Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants

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ABSTRACT

Acid mine drainage (AMD) sludge, a waste product from coal mine water treatment, was used in this study as an adsorbent to develop a cost-effective treatment approach to phosphorus removal from municipal secondary effluents. Batch tests were carried out to study the effects of pH, temperature, concentration, and contact time for phosphorus removal from wastewater. Batch tests were followed by continuous flow tests using a continuous stirred tank reactor (CSTR). Adsorption of orthophosphate onto AMD sludge particles followed the *Freundlich* isotherm model with an adsorption capacity ranging from 9.89 to 31.97 mg/g when the final effluent concentration increased from 0.21 to 13.61 mg P/L. P adsorption was found to be a rather rapid process and neutral or acidic pH enhanced phosphorus removal. Based on a thermodynamic assessment, P adsorption by AMD sludge was found to be endothermic; consequently, an increase in temperature could also favor phosphorus adsorption. Results from batch tests showed that leaching of metals common to AMD sludges was not likely to be a major issue of concern over the typical pH range (6–8) of secondary wastewater effluents. CSTR tests with three types of water (synthetic wastewater, river water, and municipal secondary effluent) illustrated that P adsorption by AMD sludge was relatively independent of the presence of other ionic species. In treating municipal secondary effluent, a phosphorus removal efficiency in excess of 98% was obtained. Results of this study indicated that it was very promising to utilize AMD sludge for phosphorus removal from secondary effluents and may be relevant to future efforts focused on the control of eutrophication in surface waters.

1. Introduction

The release of phosphorus (P) from municipal wastewater treatment effluents into the environment is one major cause of eutrophication in receiving water bodies (Oleszkiewicz and Barnard, 2006; Edwards and Withers, 2007). In order to mitigate the growth of aquatic plants and phytoplanktonic algae, environmental agencies are required to develop phosphorus total maximum daily load (TMDL) for many watersheds (Havens and Schelske, 2001; Walker, 2003). In addition to TMDL requirements, some regulations can require the phosphorus concentration in wastewater effluents to be as low as 50 μg/L (Genz et al., 2004). Phosphorus exists in municipal wastewaters in different forms, including total phosphorus, soluble phosphorus, and particulate phosphorus. In general, primary and secondary treatment is

effective in removing particulate phosphorus. Phosphorus in the secondary effluents is mostly soluble and is present as orthophosphate (Duenas et al., 2003). Furthermore, only orthophosphate is consumed for phytoplankton growth causing eutrophication in surface water bodies (Selig et al., 2002). Consequently, tertiary treatment of secondary municipal effluents to remove orthophosphate has become increasingly necessary to meet environmental regulations worldwide.

There are a wide range of technologies available to remove phosphorus from wastewaters, such as chemical precipitation, biological treatment, adsorption processes, constructed wetlands, and a number of wastewater-and-sludge-based methods (Morse et al., 1998; de-Bashan and Bashan, 2004), which typically require considerable capital investment and maintenance costs for infrastructure and reagents. Thus, it is desirable to develop cost-effective processes for phosphorus removal from secondary wastewater effluents. In particular, P adsorption using iron oxide/hydroxide and aluminum hydroxide has been recently studied and found to be successful.

Kang et al. (2003) evaluated the adsorption of orthophosphate by iron oxide particles (ferrihydrite, goethite, and hematite) and found that ferrihydrite was most effective in removing phosphorus to a very low concentration. For ferrihydrite, the *Freundlich* isotherm parameters were $K = 19.4\,\text{mg P/g}$ and $n = 0.293$. Genz et al. (2004) studied the advanced phosphorus removal from membrane bioreactor effluents using activated aluminum oxide and granular ferric hydroxide (GFH). Both adsorbents were proven to be suitable for potential application in fixed bed adsorbers, while GFH showed better affinity and adsorption capacity at low phosphorus concentrations. The adsorption capacity of GFH ranged from 7.9 to 12.3 mg P/g, when equilibrium P concentrations increased from 0.1 to 0.3 mg P/L. Recovered ochre (i.e., $Fe(OH)_3$ or $FeO \cdot OH$-rich sludge) was tested for phosphorus removal from wastewater (Heal et al., 2004). It was found that ochre had a high adsorption capacity due to its high content of iron oxide/hydroxide (maximum adsorption capacity 17.8–21.5 mg P/g), and its potential to treat sewage effluent and agricultural runoff was assessed. Adler and Sibrell (2003) investigated the use of flocs from acid mine water neutralization to reduce the loss of soluble phosphorus from agricultural and animal wastewater, and found iron and aluminum-rich flocs were effective in controlling the release of soluble phosphorus from soil and manure. The adsorption capacities of acid mine drainage (AMD) flocs ranged from 10 to 20 mg P/g at an equilibrium concentration of 1 mg P/L. Galarneau and Gehr (1997) studied the capacity of aluminum hydroxide as an adsorbent to remove various forms of phosphorus. At a dose of 8 mol Al/mol P, the removal efficiency was 95%, 95%, and 40% for orthophosphate, condensed phosphate, and organic phosphate, respectively. Spent alum sludge, a byproduct from water treatment (mostly Al(OH)₃), was also demonstrated to be effective in the removal of phosphorus from wastewater (Yang et al., 2006). The maximum adsorption capacities ranged from 0.7 to 3.5 mg P/g when pH varied from 9.0 to 4.3. Furthermore, quartz particles coated with iron and aluminum oxides were evaluated as a filter media to remove phosphorus from wastewater (Arias et al., 2006). The maximum adsorption capacity was 4.4 mg/g of Fe-oxide-coated particles.

