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Mechanistic study of P retention by dewatered waterworks sludges

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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 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.

Keywords: adsorption capacity, aluminium sludges, dewatered waterworks sludges, ferric sludges, phosphorus

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 U.S. 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, 0.1g samples of each of the sludges (air dried and ground to particle size <2mm) 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 hours, 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˚ to 80˚ 2θ with scanning speed at 0.02° 2θ per 0.5 second. To quantify the amorphous Al and Fe oxides of the sludges, ammonium oxalate-extractable Al and Fe were measured according to the method described by McKeague and Day (1966).

2.2 Adsorption isotherm study

P sorption maxima of the dewatered water sludges was determined by equilibrating 1g each of the dewatered sludges samples in 200 ml acid-washed polyethylene bottles. The bottles contain 100 ml solution at three pH values (4, 7 and 9); and seven initial P concentrations (5, 10, 20, 40, 80, 160 and 320 mg-P/l). Hydrochloric acid (0.01M) and potassium hydroxide (0.1M) were used for pH adjustment. Potassium dihydrogen phosphate (KH_2PO_4) was used to prepare P stock solution. After 48-hours pre-determined equilibration time, samples were filtered using a 0.45µm membrane filter and analysed for P using a HACH DR-3900 spectrophotometer. The mass of P adsorbed per mass of adsorbent (q) in mg/g was calculated using Eq. (1).

$$q_e = \frac{(C_o - C_e)}{m} V \qquad (1)$$

where C_o and C_e are the initial and equilibrium P concentrations, respectively in the solution (mg/l), V represents the volume of the solution (l), and m is the mass of the adsorbent (g).

The equilibrium data was fitted with Langmuir and Freundlich isotherm models; the linearized forms of which are given below, respectively in equations 2 and 3;

$$\frac{C_e}{q_e} = \frac{1}{bQ_\circ} + \frac{C_e}{Q_\circ} \qquad (2)$$

$$\log q_e = logK_f + \frac{1}{n} \log C_e \qquad (3)$$

where b is constant of Langmuir adsorption (L/g), Q is the maximum mass of P adsorbed at saturation conditions per mass unit of adsorbent (mg/g); K_f is the bonding energy related constant (L/g), and n is Freundlich heterogeneity constant.

2.3 P retention – Mechanism and linkage with inherent properties

2.3.1 Exchangeable ions and Precipitation tests

In order to investigate the possible mechanism of P retention by the sludges through calcium phosphate precipitation and/or adsorption to the precipitated aluminium and iron oxides, exchangeable ions and precipitation tests were carried out. For the exchangeable ions test, the leachability of Ca, Al and Fe from the sludges was determined by shaking 1 g each of the sludge samples in 100 ml of deionized water at three initial pH solutions (4, 7 and 9), and for

48 h at room temperature. The pH at time of equilibrium was determined using a pH meter, and the samples were then filtered using 0.45 µm membrane filters. The supernatants were analysed for Al, Ca, Fe, magnesium (Mg) and P using ICP-AES; and the leached concentrations determined were used as background concentration for the precipitation test before adding P.

Precipitation test was then conducted to determine at which pH, and Ca and P concentrations the calcium phosphate precipitation might occur. The tests were performed in conditions simulating the P adsorption experiments. Aliquots of 100 ml of deionized water were placed in 200 ml acid washed polyethylene bottles and then agitated with different concentration of Ca and/or Fe (the concentration of Ca and/or Fe was determined based on the result of the exchangeable test wherein some sludges leached Ca while some leached both Ca and Fe). Thereafter, pH was adjusted using hydrochloric acid (0.01M) and potassium hydroxide (0.1M), prior to adding the P stock solution. The mixtures were then agitated on a rotary shaker for 48h before being filtered using 0.45 µm membrane filter and then analysed for Ca, Fe and P. Any reduction in the concentrations of Ca, Fe and P after the reaction time would indicate a reaction taking place. To further probe the reaction taking place and the possible mechanism, samples of the sludges before and after reaction with the P stock solution were examined using Fourier transform infrared spectroscopy (FTIR); the spectrum was scanned from 500 to 4000 cm^{-1}.

2.3.2 Linkage with inherent properties

To identify which of the measured sludge properties gives the most explanation of variance in P retention (uptake and maximum), a multiple linear regression analysis was conducted. Pearson's correlation coefficients were computed to find out if there is high correlation between the physicochemical properties of the dewatered sludges. Due to the high correlations found between the measured physicochemical properties of the seventeen dewatered sludges, rotated principal component analysis (PCA) was performed, using Varimax rotation method, to reduce the number of predictor variables which are highly correlated (multicollinearity) from eleven single variables to three uncorrelated linearly principal components. The produced component scores were then used as predictors (independent variables) in addition to initial pH of the solution in a multiple linear regression model. P uptakes at seven initial P concentrations, P adsorption maxima and Freundlich constant were chosen as the outcome (dependent) variables.

IBM SPSS statistic software (version 20) was used for statistical analyses. The Shapiro-Wilk's test and data visualization by histograms, normal Q-Q plots and box plots were used to assess the normal distribution of the experimental data. Where data was not normally distributed, a transformation was performed for data to obtain a normal distribution.

3. Results and discussion

3.1 General physicochemical characterization

The dewatered waterworks sludges had highly variable physicochemical properties (see Table 1). The main constituent of the sludges, by weight was either aluminium (0.39 – 15.2) % or iron (0.59 – 29.8) %. It was evident that the Al and Fe contents of the sludges were dependent on the primary coagulant used during the water treatment process. Ten of the sludges were Fe-based, and the rest (including one sludge which contains both Al and Fe) were Al-based. The total specific surface areas (TSSA) of the sludges ranged from 97 to 468 m^2/g (see Table 1).

