P removal to that of $Al_2(SO_4)_3$ previously [17]. The present study quantifies P removal using Ti-based coagulant at various conditions, and determines the optimal Ti concentration and controlled pH (pH_C) to maximize P removal. A preliminary pilot experiment was also performed to test the applicability of Ti-based salt coagulation in municipal wastewater treatment.

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2. Materials and method

2.1. Synthetic wastewater and chemicals

Synthetic wastewater was prepared using KH_2PO_4 (2 mg P/L). To obtain various A_T, 50–150 mg $CaCO_3$/L of $NaHCO_3$ was added. $TiCl_4$ solution (20%) and polytitanium tetrachloride (PTC) (OH/Ti ratio, $0.3 \le B \le 3.0$) were obtained from Photo & Environment Technology Co. Ltd. (South Korea), and were used as received.

2.2. Jar test

Jar tests were conducted to determine the optimal coagulant dose and pH for $TiCl_4$ and PTC. Coagulation and flocculation were conducted using a jar-test apparatus (FC6S, VELP Scientifica, Italy) under various chemical concentration or B value. In each test, 500 mL of solution was poured into a 1-L glass beaker. During each test, chemical addition was followed immediately by rapid mixing (120 rpm) for 1 min, and then by slow mixing (30 rpm) for 20 min. The mixing was then stopped to allow the aggregated flocs to settle for 30 min. To achieve the desired pH_I (5.5–8.5), an appropriate amount of 1 N HCl or NaOH was added; pH_F of the solutions were recorded at the end of the processes.

To observe how $TiCl_4$ coagulated P under pH_C [1,18], the pH was continuously measuring after adding coagulants. To maintain pH_C, the pH was maintained at (2.0–6.0) ± 0.1 by adding 1 N HCl or NaOH.

2.3. Experimental design for response surface analysis

Response surface analysis (RSA) was used to optimize the coagulation-flocculation in jar-test experiments. RSA designs experiments and builds mathematical models to evaluate the effects of several factors and to identify optimal conditions for desired responses with the fewest experiments [19]. RSA was used to evaluate the relative significance of $TiCl_4$ concentration ([$TiCl_4$]) and pH_C, and to determine the conditions under which P removal is maximum within the experimental range of [$TiCl_4$] and pH_C. The experiment used the central composite design and consisted of a 2 × 2 ([$TiCl_4$] × pH_C) orthogonal design augmented by five replicates at the center point. A sequential procedure of collecting data, estimating polynomials, and verifying the adequacy of the model was used. Least squares regression was used to estimate the parameters of the response surface. Minitab 16 (Minitab Inc., USA) was used to establish the experimental design and to test polynomials.

At $pH_C \ge 3$, the optimal [$TiCl_4$] increased as pH_C was increased (data not shown). For 99.1% P removal, the optimal [$TiCl_4$] was 0.17 mM at $pH_C = 3$. However, at [$TiCl_4$] = 0.31 mM, the P-removal efficiency was 97.9% for $pH_C = 4$, and 81.0% for $pH_C = 6$. The P-removal efficiency was not stable at $pH_C = 2$. On the basis of these results, the ranges of independent variables chosen for this study were $0.10 \le [TiCl_4] \le 0.30$ mM and $3.0 \le pH_C \le 6.0$. Conditions at the center point were [$TiCl_4$] = 0.20 mM and $pH_C = 4.5$. Observations at the center point were replicated to estimate the experimental error.

2.4. Pilot plant

To verify the practicability of using Ti salt to coagulate P, a field experiment was conducted by sequential coagulation, flocculation, and sedimentation processes on a pilot municipal wastewater treatment system with a capacity of 14.4 m^3/d. Wastewater pumped into rapid coagulation tank was mixed thoroughly with coagulants for 1 min at 100 rpm. The pilot plant drew raw wastewater from influent (secondary clarifier effluent) into the P-removal facility in a municipal wastewater treatment plant. The dimensions of the rapid-mixing tank were 200 × 200 × 320 mm (working volume = 10 L), those of the slow-mixing (flocculation) tank were 450 × 450 × 1136 cm (working volume = 200 L). Flocculation experiments involved a speed-adjustable paddle impeller. The raw wastewater was pumped at 14.4 m^3/d into the rapid mixing tank, then the Ti-based coagulants were added; the samples were mixed rapidly at 100 rpm for 1 min, then slowly at 30 rpm for 20 min.

