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### Reuse of Aluminum-based Water Treatment Sludge to Immobilize a Wide Range of Phosphorus Contamination: Equilibrium Study with Different Isotherm Models

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## Reuse of Aluminum-based Water Treatment Sludge to Immobilize a Wide Range of Phosphorus Contamination: Equilibrium Study with Different Isotherm Models

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**Abstract:** The adsorption equilibrium of a wide range of phosphorus species by an aluminum-based water treatment sludge (Al-WTS) was examined in this study. Four kinds of adsorption-isotherm models, namely Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich, were used to fit the adsorption equilibrium data. In order to optimize the adsorption-isotherm model, correlation coefficient ( $R^2$ ) and four error functions were employed to facilitate the evaluation of fitting accuracy. Experiments have demonstrated that the Al-WTS may be an excellent raw material to adsorb P in a polluted aqueous environment with adsorption ability in the order of  $\text{KH}_2\text{PO}_4$  (ortho-P) >  $\text{Na}(\text{PO}_3)_6$  (poly-P) >  $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P} \cdot \text{H}_2\text{O}$  (organic-P). More importantly, this study provides an entire comparison of the four isotherms in describing the P adsorption behavior. By considering both the standard least-square based  $R^2$  and the results of four error functions analysis, this study reveals that the Freundlich isotherm appears to be the best model to fit the experimental equilibrium data. Langmuir and Temkin isotherms are also good models in current experimental conditions while the Dubinin-Radushkevich isotherm poorly described the adsorption behavior. The error analysis in this study provides vital evidence to reflect its role in facilitating the optimization in the adsorption

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isotherm study. Obviously,  $R^2$  seems inadequate in optimizing multi-isotherm models due to its inherent bias resulting from the least-squares linearization.

**Keywords:** Adsorption, aluminum, disposal, drinking water treatment sludge, phosphorus removal, reuse, wastewater treatment

## INTRODUCTION

The generation of coagulant residual sludge may remain unavoidable with the current water treatment technologies. Aluminum based water treatment sludge (Al-WTS) is generated at those water treatment plants where aluminum sulphate is used as the primary coagulant together with organic polymer as co-coagulant. Such sludge contains removed color, turbidity, and humic substances from source water, plus added aluminum sulphate and residual polymers. Due to the differences in the quality of the raw water and the varied treatment chemicals and processes in practice, Al-WTS can significantly vary in their characteristics (1, 2).

At present, no EU legislation is specifically concerned with Al-WTS and it is yet to be classified as hazardous under any EU legislation including the EU directive, 91/271/EEC (3). However, the increasing amounts of Al-WTS produced daily are triggering considerable environmental and economic concerns as well as disposal issues. In Ireland alone, the current estimated annual production of 15,000 to 18,000 tonnes of the dried solids is predicted to be doubled by the end of the next decade. As in most European countries, Al-WTS is currently being treated as a landfill waste in Ireland and it has become mandatory for water companies to dispose of the sludge appropriately. However, the options for recovery/recycling of Al-WTS are generally not well-developed as economically viable options for application in Ireland (4). Thus, the search for cost-effective and eco-friendly disposal option(s) becomes an urgent priority.

On the other hand, the targets of phosphorus (P) control set by Phosphorus Regulation 1998 of the Irish Environmental Protection Agency (Water Quality Standards for Phosphorus, 1998 (SI 258 of 1998); [www.epa.ie](http://www.epa.ie)) remain a very considerable challenge for the vast majority of local authorities although the monitoring indicated that the majority of Ireland's rivers and lakes are not polluted. There is evidence to suggest that problems remain in a number of rivers as a result of municipal pollution and ineffective wastewater treatment, especially P removal facilities (5).

Interestingly, it is noted that, due to the feature of generation of Al-WTS, aluminum hydroxide components become the important composition of the sludge once it has been dewatered. This raises a possibility of reusing such kind of sludge as a valuable material for P control since aluminum ion in Al-WTS has shown a strong affinity for P and can enhance adsorption and chemical precipitation processes. Past studies particularly in recent years

have extensively demonstrated the P adsorption ability of Al-WTS (6–10). According to Ippolito et al. (11), a high phosphorus-binding capacity of approximate 12.5 g P/kg Al-WTS was reported while Dayton and Basta (12) claimed a capacity ranged from 10.4 to 37.0 g P/kg Al-WTS by examining 18 WTS in the U.S. Zhao et al. (13) studied the possibility to reuse dewatered Al-WTS cakes as the main substrate in a reed bed system for P-enriched wastewater treatment. In addition, Chu (14) investigated the dye removal from textile industrial effluent using Al-WTS. Basibuyuk and Kalat (15) reported the use of waterworks sludge for the treatment of vegetable oil refinery industry wastewater. In order to enhance particulate pollutant removal in primary sewage treatment, the feasibility of reuse Al-WTS was studied by Guan et al. (16). The concept lies in the utilization of a large portion of insoluble aluminum hydroxides in the sludge as a coagulant in chemical coagulation/flocculation. More recently, Makris et al. (17, 18) investigated the use of Al-WTS as sorbent for perchlorate and arsenic removals.