TC and organic carbon (OC) of the Al- and Fe-based sludges ranged from 53.7 to 177.4 and 53.1 to 177.4 mg/g, respectively as shown in Table 1. Also, it can be seen that there is negligible difference between the TC and OC content of the sludges. This implies that the content of most common inorganic carbon in the sludges; i.e. calcium carbonate and calcium magnesium carbonate is minimal. TC has a negative impact on the P adsorption capacity of dewatered sludges by retarding P diffusion into the micropores (Makris et al., 2005). However, Yang et al. (2006) found that during the adsorption process, OC exchanges with P which replaces it on the surface of the sludges, thus implying that more exchangeable OC can enhance P retention by the sludges. In our study, it was not possible to isolate the effect of TC and OC on P retention; however, results of the FTIR test shows that the carboxyl group bands was changed after the sludges reacted with P, indicating the replacement of OC with the phosphate ions on the surface of the sludge. The XRD diffraction patterns reveal sharp diffraction characteristic (peaks) for GU, BS, HO, CA, AR, HU, SF and CF sludges; and these were defined as: quartz for HO, HU and CF; graphite and iron molybdenum for GU; Lithium phosphate and calcium manganese oxide for CA; cronusite and lavendulan for AR, graphite for SF and mica and nimite-1 in addition to quartz for CF (see Table 1). Interestingly, the two mineral peaks (mica and nimite-1) of CF which is a Fe-based sludge, contain iron and aluminium ions. This indicates that the iron and aluminium metals alloys are in crystalline form. This might impact on the adsorption behaviour of the CF sludge via reduction of the available reactive surfaces for P retention. In addition, two crystalline peaks of graphite from carbon for GU and SF which are both Al-based sludges, would suggest reduced cation and anion ions leachability from these sludges, and this could restrict the adsorption process into aluminium oxide especially for the SF sludge which has a high TC content.

Table 1 Physicochemical properties of the seventeen dewatered waterworks sludges

Properties		GU	BS	MO	HO	CA	WD	FO	HH	AR	OS	HU	WY	WA	BU	SF	CF	BG
Al	mg/g	112.81	4.59	3.89	65.35	6.80	104.22	21.16	5.16	5.87	105.34	151.88	4.84	108.78	5.80	122.29	50.05	7.71
Ca		1.16	6.83	2.65	1.90	3.33	1.80	3.17	3.06	24.87	0.88	3.21	0.89	0.93	1.47	0.63	12.56	6.67
Fe		17.00	298.10	257.80	143.29	255.46	9.75	241.69	193.85	277.72	28.73	8.25	287.34	5.94	212.09	13.91	245.79	257.99
P		0.24	0.61	0.39	0.65	0.29	0.70	0.43	0.44	0.35	0.60	4.78	0.77	0.68	0.61	0.47	3.19	1.70
Mg		0.66	0.47	0.20	1.38	0.43	0.44	0.25	0.81	0.28	0.79	0.97	0.23	0.57	0.31	0.20	9.15	0.47
Mn		0.33	0.94	0.79	0.57	0.45	0.29	2.32	0.37	0.52	0.40	0.66	1.28	0.43	0.17	0.42	1.55	1.27
Zn		1.02	0.19	0.40	1.71	0.09	0.47	0.09	1.85	0.08	1.71	0.12	0.16	1.22	1.74	0.84	0.28	0.50
Al_{oxa}		110.12	1.14	1.85	58.63	1.02	95.28	17.36	1.36	2.99	88.26	105.51	3.46	96.02	4.67	75.68	2.62	4.14
Fe_{oxa}		13.35	143.08	149.52	72.41	144.48	3.68	121.33	121.38	113.63	14.42	2.52	146.37	4.64	138.48	6.96	118.09	101.10
p_{oxa}		0.22	0.23	0.24	0.34	0.28	0.28	0.23	0.30	0.21	0.27	0.69	0.34	0.30	0.25	0.28	0.24	0.52
Cl^-		0.11	0.22	0.16	0.16	0.21	0.24	0.30	0.33	0.59	0.11	0.22	0.27	0.14	0.22	0.56	0.76	0.48
SO_4		0.81	4.06	6.93	3.86	7.45	1.88	4.26	4.51	6.32	1.19	2.72	8.55	0.33	2.81	0.26	0.71	0.22
TC		119.6	110.8	117.4	105.2	115.9	119.6	137.	161.9	88.62	170.6	75.21	113.7	154.4	154	177.4	53.7	144.4
OC		118.9	110.8	117.4	105.2	115.9	119.1	137	161.9	88.62	170.1	74.2	113.7	154	153.6	177.4	53.1	144.4
TSSA	m^2/g	364.1	203.4	186.4	414.5	219.8	468	120.3	131.9	97.02	206.9	390.4	132.3	210.1	157.2	181.8	296.3	125.2
EC	µs/cm	455.5	522.8	488.3	665.7	410.7	723.1	378	375.8	1239.3	421.3	541.5	843.4	688	828	329.2	1073.1	471.1
PH	---	6.26	5.47	4.48	5.49	4.09	6.27	5.49	4.55	6.64	6.05	7.06	4.3	6.31	4.75	6.13	6.99	5.89
Crystalline minerals		Graphite, Iron Molybdenum	Lithium boride	----	Quartz	Lithium phosphate, Calcium manganese oxide	----	----	----	Cronusite, Lavendulen	----	Quartz	----	----	----	Graphite	Quartz, Mica, Nimite-1	---

In general, XRD patterns for the sluges showed apparent poorly ordered particle distribution of Al and Fe minerals within the Al- and Fe-based sludges (with the exception of CF); this implies that the Al and Fe sludges are in the amorphous phases. Amorphous oxide phases are assumed to be extracted with acidified ammonium oxalate and associated with non-crystalline phase of metal oxides. Thus, the quantity of Al_{oxa} and Fe_{oxa} in the sludges were determined using this method. Results show that the amorphous Al and Fe oxides represent 61.9 to 97.6% of total Al for the Al-based sludges and 39.2 to 65.3% of total Fe for the Fe-based sludges (see table 1). P uptake is strongly linked to amorphous Al and Fe concentrations and the variation in oxalate extractable Al and Fe has been shown to account for differences in P retention by dewatered waterworks sludges (Dayton and Basta, 2005; Elliott et al., 2002).