AMD, produced at both active and abandoned mines, is generally characterized by low pH and often high concentrations of dissolved metals (Fe, Al, Mn, and trace metals such as Pb, Cu, and Zn), resulting in environmental problems across the globe (Johnson and Hallberg, 2005). Typical AMD treatment processes rely on the removal of dissolved metals via precipitation. As a residual of this treatment approach, large volumes of sludge are produced. These sludges are a mixture of metal oxides/hydroxides and solids content is very low (1–5%). When compounded by the low economic value of the waste sludge, substantial difficulties in dewatering, and the high cost of off-site hauling, the ultimate disposal of AMD sludge is problematic (Ackman, 1982; Dempsey et al., 2001; Viadero et al., 2006). In an AMD site treating a flow of 100–400 gal/min (400–1500 L/min) in West Virginia, USA, approximately $30{,}000\,\text{m}^3$ of sludge was generated annually (Wei et al., 2005). Consequently, a major challenge in AMD treatment is the management of large volumes of loose sludge (Ackman, 1982; Kuyucak, 1998; Wei et al., 2005). The waste sludge is usually transported by pipeline and/or truck, and is typically disposed of through one of the following methods: deep mine disposal, retained-in-pond disposal, or disposal at coal refuse areas (Ackman, 1982; Matlock et al., 2002). However, the chemical composition of AMD sludge is mostly amorphous micron- and submicron-sized metal oxide/hydroxide particles. AMD sludge generally has a high specific surface area and numerous functional groups which are chemically active in an aqueous environment (Kirby et al., 1999; Cornell and Schwertmann, 2003; Wei and Viadero, 2007).

To date, very little work has been reported in the peer-reviewed literature on the beneficial use of AMD sludge for phosphorus removal. However, given the wide range of studies successfully reporting P removal from wastewaters using Fe and/or Al hydroxide sludges, it was hypothesized that the AMD sludge containing a mixture of iron and aluminum hydroxide precipitates would be a suitable medium for the adsorption of dissolved orthophosphate from solution. The goal of this study was to develop a potentially low-cost, sustainable treatment approach to phosphorus removal from secondary wastewater effluents in which a waste product from the mining industry is used for further benefit. Batch tests were carried out to study the adsorption kinetics, isotherms, and adsorptive thermodynamics in conjunction with studies on the effects of pH, temperature, concentration, and contact time for phosphorus removal from wastewater. Batch tests were followed by continuous flow tests using a continuous stirred tank reactor (CSTR). Based on the outcomes of these studies, the applications and implications of using AMD sludge as a tertiary process in municipal wastewater treatment were discussed.

2.   Materials and methods

2.1.   Adsorbent

AMD sludge was used as adsorbent in this study. The sludge was collected from a bond-forfeited treatment site in north central West Virginia, USA, where AMD was actively treated with hydrogen peroxide and anhydrous ammonia. The sludge

was approximately one month old upon collection. The collected sludge was sieved through a fine screen (100 mesh) to remove the debris and sand entrained from the settling pond and was stored in a sealed 19-L (5-gal) container at $4\,^\circ$C. The sludge suspension was very stable without the occurrence of apparent settling during storage. The total solids content of the sludge was 4.31% by weight and the pH was ~8.1. Based on elemental analysis, the AMD sludge was composed mainly of iron and aluminum hydroxides (Fe 26.1%, Al 9.5%, Ca 2.6%, Mg 0.6%, Mn 0.2%, Zn 0.2%, Ni 0.1%, and Si 4.1%; analyzed on a dry weight basis). Before adsorption tests, the AMD sludge was mixed homogeneously and sludge samples were taken. Wet sludge (4.31% solids) was applied directly as adsorbent without drying because sludge drying was energy and time consuming. Further, subsequent rehydration of dried samples could have affected the surface area and the number and character of surface-active sites available for phosphorus adsorption. However, the amount of adsorbent applied during each test is reported in grams based on its dry weight (unless otherwise noted) in order to follow the convention of typical adsorption studies.

2.2. Adsorbate

Since orthophosphate is the primary form of phosphorus responsible for eutrophication (Selig et al., 2002; Duenas et al., 2003), potassium dihydrogen phosphate (KH_2PO_4, CAS#: 7778-77-0), acquired from *Fisher Scientific* (Fair Lawn, NJ), was used in adsorption tests as the source of orthophosphate without further purification. A stock orthophosphate solution of 20 mg P/L was prepared with laboratory-grade water and used throughout the study, unless otherwise noted.

2.3. Batch adsorption studies

Batch studies were performed to examine orthophosphate adsorption onto AMD sludge by agitating 500 mL of a synthetic wastewater (20 mg P/L) dosed with predetermined amounts of AMD sludge using a *Phipps and Bird* stirrer at 150 rpm. After adsorption equilibrium was reached (determined through laboratory tests), samples were taken and phosphorus concentrations were determined. Experiments were conducted to evaluate the effects of pH, temperature, P concentration, contact time, and adsorbent dosage. The pH of the suspensions of orthophosphate and AMD sludge was maintained at the desired ranges by addition of either 1 M NaOH or 0.5 M H_2SO_4 solution during adsorption tests. All adsorption tests were carried out in triplicate.

For adsorption isotherm study, different amounts of AMD sludge (0.0–1.0 g) were added to 500 mL of orthophosphate solution and mixed for 1 h at $20\,^\circ$C and pH 7 ± 0.1. To examine adsorption kinetics, 0.5 g of AMD sludge was added to 500 mL of stock orthophosphate solution and agitated for periods of time ranging from 5 to 120 min at pH 7 ± 0.1, before samples were taken to determine orthophosphate concentration. Based on contact time test, it was found that 1 h mixing was sufficient for the adsorption to reach equilibrium. To test the effect of system pH, suspensions of 0.3 g AMD sludge and 500 mL of orthophosphate solution were adjusted in 0.5 standard unit intervals with NaOH or H_2SO_4 to a target pH ranging from 5.0 to 8.5 and mixed for 1 h at $20\,^\circ$C.