2.5. Analytical methods

P concentration was determined by the ascorbic acid method [20] using a UV–Vis Spectrophotometer (Biochrom., Libra S60, UK). pH was measured using a pH electrode (UB-10, Denver instrument, USA). A_T was measured by titration [20].

3. Results and discussion

3.1. Influence of alkalinity on phosphorus removal and final pH with $TiCl_4$ dosage

P-removal ability of $TiCl_4$ decreased as A_T increased. [$TiCl_4$] required to achieve 98–99% P removal was 0.25 mM at 50 mg $CaCO_3$/L, 0.31 mM at 100 mg $CaCO_3$/L, and 0.49 mM at 150 mg $CaCO_3$/L (Fig. 1(a)). This trend may be a result of the strong buffering effect of bicarbonate, which combines with most of the H^+ that is released during hydrolysis of Ti salt [9]; as a result, the pH might be prevented from dropping to the acidity required for Ti-salt sedimentation [9]. Therefore, Ti salts are suitable for treating wastewater with low A_T [8,9]. However, when A_T is zero or very low, the amount of H^+ derived from $TiCl_4$ hydrolysis can be so high that pH would be depressed, so P removal is poor [9]. In contrast, A_T (6–12 mM of $NaHCO_3$) does not affect P coagulation when $FeCl_3$ is used, partly because this process has

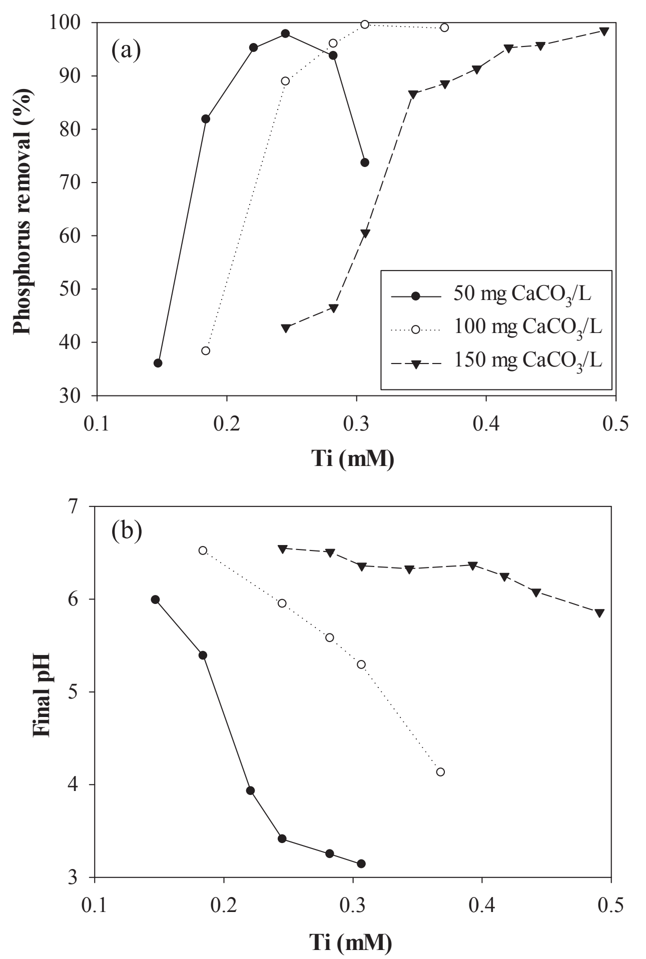

Fig. 1. Effect of $TiCl_4$ concentration on phosphorus removal (a) and final pH (b) at alkalinity 50–150 mg $CaCO_3$/L.