3.2 Adsorption isotherm study

Figure 1 shows the isotherm of P uptake by the sludges. For ease of comparison, the Al- and Fe-based sludges were grouped separately. To determine if there was any significant difference in P uptake between the sludges; a one-way ANOVA was used. The results revealed significant differences in P uptake between the sludges (p= 0.002). These findings are consistent with those of Makris et al. (2005) who studied the P sorption/desorption characteristics and kinetics for seven dewatered waterworks sludges and found that the Al-based sludges had higher adsorption capacity than the Fe-based sludges.

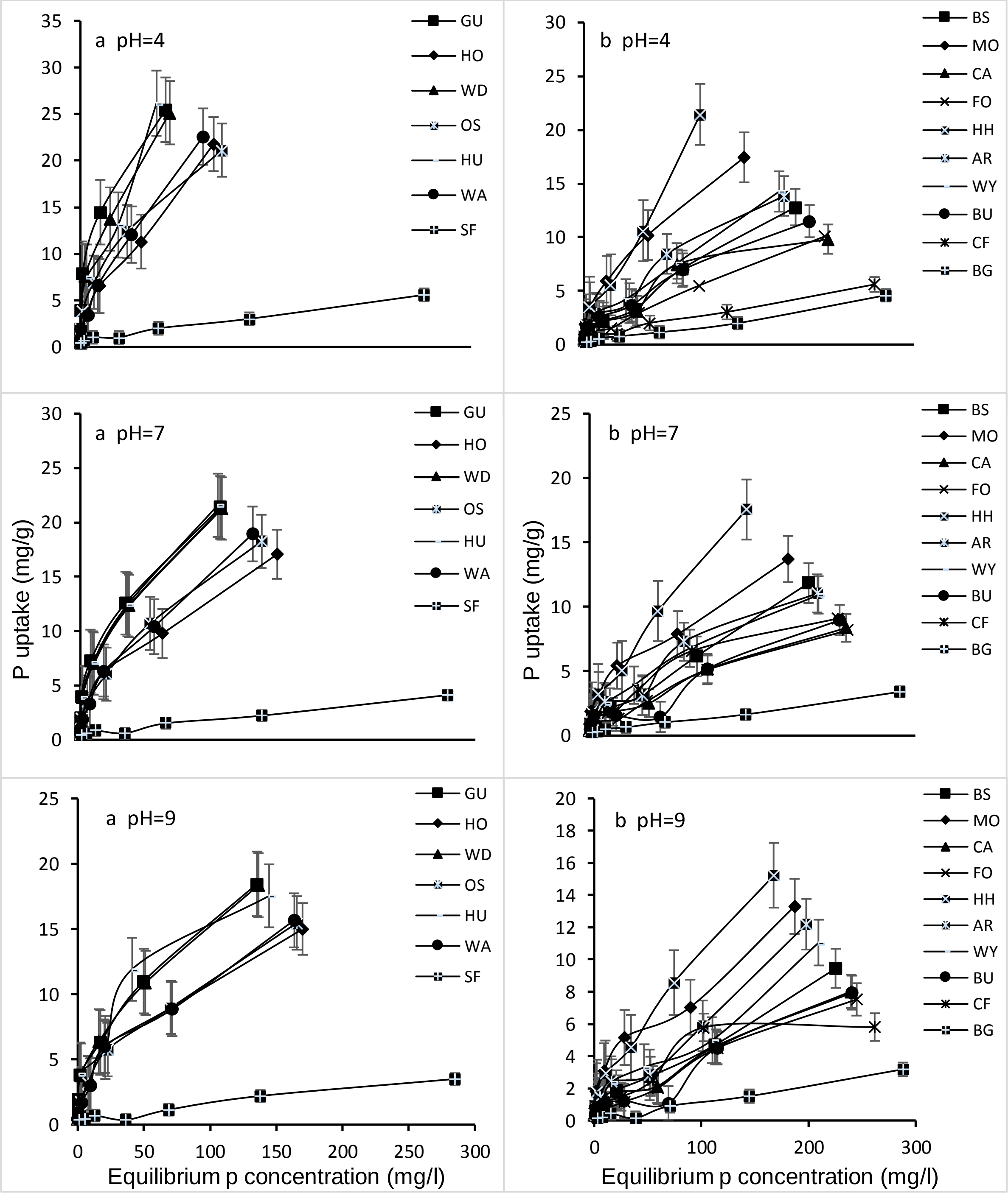

Figure 1 Isotherms of P uptake by the seventeen dewatered water sludges (at initial pHs of 4, 7 and 9; t=48 hours; plots to the left and right refer to, respectively, aluminium- and iron-based sludges).

Further data analysis show that the P adsorption data was well fitted with the Freundlich model; and that the adsorption density value for all the sludges was > 1 and ranged from 1.40 to 2.79. For most sludges, the bonding energy related constant decreased as the adsorption density increased, in accordance with preferential adsorption occupying surface sites in order from strongest to weakest binding strength (Apak, 2013).