Although adsorption of P by Al-WTS had been well-documented, it is noted that P adsorption has been studied predominately in orthophosphate while information on the adsorption behavior of other different species of P are evidently lacking in literature. Furthermore, with regard to the description of P adsorption process by Al-WTS, there is limited information in the literature on the application of different isotherms although the Langmuir isotherm was widely used (1, 19, 20). In this study, three phosphate species (orthophosphate, polyphosphate, and organic phosphate) commonly found in municipal wastewater were studied for equilibrium adsorption using an Irish Al-WTS. The adsorption ability of these three phosphates was investigated. Four adsorption isotherms, i.e., the Langmuir, the Freundlich, the Temkin, and the Dubinin-Radushkevich isotherms, were employed to fit the experimental equilibrium data to describe how different species of phosphorus interact with the Al-WTS (sorbent). In order to optimize the most appropriate correlation for the equilibrium curve, adsorption isotherms were evaluated by error analysis with four error functions. The significance of this study lies in providing experimental evidence in Al-WTS to aid in P pollution control with optimal adsorption isotherm.

## MATERIALS AND METHODS

### Al-based WTS

An aluminum-based water treatment sludge was used as adsorbent in this study. Initially, the dewatered Al-WTS cakes were collected from the dewatering unit of the Ballymore-Eustace Water Treatment Plant located in Co. Kildare, South Dublin, Ireland. The plant uses aluminum sulphate as a coagulant to treat reservoir water via the traditional processes of flocculation, sedimentation, filtration, and disinfection, to produce about 230,000 m<sup>3</sup>/d of potable water for Dublin city. The raw water with a color of 105 Hazens flows

through a series of tunnels under gravity from the Poulaphuca reservoir, 1.5 km away from the plant. The dosage of aluminum sulphate ranges from 42 to 60 mg/l. Water treatment sludges from a sedimentation tank together with a back washing stream from a filtration tank were thickened and then conditioned with organic polymer and finally dewatered by a filter press to produce sludge cakes for landfill as final disposal. The major elemental components of the dewatered Al-WTS used in this study as determined by ICP-analysis were 46%  $\text{Al}_2\text{O}_3$ , 1.2%  $\text{Fe}_2\text{O}_3$ , 1.2%  $\text{CaO}$  and 10% humic acids classified as TOC (10). The collected solids Al-WTS cakes (with moisture content of 72–75%) were air-dried and then ground and sieved to various sizes to prepare the testing Al-WTS samples. Two kinds of samples of the sieved sludge with different sizes were used in this study, i.e., the sample with size range of 0.06–0.13 mm (regarded as fine Al-WTS) and 0.25–0.45 mm (regarded as coarse Al-WTS), respectively. The moisture content of the prepared sludge samples (air-dried) was 23.4–23.7%.

### Phosphorus Aqueous Solutions

The phosphorus aqueous solutions used for batch adsorption tests were prepared by dissolving carefully weighed phosphorus salts in distilled water. Three types of phosphate suspensions were prepared separately; orthophosphate (potassium dihydrogen phosphate: Riedel De Haen  $\text{KH}_2\text{PO}_4$ , AnalaR grade), polyphosphate (sodium hexametaphosphate: BDH  $(\text{NaPO}_3)_6$ , no grade) and organic phosphate (adenosine monophosphate: Fluka  $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P} \cdot \text{H}_2\text{O}$ , AnalaR grade). The concentrations of the prepared solutions, which tend to simulate the similar concentrations of phosphates in typical municipal wastewater (21), are as follows: orthophosphate at 14.6 mg- $\text{PO}_4^{3-}$ /l, polyphosphate at 10.8 mg- $\text{PO}_4^{3-}$ /l and organic phosphate at 3.4 mg- $\text{PO}_4^{3-}$ /l.

