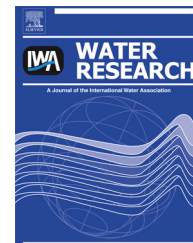




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Phosphate recovery using hybrid anion exchange: Applications to source-separated urine and combined wastewater streams

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ABSTRACT

There is increasing interest in recovering phosphorus (P) from various wastewater streams for beneficial use as fertilizer and to minimize environmental impacts of excess P on receiving waters. One such example is P recovery from human urine, which has a high concentration of phosphate (200–800 mg P/L) and accounts for a small volume (~1%) of total wastewater flow. Accordingly, the goal of this study was to evaluate the potential to recover P from source-separated and combined wastewater streams that included undiluted human urine, urine diluted with tap water, greywater, mixture of urine and greywater, anaerobic digester supernatant, and secondary wastewater effluent. A hybrid anion exchange (HAIX) resin containing hydrous ferric oxide was used to recover P because of its selectivity for phosphate and the option to precipitate P minerals in the waste regeneration solution. The P recovery potential was fresh urine > hydrolyzed urine > greywater > biological wastewater effluent > anaerobic digester supernatant. The maximum loading of P on HAIX resin was fresh urine > hydrolyzed urine > anaerobic digester supernatant ≈ greywater > biological wastewater effluent. Results indicated that the sorption capacity of HAIX resin for phosphate and the total P recovery potential were greater for source-separated urine than the combined wastewater streams of secondary wastewater effluent and anaerobic digester supernatant. Dilution of urine with tap water decreased the phosphate loading on HAIX resin. The results of this work advance the current understanding of nutrient recovery from complex wastewater streams by sorption processes.

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1. Introduction

Phosphate rock is the main source of phosphorus (P) in fertilizers and is essential for high crop yields in agriculture (Schröder et al., 2011). Phosphate rock is also a non-renewable resource that is under threat of depletion (Van Vuuren et al., 2010). Confounding this problem is a growing world population and greater food demands which will require phosphate-

based fertilizers (Childers et al., 2011). There is the potential, however, to recover P from wastewater streams for use as fertilizer (Cabeza et al., 2011) in order to lessen the problem of limited phosphate rock supply. Not only could P recovery from wastewater contribute to more sustainable P management (Cordell et al., 2011), but it could also reduce P loading to receiving waters. It is known that wastewater treatment plants are a point-source of excess P to receiving waters (Carey

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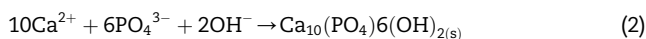
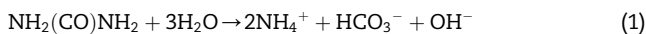
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and Migliaccio, 2009), which can cause eutrophication and degraded water quality. One approach to P recovery is the precipitation of struvite at the wastewater plant, e.g., membrane concentrate from aerobic or anaerobic treatment (Bradford-Hartke et al., 2012) or filtrate from sludge belt filter press (Lew et al., 2011). A more radical approach to P recovery is source separation and treatment of urine, which accounts for ~1% of wastewater by volume, yet contributes ~50% of the total P load to wastewater (Larsen and Gujer, 1996; Wilsenach and van Loosdrecht, 2006).

Recent studies on source separation and treatment of urine outline many of the potential benefits that could come from this technique such as lower energy requirements for wastewater treatment (Wilsenach and van Loosdrecht, 2006), water conservation, nutrient recovery, and decreased loading of nutrients (Larsen et al., 2009) and pharmaceuticals (Lamichhane and Babcock, 2012) to the environment. Urine source-separation is accomplished using waterless urinals and no-mix toilets, which can be used to collect undiluted or low diluted urine in storage tanks (Rossi et al., 2009). However, treatment of urine poses challenges due to its complicated chemistry (Maurer et al., 2006). The composition of urine changes from fresh urine to hydrolyzed urine once it leaves the human body and flows through urinals, toilets, and wastewater piping. The change in composition is due to urea hydrolysis that is facilitated by urease-positive bacteria (Mobley and Hausinger, 1989), which are assumed to be present in toilets, urinals, and wastewater collection systems. The hydrolysis of urea creates ammonium, bicarbonate, and increases pH (Eq. (1)) (Mobley and Hausinger, 1989). Urea hydrolysis can occur in minutes to hours in undiluted urine, and causes loss of phosphate through precipitation of hydroxyapatite (Eq. (2)) and struvite (Eq. (3)) (Udert et al., 2003a). In conventional urinals and toilets, dilution of urine with tap water can cause phosphate precipitation if calcium or magnesium are present (Udert et al., 2003b). Thus the potential to recover P from urine changes as the composition of urine changes, e.g., fresh urine, hydrolyzed urine, urine diluted with tap water or mixed with greywater.