P adsorption capacities obtained from the fitting of the Langmuir model (see figure 2) shows generally that sludges had variable adsorption capacities which increased with decrease initial pH solution. This suggests that P adsorption by the sludges is favourable at acidic conditions. It should be noted that the adsorption capacities reported herein relate to the equilibrium concentration of P in solution. Therefore, using the adsorbents at very low P concentration means the process would be operating under the most unfavourable condition. To compare the P adsorption capacity (as determined by the Langmuir model for those sludges with good fitting); one-way ANOVA analysis was used. The results of the test showed that there was significant difference in adsorption capacities between the Al- and Fe-based sludges ($P< 0.001$). This is in agreement with Makris et al. (2005) which showed higher P adsorption capacity for Al-based sludge than Fe-based sludges. Elliott et al. (2002) also reported similar findings in P adsorption between Al- and Fe-based sludges. In addition, the adsorption capacity is related with SSA which in turn depends on the metal oxide. Makris et al. (2004) found that Al-based sludges have higher SSA than Fe-based sludges, resulting in the differences in their adsorption capacities. In our study, higher TSSA and P adsorption capacity were found for Al-based sludges with the exception of SF sludge. The SF sludge has the highest carbon content (crystalline – graphite) which restricts the contact surfaces available for P retention.

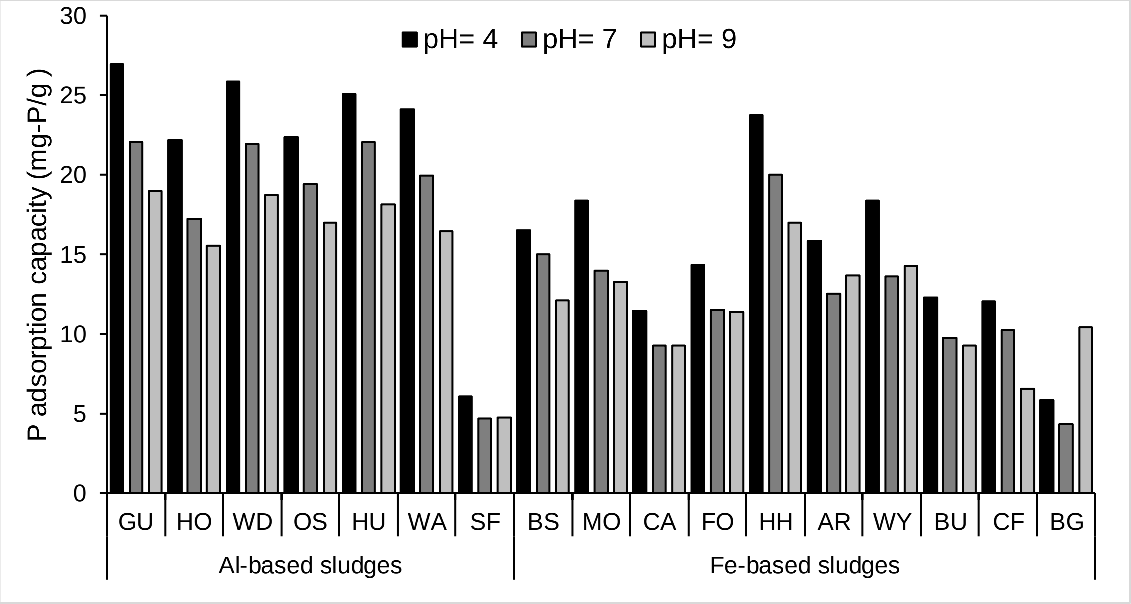

Figure 2 P adsorption capacities of Al- and Fe-based sludges calculated from fitting Langmuir model at three initial pH solution values.

3.3 P retention – Mechanisms

Table 2 presents results of the exchangeable ions test. Results show that the cations concentrations decreased as the initial solution pH increased. The pH at equilibrium was either increased or decreased relative to the initial pH. This could be explained by the fact that during the agitation, the hydroxyl groups on the surface of the sludge and also cations and anions (as Ca, Mg, Cl-, SO_4^{2-}, TOC) released into the solution influence the increase or decrease of the pH from its initial value. The P released from the sludges was low across the three initial pHs. This P originates from the raw water and becomes part of the structure of the dewatered sludges; and it is minimally released over time (Makris, 2004). The concentration of Ca released across the three initial pHs was generally higher than that observed for the other cations and ranged from 3.0 mg/l to 34.5 mg/l at initial pH 4. The amount of exchangeable Ca was proportional with Ca content of the sludges with the exception of GU and SF, both of which contain carbon as graphite (crystalline), resulting in low exchangeable ions. In addition, significant Fe concentrations were observed for BS, CA, HH and WY sludges with 1.38; 3.73; 2.36 and 1.54 mg/l of Fe respectively at initial pH 4. The pHs were acidic for most of the sludges except for AR, HU and CF which all had approximately neutral equilibrium pH. The neutral pH of the three sludges resulted from the combination of the initial pH and pH at equilibrium, combined with increased Ca concentration which might then encourage calcium phosphate precipitation (Del Bubba et al., 2003).

Table 2 Equilibrium pH and the released concentrations of aluminium, iron, calcium, magnesium and phosphorus after agitating one gram of each sludge in 100 ml of deionized water with three initial pH values for 48 h (n=2)

