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Mechanistic study of P retention by dewatered waterworks sludges

T. Al-Tahmazi [a,b], A.O. Babatunde [a,*]

[a] Hydro-environmental Research Centre, Energy and Environment Theme, Cardiff University School of Engineering, Queen's Buildings, The Parade, CF24 3AA, Cardiff, Wales, UK

[b] College of Engineering, University of Karbala, Karbala, Iraq

HIGHLIGHTS

- Dewatered Al and Fe waterworks sludges are good materials for P retention.
- Aluminium sludges tend to have higher P adsorption capacities than iron sludges.
- At least, 5.8 mg of P was retained by each gram of the sludges.
- Metal content and surface area explained most variance in P retention.
- P retention via surface complexation, ligand exchange, and/or precipitation.

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ABSTRACT

Eutrophication caused by excess phosphorus (P) loading poses serious environmental risk to freshwater bodies around the world. Advancing our fundamental understanding towards practical reduction of this risk using novel industrial by-products as P adsorbents is the focus of this study. The study examined the combined effect of solution chemistry and the inherent properties of a novel adsorbent (dewatered waterworks sludges) on their P retention. The overall aim was to contribute to a mechanistic understanding of P retention by the sludges; and to better understand what properties regulate their P retention. Results confirm a strong but variable affinity for P by the sludges. Aluminium (Al)-based sludges generally had higher total specific surface areas; and tended to have higher P sorption capacities (6.09–26.95 mg-P/g) than iron (Fe)-based sludges (5.83–23.75 mg-P/g). In most cases, adsorption data was well fitted with the Freundlich model. However, data for two of the Al-based sludges was best described by the Langmuir model with very minimal leaching of Al, Calcium (Ca) and sulphate (SO_4^{2-}) ions observed; indicating surface complexation via P binding into the Al hydr(oxide) as the main mechanism for these Al-based sludges.

Principal component and multiple linear regression analyses revealed that the metal content (Al, Fe, $Al_{oxalate}$ and $Fe_{oxalate}$) and total specific surface area components had the most significant explanation for the variance of: (i) P-uptake at different initial P concentrations; (ii) the adsorption maxima; and (iii) the Freundlich constant (K_f); ($p < 0.001$). Total carbon (TC), organic carbon, Ca content and exchangeable Ca components explained a significant reasonable variance in P-uptake and K_f. This explanation was demonstrated for the role of Ca content in chemical P precipitation mechanism; and also for exchanging TC sites on the surface of the sludges with phosphate ions via ligand exchange mechanism. Overall, giving the combined effect of intrinsic sludge properties and solution

* Corresponding author.
E-mail address: babatundea@cardiff.ac.uk (A.O. Babatunde).

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chemistry; dewatered waterworks sludges with high reactive metal content (Al and Fe), Ca and SO_4^{2-} ions, and total specific surface area would be the best choice for P retention in practical applications.

1. Introduction

Eutrophication caused by excess phosphorus (P) loading poses serious environmental risk to freshwater bodies around the world. It has now become a global environmental concern particularly with waters worldwide experiencing major increases in P concentrations leading to additional drinking water treatment, decreased biodiversity and loss of recreational value. For example, P fluxes to oceans have increased approximately 2.8-fold since the industrial revolution and over 400 coastal dead zones can be found at the mouths of rivers discharging P (Diaz and Rosenberg, 2008). Surveys in the United States and the European Union (EU) estimates that 78% and 65% of their coastal areas, respectively, exhibit symptoms of eutrophication (Mayer et al., 2013); whilst inland waters are equally at risk. According to the US Environmental Protection Agency, eutrophication is the biggest overall source of impairment of the nation's rivers and streams, lakes and reservoirs, and estuaries; while in the EU, approximately 50% of all lakes have total P (TP) at levels which pose a risk of eutrophication (Bogestrand, 2004). In the UK, the Technical Advisory Group has advised that 65% of England's rivers fail current P limits with lakes being more sensitive to contamination (Wood et al., 2007).

In order to prevent eutrophication of inland and coastal waters, legislation on P discharge into the surrounding environment is becoming stricter worldwide and many water companies now face additional treatment requirements to reduce P in their final effluent discharges. Consequently, water companies are now faced with the prospect of having to implement additional treatment methods in order to supplement their traditional biological, chemical and physical processes for reducing P. However, finding the best application to reduce P can be challenging, particularly when low consents are required, coupled with the expectation to strive towards recovering the P.

In this regards, P removal via adsorption on novel materials and by-products is gaining increased attention as an environmentally friendly and cost-effective means of removing and reducing P in wastewater streams, and enabling its recovery. This study focuses on one of such novel by-products, dewatered waterworks sludges which is a widely available by-product of drinking water purification processes; and which have been shown to be effective adsorbent for P (Babatunde et al., 2009). However, while the sludges can retain P and therefore be used as an adsorbent for P removal; there is a need to further investigate the factors that influence their P retention behaviour. This is because drinking water treatment plants use different water sources and different coagulants and polyelectrolytes; and therefore, they produce sludges with variable elemental compositions and characteristics. Whilst some studies have examined the influence of either solution chemistry or physicochemical characteristics of the sludges on their P retention; investigation into their combined effects over a wide range of samples from various sources has been limited. This is, however, crucial for improving our mechanistic understanding of their P retention behaviour and for their effective practical use for P removal.

Therefore, the specific objectives of this study were: (i) to evaluate the physicochemical properties of seventeen dewatered waterworks sludges from different sources; and together with the solution chemistry effects, relate these to their P retention behaviour; (ii) to probe the characteristics of P retention by the dewatered waterworks sludges; and (iii) to investigate and determine the mechanisms involved in P retention by the sludges.

2. Material and methods

2.1. General physicochemical characterization

Dewatered waterworks sludges were collected from seventeen drinking water treatment works located in the United Kingdom. The treatment plant locations are kept anonymous on request; and samples obtained were simply labelled using a sequential alphabetic code generated from the location names. To determine the chemical composition, 0.1 g samples of each of the sludges (air dried and ground to particle size <2 mm) was digested with 3 mL of HCl and 3 mL of HNO_3 in a microwave and analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Chloride, sulphate and exchangeable calcium ions were determined by extraction with deionized water at a 1:10 solid:liquid ratio for 4 h, followed by filtration with 0.45 μm membrane filters. The chloride and sulphate ions were measured using Ion Chromatography (ICS—2000 Ion Chromatography system) while Ca concentration was measured using ICP-AES. Total carbon (TC) and OC were determined by Total Organic Carbon Analyzer (TOC-V CSH (Shimadzu)); pH was determined following the British Standards institution method (British Standards Institution, 1990). The total surface area was measured with the sludges in a wet condition using Ethylene Glycol Monoethyl Ether (EGME) method. The method determines both the internal and external surface areas where adsorption and ion exchange take place (see Cerato and Lutenegger, 2002 for the measuring procedure). The morphological structure of the sludges was examined by X-ray diffraction (XRD); the scattering angles ranged from 2°