A thermostatic water bath (*Fisher Isotemp*) was used to examine the effect of temperature on phosphorus adsorption by AMD sludge. First, 500 mL of orthophosphate solution was mixed in a beaker until the target temperature was reached. Then, 0.3 g adsorbent was added and mixing continued for 1 h at pH 7 ± 0.1. Test temperatures ranged from 5 to $50\,^\circ$C at 5 or $10\,^\circ$C intervals. Temperatures below $20\,^\circ$C were maintained by adding ice to the water bath during testing.

2.4. Continuous adsorption studies

Continuous adsorption was carried out by using a CSTR (Fig. 1). The three types of water used in CSTR tests were: (1) a synthetic wastewater, same as the batch adsorption tests (20 mg P/L), (2) surface water from the Monongahela (Mon) River near Morgantown, West Virginia, USA, which was dosed to 20 mg P/L, and (3) secondary effluent from an operating publicly owned treatment works (POTW). The synthetic wastewater was used to test for potential differences in phosphorus removal between CSTR systems and batch operations. However, since the synthetic wastewater was prepared with deionized water, the potential effects of competing ions, especially anions (SO_4^{2-}, or Cl^-), was unknown. Consequently, surface water from a local river was collected and tested. In order to compare the removal effectiveness with and without competing ions, the river water was dosed to the same phosphorus concentration used in experiments with the synthetic wastewater. Finally, the actual effluent was tested to demonstrate the effectiveness of phosphorus adsorption with AMD sludge. Typical water quality data for the Mon River and secondary effluent from a POTW used in this study are presented in Table 1.

At the start of each test, a 2-L CSTR was filled with the wastewater. Phosphorus-containing water was then continuously fed into the CSTR at a flow rate of 2 L/h with a variable flow pump. At the same time, the well-mixed AMD sludge was fed to the reactor at a flow rate predetermined to achieve different sludge dosages (0.35, 0.5, or 1.0 g (dry weight) per liter wastewater). The hydraulic residence time (1 or 2 h) of the CSTR was adjusted by varying the feed rate of the
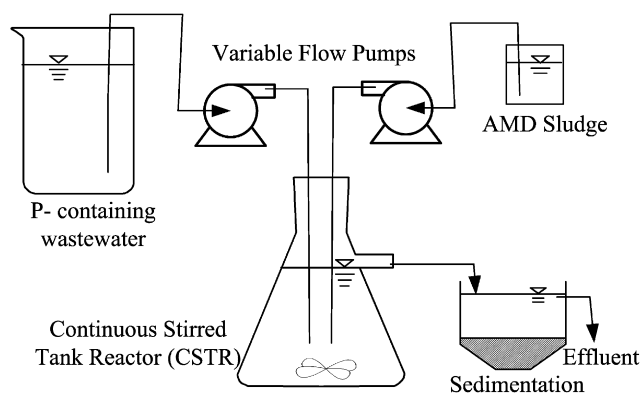

Fig. 1 – Schematic of laboratory CSTR testing system.

Table 1 – The physicochemical characteristics of water samples from Monongahela River and a POTW secondary effluent (concentration in mg/L except pH)

Item	Monongahela River sample	POTW secondary effluent
Acidity	7.86 as CaCO$_3$	24.27 as CaCO$_3$
Alkalinity	67.20 as CaCO$_3$	102.52 as CaCO$_3$
pH	7.75	6.91
Chloride	13.5	76.5
TSS	3.05	7.54
Sulfate	697.0	166.6
Nitrate	0.613	0.450
Nitrite	0.042	0.241
Ammonia	0.295	4.45
P (ortho)	0.016	1.80
Mn	0.12	0.65
Fe	0.27	0.15
Ca	38.6	48.0
Mg	9.70	8.44
Al	0.37	0.18

wastewater. The system was operated continuously for a period of 3–5 h until equilibrium was reached. The resulting effluent was sampled at certain time intervals (10–25 min). All tests were conducted in triplicate and the mean values were reported (variability of triplicate data was within $\pm$5% of the mean). No pH adjustment was made in CSTR tests, although pH was monitored every time water samples were taken.

2.5. Phosphorus analyses

Orthophosphate was measured according to Standard Method 4500-P E (APHA, 1998) with a method detection limit (MDL) of 0.01 mg P/L. Ascorbic acid, ammonium molybdate, and potassium antimonyl tartrate were used for color development and the orthophosphate concentration was determined using a Genesys 10uv spectrophotometer based on a calibration curve between absorbance and concentration at a wavelength of 880 nm. Prior to measurement, the solids in the water samples were removed via centrifugation for 10 min at 4000 rpm (Sorvall RC-5C centrifuge) and the supernatant was filtered through 0.45 μm membrane (Millipore). For quality control and assurance, blank and spiked samples were treated the same way as water samples to assess potential sample contamination and determine "analytic recovery" of phosphorus. Further, P analysis was completed the same day as testing and the membrane filters were soaked in distilled water for 24 h prior to use, according to Standard Method 4500-P B (APHA, 1998).

2.6. Metal leaching tests

Metal leaching experiments were carried out to determine if metals were leaching from the AMD sludge during adsorption. The tests were performed by agitating a 500 mL sample of orthophosphate solution dosed with 0.5 g AMD sludge for 1 h at a pH ranging from 5 to 9, in 1 standard unit increments. After agitation, samples were taken and filtered through a

0.45 μm membrane. The concentrations of dissolved metals (Fe, Al, Mn, Zn, Ni, and Cu) in the filtrate were determined according to Standard Method 3111 (APHA, 1998), using an atomic absorption spectrometer (Perkin Elmer 3100; MDLs are presented in Table 3). All experimental controls were performed using 500 mL of deionized water (0 mg/L orthophosphate) and 0.5 g AMD sludge at pH ~8.1.