sludge	pH^{*} 4						pH^{*} 7						pH^{*} 9					
	pH^{**}	Al mg/l	Ca mg/l	Fe mg/l	Mg mg/l	P mg/l	PH^{**}	Al mg/l	Ca mg/l	Fe mg/l	Mg mg/l	P mg/l	PH^{**}	Al mg/l	Ca mg/l	Fe mg/l	Mg mg/l	P mg/l
GU	5.93	0.027	4.345	0.003	0.447	0.549	6.07	0.018	3.228	0.001	0.428	0.441	6.08	0.016	2.939	0.001	0.411	0.402
BS	5.15	0.024	13.17	1.381	1.251	0.413	5.23	0.038	11.95	1.31	1.179	0.407	5.25	0.028	11.3	1.167	1.127	0.381
MO	4.28	0.346	6.679	0.909	0.709	0.384	4.35	0.259	6.141	0.892	0.701	0.378	4.38	0.235	6.072	0.889	0.714	0.373
HO	5.36	0.121	11.94	0.146	0.928	0.391	5.49	0.095	11.21	0.095	0.875	0.375	5.47	0.075	10.11	0.064	0.888	0.357
CA	4.25	0.554	12.28	3.734	1.068	0.355	4.28	0.442	11.58	3.526	1.035	0.354	4.29	0.43	11.73	3.567	1.03	0.334
WD	5.76	0.045	7.778	0.0012	0.919	0.377	5.98	0.015	6.929	0.0011	0.92	0.353	6.11	0.017	7.299	0.001	0.911	0.352
FO	5.35	0.032	8.923	0.035	0.724	0.402	5.52	0.031	7.541	0.068	0.72	0.395	5.53	0.029	6.494	0.086	0.593	0.379
HH	4.93	0.319	4.596	2.363	0.594	0.382	5.05	0.222	3.138	2.161	0.425	0.376	5.06	0.291	3.707	2.619	0.488	0.366
AR	7.33	0.033	34.50	1.081	0.524	0.388	7.41	0.021	33.88	0.959	0.504	0.379	7.42	0.007	33.21	0.612	0.5	0.375
OS	5.37	0.072	3.955	0.009	0.704	0.38	5.74	0.028	2.709	0.008	0.601	0.371	5.75	0.027	2.822	0.0075	0.597	0.326
HU	7.08	0.011	12.06	0.001	0.944	0.4	7.10	0.01	11.43	0.001	0.981	0.398	7.15	0.01	10.9	0.001	0.981	0.392
WY	3.85	0.669	6.495	1.541	0.581	0.392	3.96	0.657	6.028	1.497	0.561	0.342	3.96	0.542	5.823	1.357	0.521	0.334
WA	4.75	1.58	5.257	0.006	0.489	0.346	4.81	0.932	5.049	0.005	0.497	0.344	4.81	0.916	4.736	0.003	0.463	0.299
BU	4.15	0.635	5.841	0.400	0.718	0.351	4.25	0.425	5.459	0.33	0.706	0.347	4.29	0.349	5.444	0.303	0.699	0.312
SF	4.87	0.051	2.964	0.003	0.938	0.621	5.89	0.042	2.404	0.002	0.227	0.548	5.99	0.04	2.213	0.001	0.215	0.401
CF	7.46	0.045	13.64	0.195	0.938	0.396	7.58	0.032	10.14	0.065	0.761	0.395	7.59	0.026	9.388	0.051	0.692	0.371
BG	6.50	0.04	3.431	0.098	0.423	0.378	6.64	0.032	2.361	0.094	0.332	0.378	6.66	0.029	2.325	0.047	0.327	0.356

* initial pH solution, ** pH at equilibrium time (after 48 hrs agitation)

Furthermore, precipitation test was conducted to determine the conditions of pH, Ca, Fe and P concentrations which might cause phosphate precipitation. To decide which equilibrium pH, and Ca and Fe concentrations across the three initial pHs should be used in the precipitation test; a one-way ANOVA analysis was performed to find out if there is any significant differences in these values across the initial pHs. The results showed that there was no significant differences in the variation of the pH at equilibrium and the Ca and Fe concentrations ($p > 0.05$). Thus, different samples with different pH values and Ca and Fe concentrations were used depending on the exchangeable ions test; while the P concentration values used were based on the change in P uptake over the range of initial P concentrations. Results obtained (not shown) indicate that no significant changes between initial and final concentration of both Ca and P to precipitate calcium phosphate minerals occurred at pH less than 7.3. Whereas at pH > 7.3, preliminary phosphate retention via precipitation mechanism was found at high initial P concentrations. Based on the molar ratio of Ca to P (0.5), it can be proposed that monocalcium phosphate was the precipitated metal. The formation of monocalcium phosphate metal is dependent on the availability of phosphoric acid (H_3PO_4), which is one of the orthophosphate species; in addition to calcium at alkaline condition. The amount of H_3PO_4 is minimal at neutral to alkaline pH solution, thus the calcium phosphate precipitation in this study can be considered to be minimal. The P precipitation retention mechanism as calcium phosphate minerals will spontaneously occur and is the dominant mechanism at pH > 8 (Khelifi et al., 2002; Søvik and Kløve, 2005). In this study, high equilibrium pH (> 7.3) was observed for AR and CF sludges, both of which also have the highest Ca content (table 1) and exchangeable Ca (table 2). In these conditions, P retention by calcium phosphate precipitation is minimal and P adsorption by Al and Fe oxides are the main possible mechanisms for the AR and CF sludges.

For samples that contained Fe ions, prior to reaction with the phosphate ions; the initial Fe precipitated as iron oxides when the dissolved Fe had reacted with sodium hydroxide ions which had been added for pH adjustment. Thus the final Fe concentrations were minimal and below the limit of detection. After adding the P stock solution, the iron precipitates have the ability to adsorb phosphate ions via surface complexation mechanism through the formation of inner sphere and/or outer sphere complexes with the iron precipitates.