The focus of current research on P recovery from urine is through struvite precipitation, e.g., in fully automated reactors (Antonini et al., 2011), in simple hand-operated reactors (Etter et al., 2011), or by electrolytic magnesium dosage (Hug and Udert, 2013). A promising approach for P recovery from urine is hybrid anion exchange (HAIX), which has not been tested in urine but has been evaluated in wastewaters (Blaney et al., 2007; Martin et al., 2009). Because conventional strong-base anion exchange resins have a higher selectivity for sulfate over phosphate (Gregory and Dhond, 1972), HAIX resins were developed for selective removal of phosphate over competing anions like sulfate (Blaney et al., 2007; Pan et al., 2009; Sengupta and Pandit, 2011). HAIX resin consists of strong-base anion exchange resin with immobilized metal or impregnated metal oxide nanoparticles. Previous research

has tested HAIX resins with Zr(IV) (Awual et al., 2011; Zhu and Jyo, 2005), Cu(II) (Zhao and Sengupta, 1998), and Fe(III) (Blaney et al., 2007) all of which form inner-sphere complexes between metal and phosphate. The inner-sphere complex can preferentially remove phosphate in the presence of competing anions such as chloride, sulfate, or bicarbonate (Pan et al., 2009). This is contrary to typical ion-exchange which forms outer-sphere complexes and favors the ion with the higher valence, typically sulfate (Helfferich, 1995). HAIX resin containing Fe(III) (hereafter HAIX-Fe) was selected for this study because it is commercially available, and has been tested for phosphate removal from lake and stream water (Boyer et al., 2011), domestic secondary wastewater effluent (Blaney et al., 2007; Martin et al., 2009), industrial wastewater effluent (Pan et al., 2009), reverse osmosis concentrate from wastewater treatment (Kumar et al., 2007), and sludge liquor from wastewater treatment (Bottini and Rizzo, 2012). HAIX-Fe resin exhausted with phosphate is effectively regenerated using caustic brine solution with >80% phosphate recovery (Blaney et al., 2007; Sengupta and Pandit, 2011) and solid-phase fertilizers (struvite and calcium phosphate) can be precipitated from the waste regeneration solution (Kumar et al., 2007; Sengupta and Pandit, 2011).

Despite the opportunities for P recovery from source-separated urine, several gaps in knowledge are preventing the implementation of this strategy. Foremost, there is no previous research on the removal of phosphate from urine using HAIX resin. While some research has evaluated the effect of diluted urine on ion-exchange using clinoptilolite (Kocatürk and Baykal, 2012), there is no data on how dilution of urine affects phosphate removal using HAIX resin. There is also no previous work that has examined which wastewater stream is most effective for P recovery when considering maximum recovery potential for P and sorption chemistry. Accordingly, the goal of this study was to evaluate the potential to recover P from source-separated urine and combined wastewater streams that included undiluted urine, urine diluted with tap water, greywater, mixture of urine and greywater, anaerobic digester supernatant, and secondary wastewater effluent. The specific waste streams were chosen because they comprise the major waste streams that make up domestic wastewater (Kujawa-Roeleveld and Zeeman, 2006). The specific objectives were: (1) to evaluate the sorption capacity and selectivity of HAIX-Fe resin for phosphate in fresh and hydrolyzed urine, greywater, anaerobic digester supernatant, and secondary wastewater effluent; (2) to evaluate the effect of diluting urine with tap water and mixing urine with greywater on the sorption capacity and selectivity of HAIX-Fe resin for phosphate; and (3) to identify the most efficient location to recover P starting at the point of urine generation and through wastewater treatment.

2. Materials and methods

2.1. Materials

2.1.1. Domestic wastewaters streams

Synthetic wastewaters including fresh urine (urine-F), hydrolyzed urine (urine-H), anaerobic digester supernatant

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