3. Results and discussion

3.1. Effect of sludge dose and contact time

The relationship between effluent P concentration and AMD sludge dose is presented in Fig. 2(a). The effluent P concentration decreased rapidly as the AMD sludge dose increased from low doses to 1.0 g/L, where an effluent concentration of 1.02 mg P/L (equivalent to 95% P removal) was achieved. When the sludge dose was increased above 1.0 g/L, the decrease in effluent P concentration was trivial (effluent concentration of
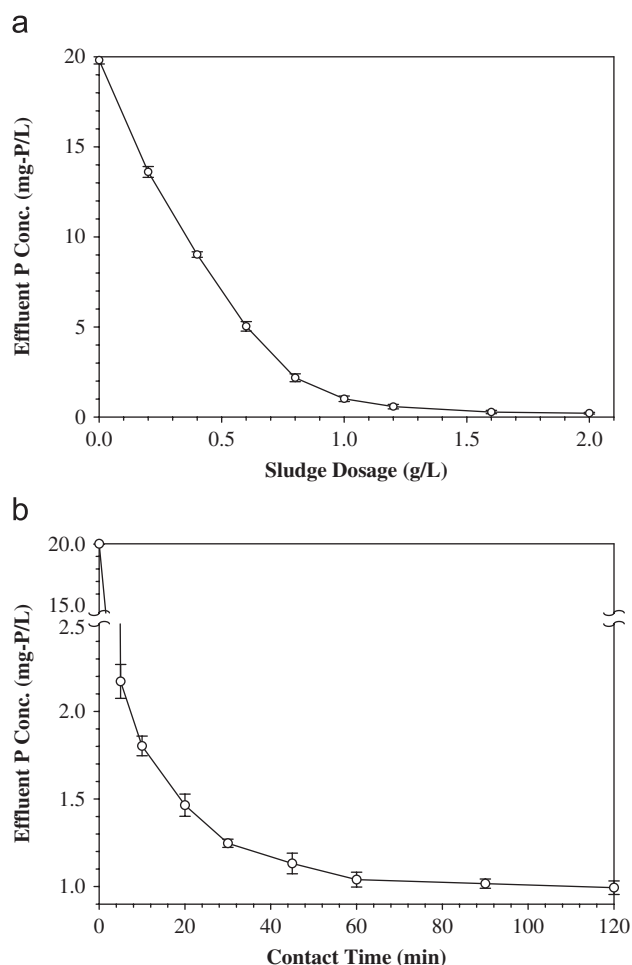

Fig. 2 – Effect of AMD sludge dosage and contact time on effluent P concentration (mean $\pm$ 1 standard deviation). (a) sludge dose (initial concentration 20 mg P/L; 20 °C; pH 7.0 $\pm$ 0.1; mixing time 1 h; dosage 0–2.0 g/L); (b) contact time (sludge dosage 1 g/L; 20 °C; pH 7.0 $\pm$ 0.1; initial concentration 20 mg P/L).

0.21 mg/L at a sludge dose of 2.0 g/L). Considering 20 mg P/L was a rather high concentration in wastewater effluent, the dose of 1.0 g/L was used in subsequent adsorption tests, unless stated otherwise. The effect of contact time on effluent P concentration is shown in Fig. 2(b). In the first 5 min, rapid phosphorus removal was observed and a P removal of 89% was determined. Thereafter, a gradual decrease in effluent P concentration occurred as mixing time was increased up to 1 h. The effluent P concentration decrease was trivial after 1 h mixing, which suggested that the equilibrium of orthophosphate adsorption onto the AMD sludge particles was reached. Consequently, 1 h mixing was used as the contact time in all further studies of adsorption at equilibrium. Similar results were found in the literature on the rapid adsorption rate of dyes using AMD sludge (Wei and Viadero, 2007) and fly ash (Acemioglu, 2004) as adsorbents.

3.2. Effect of pH, temperature, and adsorption thermodynamics

System pH during adsorption has a significant effect on the surface characteristics of the adsorbent particles, and consequently, overall adsorption performance. Illustrated in Fig. 3(a) is the effect of pH on effluent P concentration (sludge dose of 0.6 g/L was used). It was observed that effluent P concentration increased with an increasing pH, indicating orthophosphate adsorption by AMD sludge was inhibited at high pH. The result was consistent with the P adsorption study using granulated ferric hydroxide (Genz et al., 2004). Thus, neutral or slightly acidic pH was indicated when using AMD sludge for the removal of dissolved phosphorus from solution. It should be noted that pH lower than 5 or greater than 8.5 was not examined due to concerns related to metal re-solubilization.

Phosphorus removal using AMD sludge was essentially an anionic adsorption process. AMD sludge used in this study consisted mainly of iron and aluminum oxides/hydroxides. In aqueous solution, protonation and deprotonation might take place at the hydroxyl sites on the surface of metal hydroxides (M-OH), depending on the system pH, which could result in a change of surface charges. The point of zero charge (PZC) of iron and aluminum hydroxides reported in the literature ranged from 8 to 9 (Cornell and Schwertmann, 2003; Sparks, 2003), indicating the surfaces of AMD sludge particles were positively charged at pH less than 8, which would favor the adsorption of anionic orthophosphate ions. Improved adsorption at lower pH as shown in Fig. 3(a) provided further confirmation that adsorption was enhanced due to the attraction between the anionic phosphate ions and the positively changed surfaces of sludge particles.