The P retention mechanism was further investigated by analysing the FTIR spectra of the sludges before and after reaction with the phosphate ions (see figure 3). Results reveal that without phosphate adsorption, the FTIR spectra of the sludges had a strong hydroxyl stretching (e.g. 3200 cm^{-1} for BS and HU) and bending (1558 cm^{-1} for BS and HU) vibrations, which are due to physically adsorbed water molecules; while the band at 1413 and 1386 cm^{-1} could be assigned to stretching vibration of C-O and deformation vibration of C-H for carboxyl functional groups (Izquierdo et al., 2012). Additionally, deformation vibrations of multi-centred hydroxyl groups of iron and aluminium oxides (Fe-OH, Al-OH) of the sludges were observed at 1028 cm^{-1} bands for the Fe-based sludge and two bands of 1066 and 977 cm^{-1} for the Al-based sludges (Zhang et al., 2007). After reaction with phosphate ions, the FTIR spectrums of the sludges showed clear changes. The peaks of physically adsorbed water and stretching and deformation of carboxyl groups became broad and intensive which is attributed to replacement of H_2O, C-O and C-H during the phosphate adsorption. Moreover, the peaks of bending vibration of multi-centred hydroxyl groups for Fe-OH and Al-OH completely disappeared, while a new broad and intensive peak appeared at 1018 and 1004 cm-1 for Fe and Al oxides respectively. This peak could be attributed to the formation of inner sphere surface complexation between phosphate ions and oxides (Persson et al., 1996); and outer sphere surface by exchanging phosphate ions with hydroxyl group on the surface of dewatered sludge. The FTIR results indicate that the surface complexation of inner and outer sphere played a key role in the adsorption mechanism.

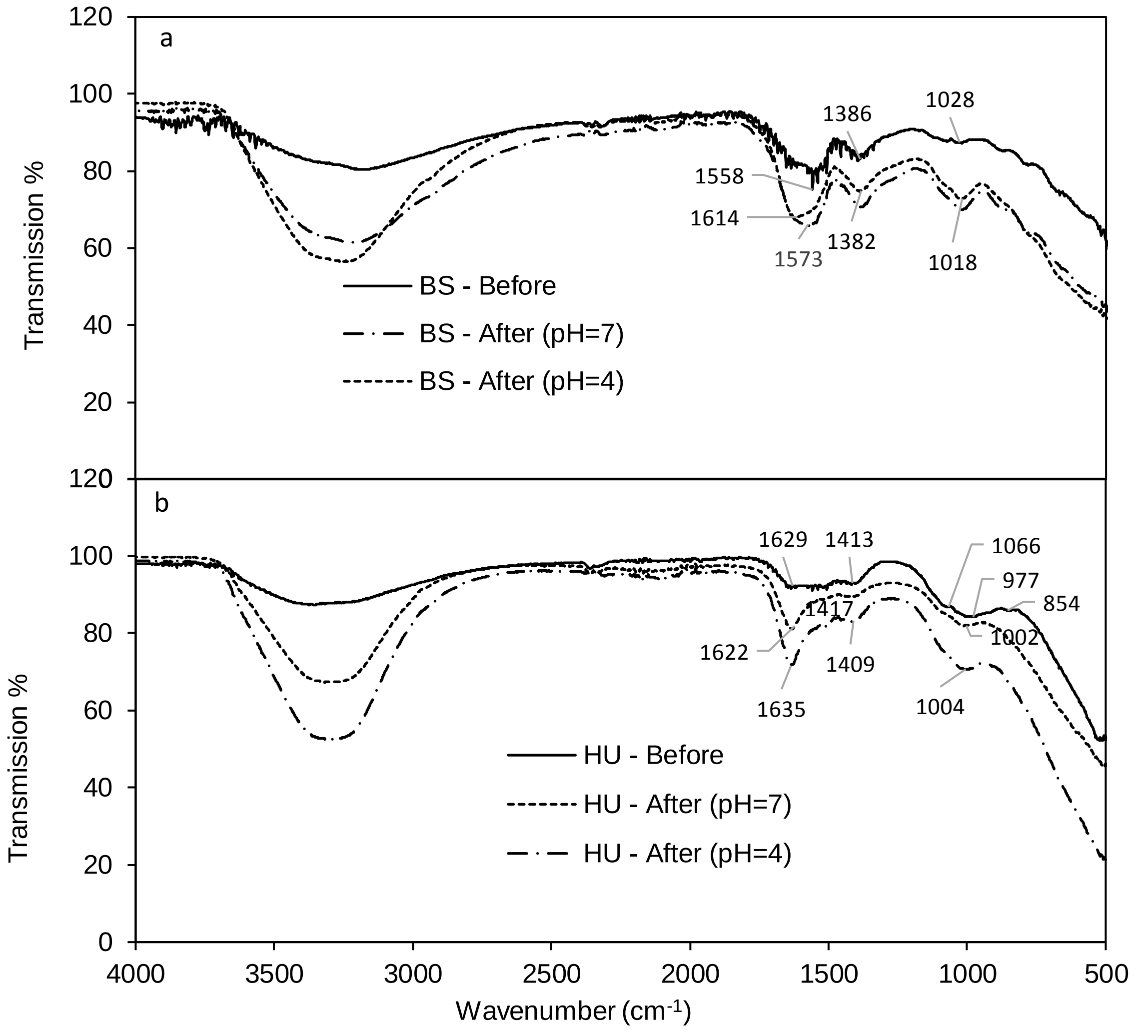

Figure 3 FTIR spectra of (a) Fe-based sludge and (b) Al-based sludge; before and after adsorption test with 10 mg/l initial P concentration at pH 4 and 7.

3.4 P retention –Linkage with inherent properties

The results of the principal component analysis are presented in Table 3. The properties which combine in the same principal component (PC) could be identified as; PC1- metal content and TSSA - related component (high loadings for Al, Fe, Al_{oxa}, Fe_{oxa} and TSSA, total variance = 42.75%); PC2- Ca content, exchangeable Ca (Ca_{ex}), TC, total organic carbon (TOC) related component (total variance = 34.56%); and PC3 - SO_4^{2-} content and sludge pH related component (total variance = 16.48%). Combined, the three PCs could explain 93.8% of the total variance in the physicochemical characteristics. The scores of the three PCs and initial pH of the incubation solution were then used as predictors in multiple regression analysis, where the outcome variable was the amount of P removed at different initial P concentrations.

The largest and most significant explanation in variability of P removal was found at initial P concentration of 80 mg/l. When PC1 was entered first, it accounted for 52.9% of variance in P-uptake ($p < 0.001$). When PC2 was entered next into the model, an additional 4.5% significant P removal was recorded ($p < 0.05$); and when PC3 and the initial pH of incubation solution were entered, a 2.9% and 4.4% explanation, respectively of significant variability in P-uptake ($p< 0.05$) was obtained. Thus the total significant variance in P-uptake in the linear regression model that could be explained by these characteristics of the sludges and initial pH solution was 64.6% ($p < 0.001$). In the case of 160 mg/l and 320mg/l initial P concentrations, the multiple linear regression analysis exhibited similar pattern, but the total explainable variance in P-uptake became less by excluding the effect of sulphate content and pH related component (PC3). By following the same procedure for the lower initial P concentration, the total explainable variance in P-uptakes by the three predictors (initial pH solution was excluded) increased with increasing initial P concentration except for the P-uptake at 5 mg/l initial P concentration. At 5 mg/l, PC3 and initial pH solution were not significantly linked to the P-uptake and the metal content related factor; and the Ca, Ca_{ex}, TC and TOC related factor combined together, explained 55.9% in the variance in P-uptake. The metal content related component (PC1) was the most significant predictor in explaining the variance in P-uptakes across the initial P concentration.

The same procedure above was used to determine the physicochemical characteristics of the sludges which had the most effect on the maximum P adsorption capacity as calculated by the Langmuir model. The scores of the three PCs and the initial solution pH were used as predictors in multiple linear regression analysis, where the calculated P adsorption capacity was used as the outcome variable. Combined together, PC1 and initial solution pH accounted for 44.8% significant variability of calculated P adsorption maxima, while PC2 and PC3 were not significantly correlated with the P adsorption maxima. As discussed previously, the best fit for adsorption data for all the sludges at the three pHs was given by Freundlich model. Therefore, to identify which of the physicochemical properties of the sludges had the most effect on the Freundlich bonding energy related parameter (K_f), the same procedure above was used. The significant variances in P-uptakes and adsorption parameters explained by the physicochemical properties of the sludges and initial pH solution are presented in the Table 3. The metal content and TSSA related component (PC1); Ca content, exchangeable Ca, TC and OC related component (PC2), and initial solution pH were significantly related to K_f Freundlich parameter. A total 78.4% of variability in K_f ($p < 0.001$) was explained by these predictors at significant levels < 0.001, < 0.01, and < 0.01 respectively.

Table 3 Principal component analysis of the physicochemical characteristics of the seventeen dewatered waterworks sludges; and linear regression analysis between the three principal components scores and initial pH solution as predictors, and amount of P-uptake at different initial P concentration, P adsorption capacity maxima and Freundlich P bonding energy related constant as outcomes variables.

Principal component	**PC1**	**PC2**	**PC3**
Eigenvalue	5.626	3.668	1.023
Proportion of variance (%)	42.745	34.563	16.477
Cumulative proportion of variance (%)	72.745	77.308	93.785
Rotated factor loading			
Variable	PC1	PC2	PC3
Al	**0.925**	-0.044	0.33
Fe	**-0.918**	0.255	-0.256
Al_{oxa}	**0.953**	-0.083	0.259
Fe_{oxa}	**-0.881**	0.168	-0.402
Ca	-0.596	**0.691**	0.337
Ca_{ex}	-0.154	**0.915**	-0.081
SO_4^{2}-	-0.419	0.271	**-0.801**
TC	0.019	**-0.969**	0.012
TOC	0.013	**-0.969**	0.009
TSA	**0.756**	0.563	0.027
pH	0.438	0.343	**0.805**

Independent variable	**PC1**	**PC2**	**PC3**	**pH**	**TV%**
	Percentage of explainable variance				
q_1^a	45.3^{***}	6.1^{*}	NOT Sig.	NOT Sig.	55.9^{***}
q_2^a	28.9^{***}	9.3^{**}	NOT Sig.	NOT Sig.	38.2^{***}
q_3^a	30.8^{***}	10.1^{**}	6.1^{*}	NOT Sig.	46.9^{***}
q_4^a	36.9^{***}	8.1^{**}	8.2^{**}	NOT Sig.	53.2^{***}
q_5^a	52.9^{***}	4.5^{*}	2.9^{*}	4.4^{*}	64.6^{***}
q_6^a	46.4^{***}	6.5^{**}	NOT Sig.	6.9^{*}	59.8^{***}
q_7^a	42.3^{***}	4^{*}	NOT Sig.	9.5^{**}	55.8^{***}
Q_o^b	34.4^{***}	NOT Sig.	NOT Sig.	10.4^{*}	44.8^{***}
K_f^c	66.4^{***}	6.2^{**}	NOT Sig.	5.8^{**}	78.4^{***}

* explainable variance is significant at the 0.05 level
** explainable variance is significant at the 0.01 level
*** explainable variance is significant at the 0.001 level

[a] P-uptakes ranged q1, q2, q3, q4, q5, q6, and q7 at initial P concentrations ranged 5, 10, 20, 40, 80, 160 and 320 mg/l; [b] calculated P adsorption maxima determined from fitting the linearized Langmuir model; [c]bonding energy related constant calculated from fitting the linearized Freundlich model; For the principal component table, variable with high component loading are shown in bold