The effect of temperature on effluent P concentration is presented in Fig. 3(b). A decrease in effluent P concentration was observed at higher temperatures. Consequently, the amount of phosphorus adsorbed by AMD sludge increased with temperature. Thermodynamic studies, such as the change in standard free energy (ΔG^0), enthalpy (ΔH^0_{ads}), and entropy (ΔS^0) of adsorption, helped further clarify the effect of temperature on phosphorus adsorption. Gibbs free energy of adsorption (ΔG^0) was computed based on the equilibrium

a

b

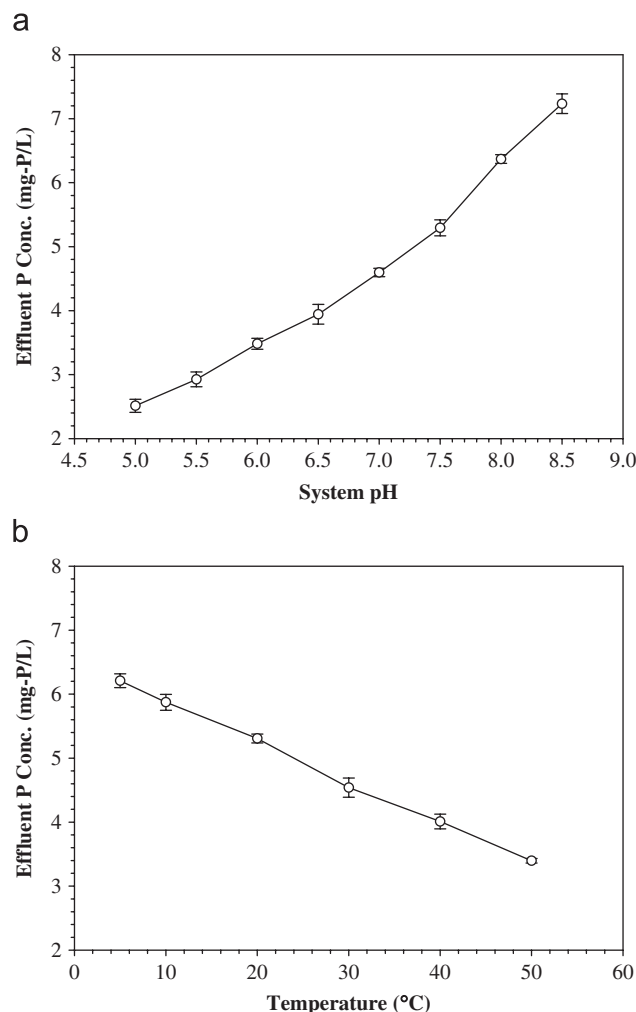

Fig. 3 – Effect of pH and temperature on effluent P concentration (mean±1 standard deviation). (a) pH (initial concentration 20 mg P/L; sludge dosage 0.6 g/L; mixing time 1 h; 20 °C); (b) temperature (initial concentration 20 mg P/L; sludge dosage 0.6 g/L; mixing time 1 h; pH 7±0.1).

constant (K_c) in the following equation:

$$\Delta G^0 = -RT \ln(K_c) \quad (1)$$

where R is the universal gas constant (8.314 kJ/kmol/K), T is the adsorption temperature in Kelvin, and K_c is equilibrium constant (ratio of the concentration of orthophosphate ions adsorbed by adsorbent to that of orthophosphate ions in the aqueous phase at equilibrium) (Namasivayam and Kavitha, 2002). The standard enthalpy (ΔH^0_{ads}) and entropy (ΔS^0) were estimated from the van't Hoff equation (Eq. (2)) via linear regression (Acemioglu, 2004):

$$\ln(K_c) = \frac{-\Delta H^0_{ads}}{RT} + \frac{\Delta S^0}{R} \quad (2)$$

The linear relationship between $\ln(K_c)$ and $1/T$ for P adsorption was found and the determined thermodynamic parameters are presented in Table 2. The negative values of Gibbs free energy (ΔG^0) suggested the spontaneity of P adsorption process over the temperature range tested.

Table 2 – Thermodynamic parameters for P adsorption by AMD sludge

Temperature ($^{\circ}$C)	K_c	ΔG^0 (kJ/mol)	Regression results	
			ΔH^0_{ads} (kJ/mol)	ΔS^0 (kJ/mol/K)
5	2.22	−6.63		
10	2.41	−7.30		
20	2.77	−8.47		
30	3.41	−10.19	12.99	0.053
40	3.99	−11.50		
50	4.89	−13.19		

Further, based on the positive value of ΔH^0_{ads}, the adsorption reaction was found to be endothermic, which was in agreement with the improvement in phosphorus removal by AMD sludge at higher temperatures (Fig. 3(b)). However, this finding was different from that of synthetic dye adsorption by AMD sludge (Wei and Viadero, 2007), where adsorption was found to be exothermic. The positive ΔS^0 indicated that adsorption of phosphorus onto AMD sludge particles resulted in an increase of randomness at the solid–liquid interface.

3.3. Adsorption isotherms

Illustrated in Fig. 4 is the relationship between equilibrium effluent P concentration and adsorption capacity of AMD sludge. The adsorption capacity increased from 9.89 to 31.97 mg/g when the final effluent P concentration increased from 0.21 to 13.61 mg P/L. Based on these data, AMD sludge was found to have a P adsorption capacity comparable to or better than reported for other metal oxide adsorbents such as recovered ochre (Heal et al., 2004), GFH (Genz et al., 2004), ferrihydrite (Kang et al., 2003), and synthetic AMD flocs (Adler and Sibrell, 2003).

The adsorption of P by AMD sludge was well described using the *Freundlich* isotherm (Eq. (3)).

$$q_e = KC_e^{1/n} \tag{3}$$

where C_e and q_e are equilibrium P concentration in solution (mg P/L) and the corresponding P adsorption capacity of AMD sludge (mg P/g), and K and $1/n$ are empirical constants determined through regression analysis. As presented in Fig. 4, a linear relationship ($r^2 = 0.953$) between q_e and C_e was observed when the data were plotted on a log–log scale. The *Freundlich* constants K and $1/n$ were 17.0 mg P/L and 0.25, respectively. Coincidentally, the outcomes of this isotherm study for P adsorption by AMD sludge were similar to those reported by Kang et al. (2003), who utilized ferrihydrite as an adsorbent for phosphorus removal ($K = 19.4$ mg P/L and $1/n = 0.29$). The similarities between isotherm constants gives further support to the assertion that iron in ferrihydrite form was responsible for most of the P adsorption by AMD sludge.