4. Conclusion

This study aimed at contributing to practical reduction of eutrophication caused by excess phosphorus (P) loading to the environment. Specifically, it was focused on advancing our fundamental understanding of P reduction by novel industrial by-products, using dewatered drinking water treatment sludge as P adsorbent. Findings have shown that aluminium (Al) and iron (Fe) based dewatered waterworks sludges have considerable variability in their physicochemical properties; and the difference in their P retention behaviour can be explained by the amount of reactive Al and Fe available, the total specific surface area, and in some cases, the presence of crystalline phases of total carbon and other minerals. Al-based sludges tended to have higher total specific surface areas and thus, higher adsorption capacity. P retention was shown to be generally through surface complexation, ligand exchange and/or precipitation. In particular, FTIR results indicate that surface complexation of inner and outer sphere played a key role in the adsorption mechanism. In almost all cases, adsorption data was well described by the Freundlich model indicating the heterogeneity of P adsorption on the surface of the sludges. However, adsorption data for two of the sludges which were Al based were best fitted with the Langmuir model, with minimal leaching of Al, Calcium and sulphate ions observed. This implies that P adsorption by surface complexation is the only possible mechanism for the two sludges.

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References

Apak, R., 2013. Adsorption of heavy metal ions on soil surfaces and similar substances: theoretical aspects. ChemInform 44.

Babatunde, a O., Zhao, Y.Q., Burke, a M., Morris, M. a, Hanrahan, J.P., 2009. Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. Environ. Pollut. 157, 2830–6.

doi:10.1016/j.envpol.2009.04.016

British Standards Institution, 1990. Methods of test for soils for civil engineering purposes (BS 1377). Part 2 Classif. tests.

Cerato, A.B., Lutenegger, A.J., 2002. Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method. Geotech. Test. J. 25, 315–321. doi:10.1520/GTJ11087J

Dayton, E. a, Basta, N.T., 2005. A Method for Determining the Phosphorus Sorption Capacity and Amorphous Aluminum of Aluminum-Based Drinking Water Treatment Residuals. J. Environ. Qual. 34, 1112. doi:10.2134/jeq2004.0230

Del Bubba, M., Arias, C. a, Brix, H., 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. Water Res. 37, 3390–400. doi:10.1016/S0043-1354(03)00231-8

Elliott, H. a, O’Connor, G. a, Lu, P., Brinton, S., 2002. Influence of water treatment residuals on phosphorus solubility and leaching. J. Environ. Qual. 31, 1362–1369. doi:10.2134/jeq2002.1362

Goldberg, S., Johnston, C.T., 2001. Mechanisms of Arsenic Adsorption on Amorphous Oxides Evaluated Using Macroscopic Measurements, Vibrational Spectroscopy, and Surface Complexation Modeling. J. Colloid Interface Sci. 234, 204–216. doi:10.1006/jcis.2000.7295

Ippolito, J. a, Barbarick, K. a, Elliott, H. a, 2011. Drinking water treatment residuals: a review of recent uses. J. Environ. Qual. 40, 1–12. doi:10.2134/jeq2010.0242

Izquierdo, M., Marzal, P., Gabaldón, C., Silvetti, M., Castaldi, P., 2012. Study of the Interaction Mechanism in the Biosorption of Copper(II) Ions onto Posidonia oceanica and Peat. CLEAN - Soil, Air, Water 40, 428–437. doi:10.1002/clen.201100303

Johansson, L., Gustafsson, J.P., 2000. Phosphate removal using blast furnace slags and opoka-mechanisms. Water Res. 34, 259–265. doi:10.1016/S0043-1354(99)00135-9

Khelifi, O., Kozuki, Y., Murakami, H., Kurata, K., Nishioka, M., 2002. Nutrients adsorption from seawater by new porous carrier made from zeolitized fly ash and slag. Mar. Pollut. Bull. 45, 311–315. doi:10.1016/S0025-326X(02)00107-8

Makris, K.C., 2004. Long-Term Stability of Sorbed Phosphorus By Drinking-Water Treatment Residuals: Mechanisms and Implications 198p.

Makris, K.C., El-Shall, H., Harris, W.G., O’Connor, G. a., Obreza, T. a., 2004. Intraparticle phosphorus diffusion in a drinking water treatment residual at room temperature. J. Colloid Interface Sci. 277, 417–423. doi:10.1016/j.jcis.2004.05.001

Makris, K.C., Harris, W.G., O’Connor, G. a., Obreza, T. a., Elliott, H. a., 2005. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. Environ. Sci. Technol. 39, 4280–4289. doi:10.1021/es0480769

McKeague, J. a., Day, J.H., 1966. DITHIONITE- AND OXALATE-EXTRACTABLE Fe AND Al AS AIDS IN DIFFERENTIATING VARIOUS CLASSES OF SOILS. Can. J. Soil Sci. 46, 13–22. doi:10.4141/cjss66-003

Persson, P., Persson, P., Nilsson, N., Nilsson, N., Sjöberg, S., Sjöberg, S., 1996. Structure and Bonding of Orthophosphate Ions at the Iron Oxide-Aqueous Interface. J. Colloid Interface Sci. 177, 263–275. doi:10.1006/jcis.1996.0030

Søvik, a. K., Kløve, B., 2005. Phosphorus retention processes in shell sand filter systems treating municipal wastewater. Ecol. Eng. 25, 168–182. doi:10.1016/j.ecoleng.2005.04.007

Yang, Y., Zhao, Y., Babatunde, a, Wang, L., Ren, Y., Han, Y., 2006. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. Sep. Purif. Technol. 51, 193–200. doi:10.1016/j.seppur.2006.01.013

Zhang, G.-S., Qu, J.-H., Liu, H.-J., Liu, R.-P., Li, G.-T., 2007. Removal Mechanism of As(III) by a Novel Fe−Mn Binary Oxide Adsorbent: Oxidation and Sorption. Environ. Sci. Technol. 41, 4613–4619. doi:10.1021/es063010u