3.4. Resolubilization of AMD sludge-bound metals

Since AMD sludge resulted from the precipitation of dissolved metals as oxides/hydroxides, particular attention was paid to the potential for metal resolubilization due to pH changes or
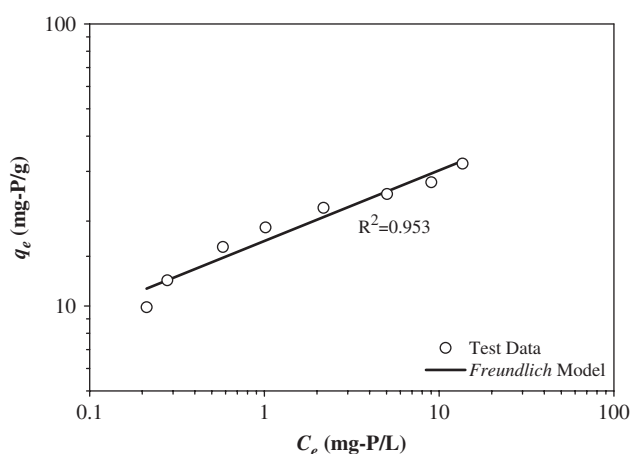

Fig. 4 – *Freundlich* isotherm of phosphorus adsorption by AMD sludge (mixing time 1 h; 20 $^{\circ}$C; pH 7.0 ± 0.1).

Table 3 – Dissolved metal concentrations (mg/L) in the effluents after P adsorption by AMD sludge at different pH[a] (initial concentration 20 mg P/L; sludge dosage 1.0 g/L; mixing 1 h; 20 $^{\circ}$C)

Metal	Fe	Al	Mn	Cu	Ni	Zn
Control[b]	<0.01	<0.1	<0.01	<0.01	<0.01	<0.01
pH 5.0	<0.01	0.1	0.24	<0.01	0.05	0.04
pH 6.0	<0.01	<0.1	0.14	<0.01	0.02	0.01
pH 7.0	<0.01	<0.1	0.01	<0.01	0.01	<0.01
pH 8.0	<0.01	<0.1	<0.01	<0.01	0.01	<0.01
pH 9.0	<0.01	0.3	<0.01	<0.01	0.02	<0.01
MDL[c]	0.01	0.1	0.01	0.01	0.01	0.01

[a] pH variation: ±0.1.
[b] Control: P concentration 0 mg/L; sludge dose 1.0 g/L; pH ~8.1.
[c] Method detection limit.

complexation reactions. Indeed, metal leaching from AMD sludge would limit the further value-added use of this byproduct from mine water treatment. The dissolved metal concentrations in the effluent of the adsorption process at pH ranging from 5 to 9 are presented in Table 3. When compared to experimental controls, some resolubilization of Mn and Al occurred at pH<6.0 and >8.0, respectively. These observations were expected based on the solubility of Mn and Al

hydroxides in water (Stumm and Morgan, 1996). At the tested pH range, no appreciable metal leaching was found for other metal elements. Consequently, it was concluded that metal resolubilization was not likely to be a major concern when phosphorus removal by AMD sludge was carried out at a pH range typical for municipal wastewater secondary effluents ($6 < pH < 8$).

3.5. Continuous CSTR adsorption studies

CSTR tests were conducted to develop insight into the potential of the AMD adsorption system for P removal from secondary effluents. The change in CSTR effluent P concentration over time for three different waters (synthetic wastewater, Mon River water, and secondary effluent from a POTW) is presented in Fig. 5(a). The P concentration decreased rapidly as CSTR testing started and P adsorption by the AMD sludge began to take place in the system. The CSTR system reached equilibrium in about 3 h, based on the little change in effluent P concentration observed for $t > 3$ h. The

equilibrium P concentration in the effluent was consistent with previous batch adsorption studies. The curves of effluent P concentration over time for the three types of water tested were in close agreement and in several instances were indistinguishable after 3 h, indicating that phosphorus removal by AMD sludge was a rather robust process capable of treating wastewaters with varying characteristics. Although there were a variety of ionic species (anionic and cationic) present in the Mon River water and secondary effluent from the POTW (Table 1), the comparable adsorption performances for three types of water revealed that P adsorption by AMD sludge was relatively independent of the presence of other ionic species. Also presented in Fig. 5(a) are the pH changes during CSTR tests. The system pH reached equilibrium typically after 2 h operation, beyond which the system pH remained constant at 7.3, 7.7, and 7.8 for POTW effluent, Mon River water, and synthetic wastewater, respectively.

Hydraulic detention time, θ_H, is an important factor for CSTR operation, which may affect the treatment capacity for a tank with a certain dimension or its treatment effectiveness. In this study, detention times of 1 and 2 h were tested. The change of P concentration in the effluent of CSTR over time using Mon River water dosed with orthophosphate stock solution to 20 mg P/L at different detention times is presented in Fig. 5(b). It was found that final effluent P concentrations at equilibrium were almost the same for hydraulic detention time at 1 and 2 h. Hydraulic detention time did not significantly affect phosphorus removal performance of AMD sludge, although it took a longer time to reach equilibrium at higher θ_H. This finding indicated that the CSTR process could be resilient in handling flow variation in full-scale processes if appropriate adjustments could be made to the AMD sludge dose. The system pH reached equilibrium after 2 h of operation and equilibrium pH for both hydraulic detention times was almost the same (pH 7.6–7.7, as shown in Fig. 5(b)).

In order to evaluate the proposed CSTR system for phosphorus removal from municipal wastewater effluent, an actual POTW effluent was tested at AMD sludge doses of 1.0, 0.5, and 0.35 g/L without the addition of extra orthophosphate salts. The actual POTW effluent contained orthophosphate at a concentration of 1.80 mg P/L (9% of the 20 mg P/L dose applied in the previous CSTR tests). Presented in Fig. 6 is the change of effluent P concentration during CSTR tests at three AMD sludge doses for the POTW effluent. It was observed that higher AMD sludge doses resulted in lower effluent P concentrations. This trend was in agreement with observations from the batch adsorption tests conducted using the synthetic wastewater. The final effluent P concentrations at sludge doses of 1.0, 0.5, and 0.35 g/L were 0.013, 0.027, and 0.034 mg/L, respectively (equivalent to phosphorus removal of 99.3%, 98.5%, and 98.1%). Consequently, it was concluded that CSTR process could be used for phosphorus removal from secondary effluents by using AMD sludge as adsorbent.

Also presented in Fig. 6 is the pH change during CSTR tests using POTW effluent. The equilibrium pH ranged from 7.3 to 7.6. Slightly higher pH was observed at higher sludge doses due to the fact that the AMD sludge contained a mixture of metal oxides/hydroxides with a higher initial pH ($\sim$8.1).
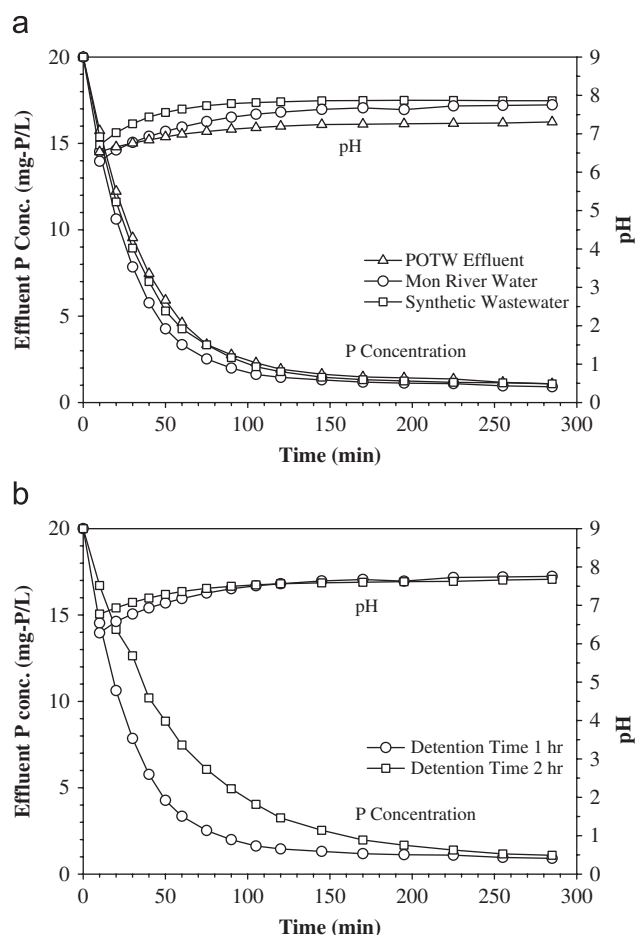
Fig. 5 – Change of effluent P concentration and pH during CSTR tests. (a) Three types of water samples (Feed rate 2 L/h; initial concentration 20 mg P/L; sludge dose 1 g/L; hydraulic detention time 1 h; 20 °C); (b) detention time (Mon River water, feed rate 1 and 2 L/h; initial concentration 20 mg P/L; sludge dose 1 g/L; 20 °C).

3.6. Implication for nutrient removal from municipal wastewater effluents

Eutrophication due to excess nutrient (especially P) loading in receiving waters is a worldwide problem with significant adverse consequences for the environmental and and
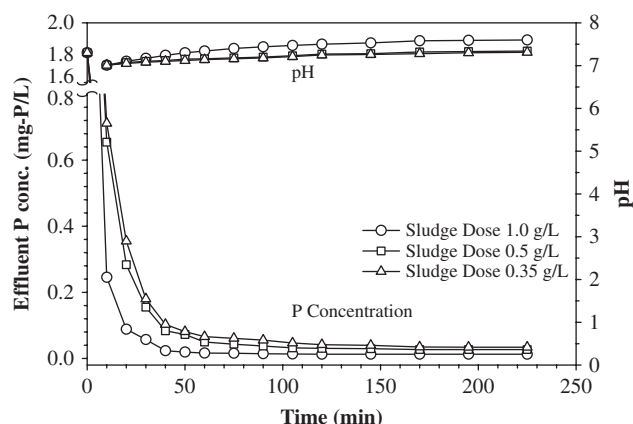

Fig. 6 – Change of effluent P concentration and pH during CSTR tests at different AMD sludge doses for actual POTW effluent (feed rate 2 L/h; hydraulic detention time 1 h; initial concentration 1.8 mg P/L; sludge dose 1.0 g/L; 20 °C).

economic futures of developed and developing nations. Consequently, the control of nutrient loading has become a high priority for environmental regulatory agencies of many countries. In particular, it is known that POTWs contribute most to point-source nutrient loading. Although newer technologies do exist for the removal of nutrients from POTW effluents, they typically involve large extensive capital investment and increased operation costs which often cannot be met—particularly in the developing world. Consequently, cost-effective technologies for nutrient removal are urgently needed.

The use of AMD sludge is very promising for P removal from POTW effluents. The process could be implemented as a CSTR-based unit operation tertiary treatment for secondary effluents. A process flow diagram is presented in Fig. 7(a and b) for a typical suspended growth wastewater treatment system and a system modified for tertiary treatment using AMD sludge adsorption. After secondary treatment, P-containing secondary effluent enters a CSTR containing AMD sludge. After phosphorus adsorption in the CSTR, the AMD sludge laden with orthophosphate can be recovered from the effluent using a variety of solid/liquid separation processes.

A second method to implement AMD sludge to remove P from POTW effluents is through the injection and complete mixing of AMD sludge with the primary effluent, prior to secondary treatment, as presented in Fig. 7(c). In this approach, there is no need for capital cost intensive tertiary
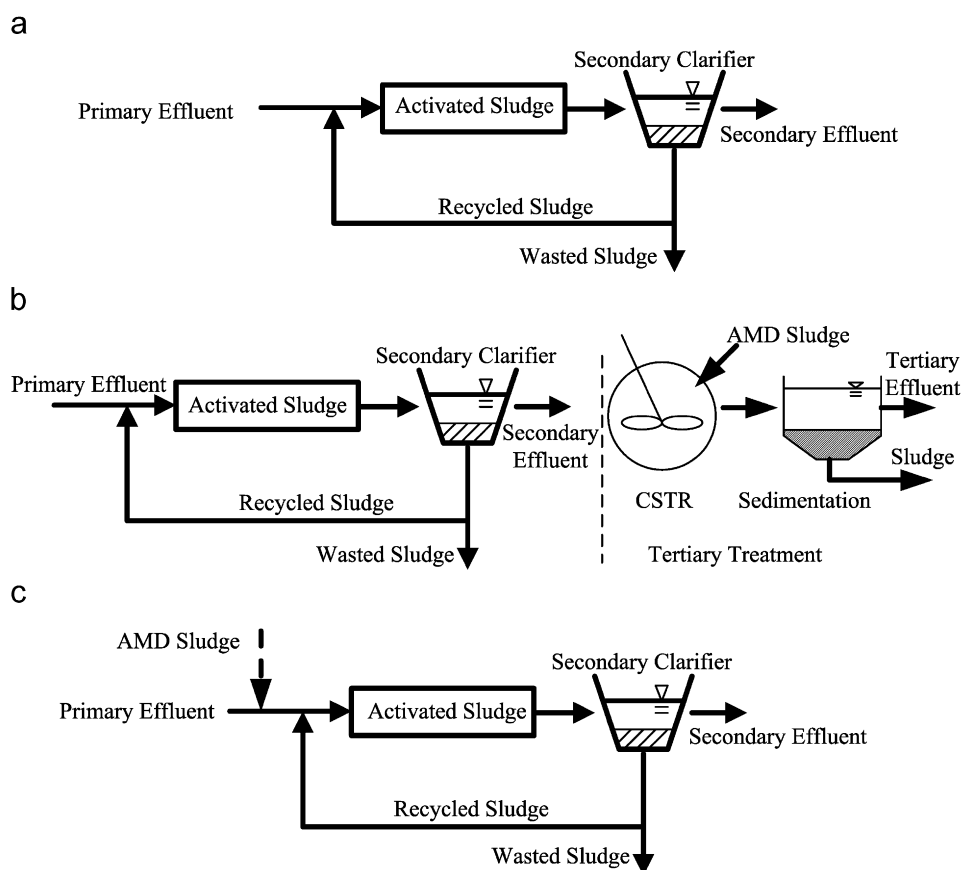

Fig. 7 – Proposed processes for phosphorus removal using AMD sludge (a) typical suspended growth secondary treatment; (b) AMD sludge adsorption tertiary treatment added to a typical suspended growth system; and (c) integration of AMD sludge-based adsorption into secondary treatment.

treatment. However, a number of key factors must be examined prior to implementing this approach. For instance, the potential effects of AMD sludge on biological processes in secondary treatment are unknown. Likewise, the presence of AMD sludge in secondary treatment processes may require changes to solid/liquid separation processes and could have effects on the further beneficial use (e.g., land application) of biosolids recovered from suspended growth systems.

Beneficial use of waste materials for pollutants removal from wastewater is a practical approach to environmental sustainability. After the adsorption capacity of AMD sludge is exhausted, the resulting P-enriched sludge could then potentially be used as a fertilizer (Dobbie et al., 2005), indicating a value-added final disposal option for AMD sludge. Although the resolubilization of metals from AMD sludge was not a major concern in this study, the variable chemical characteristics of AMD sludge from different sites and the potential presence of toxic elements could limit the full-scale application of the proposed process (Hancock, 2005).

Wet AMD sludge containing low solids (4.31%) was tested to take full advantage of the high surface area and active sites of sludge particles. However, it could be costly and impractical to transport AMD sludge with low solids to municipal wastewater treatment facilities, which might necessitate sludge mechanical dewatering or air-drying at AMD treatment sites (Heal et al., 2004). Consequently, the scale up of the proposed process requires further technical demonstration in pilot field studies to fully assess the effects of variability of sludge sources, operational practicalities, waste disposal, treatment cost–benefit tradeoff, and related regulatory issues.

4. Conclusions

The effective control of phosphorus release from municipal wastewater effluents into surface waters is known to be an effective and practical approach to decreasing eutrophication in receiving waters. Batch and continuous adsorption experiments demonstrated that a waste sludge, generated from acid mine water treatment, was very promising as adsorbent to remove phosphorus from wastewater. Phosphorus removal was found to be a beneficial use of AMD sludge prior to its final disposal. Adsorption of orthophosphate onto AMD sludge particles followed the *Freundlich* isotherm model with an adsorption capacity ranging 9.89–31.97 mg/g when the final effluent concentration increased from 0.21 to 13.61 mg P/L. In treating actual POTW effluent of 1.80 mg P/L in a continuous flow system, phosphorus removal efficiency of above 98% was obtained. The process showed potential to be used as a tertiary treatment for the secondary effluents to address P-related eutrophication problems. However, pilot studies are necessary in order to develop a full-scale process for efficient, cost-effective phosphorus removal.

Acknowledgments

R E F E R E N C E S

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