### Batch Adsorption Tests

Adsorption isotherms were studied by a series of batch adsorption tests. Different weight of prepared Al-WTS ranging between 0.1 g to 0.5 g and 100 ml of each P aqueous suspensions were poured into 100 ml plastic bottles and the pH values of the mixed suspensions were adjusted to 4.0, 5.5, 7.0, and 9.0 respectively by adding 0.1 M sulphuric acid and 0.01 M sodium hydroxide. The mixed samples were placed on a Stuart Orbital Shaker (SSL 1, Bibby Sterilin Ltd.) and agitated at 200 rpm for 24 hours for equilibrium to be achieved although different equilibration times of 17 hours (19), 24 hours (8, 11), 48 hours (10), 6 days (12), and up to 80 days (2) with initial P concentration ranged from 5.0 to 3,500 mg P/L were reported in similar studies. Preliminary experiments over the P concentrations used in this study indicated that the adsorption equilibrium was reached in 24 hours. There was

no further appreciable decrease of P concentrations in the bulk solution up to 4 days. Thus, the duration of the adsorption equilibrium isotherm experiments was chosen to be 24 hours. After 24 hours, the samples were removed from the shaker and filtered using a 0.45 Millipore membrane filters to separate the solids from the liquid for P residual monitoring.

### Phosphorus Species Analysis

The residual P concentration was determined with the molybdovanadate method 8114 (HACH) using a HACA DR-2400 spectrophotometer. Orthophosphate was determined by the colorimetric method after reaction with vanadomolybdate reagent. Polyphosphate was determined after its conversion to reactive phosphate by heating the sample at 105°C with sulphuric acid. The total phosphate was converted to reactive phosphate by heating at 105°C with sulphuric acid and potassium persulphate salts.

## ADSORPTION ISOTHERMS

### Langmuir Isotherm

Langmuir isotherm (22) is most widely used for the sorption of a pollutant from a liquid solution (20, 23, 24). The model assumes that the sorption takes place at specific homogenous sites within the adsorbent, i.e., once a sorbate molecule occupies a site, further adsorption at this site is impossible. The equation of Langmuir is represented as follows:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (1)$$

where  $q_e$  is the mass of P adsorbed on adsorbent at equilibrium (mg/g);  $C_e$  is the equilibrium concentration of P solution (mg/l);  $Q_0$  is the maximum adsorption capacity (mg/g);  $b$  is a Langmuir constant (l/mg) related to the energy of adsorption. Physically,  $b$  is a measure of the affinity of the adsorbate for the adsorbent. The linear form of Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{b Q_0} \quad (2)$$

Hence a plot of  $C_e/q_e$  versus  $C_e$  or  $1/q_e$  versus  $1/C_e$  gives a straight line from which the isotherm parameters can be determined.

### Freundlich Isotherm

Although the Freundlich isotherm (25) is an empirical equation to describe heterogeneous adsorption systems, it is the earliest known relationship

describing the adsorption equation (24). This isotherm is given as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

A linear form of the Freundlich expression is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $K_F$  is the Freundlich constant (l/g) related to the bonding energy; and  $1/n$  is the heterogeneity factor in which  $n$  is a measure of the deviation from linearity of the adsorption. The value of  $n$  indicates the degree of non-linearity between P solution concentration and adsorption as follows: if the value of  $n$  is equal to the unity, the adsorption is linear; if the value is below the unity, this implies that the adsorption process is chemical; and if the value is above unity, adsorption is a favorable physical process (26). The plot of  $\log q_e$  vs  $\log C_e$  was employed to generate the intercept value of  $K_F$  and the slope of  $1/n$ .

### Temkin Isotherm

The Temkin isotherm has been used in the following form (27, 28):

$$q_e = \frac{RT}{b_T} \ln(AC_e) \quad (5)$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b_T} \ln A + \frac{RT}{b_T} \ln C_e \quad (6)$$

where  $RT/b_T = B$ ;  $R$  is the gas constant (8.31 J/mol K) and  $T$  is the absolute temperature. The sorption data can be analyzed according to Eq. (6). Therefore a plot of  $q_e$  versus  $\ln C_e$  enables one to determine the constants  $A$  and  $b_T$ .

### Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich (29) isotherm assumes that there is a surface area where the adsorption energy is homogeneous. The Dubinin-Radushkevich equation has the following form:

$$q_e = q_m e^{-\beta \epsilon^2} \quad (7)$$

A linear form of Dubinin-Radushkevich isotherm is:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (8)$$

where  $q_m$  is the Dubinin-Radushkevich monolayer capacity (mg/g),  $\beta$  a constant related to sorption energy, and  $\varepsilon$  is the Polanyi potential which is related to the equilibrium concentration as follows

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

The constant  $\beta$  gives the mean free energy,  $E$ , of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship (27, 30):

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

### Error Analysis

For the purpose of quantitatively comparing the applicability of different adsorption isotherms in fitting to data, the following four error functions were employed for error analysis:

1. The sum of the squares of the errors (*SSE*) (26):

$$SSE = \sum_{i=1}^n (q_{e,cal} - q_{e,exp})_i^2 \quad (11)$$

2. The sum of the absolute errors (*SAE*) (26):

$$SAE = \sum_{i=1}^n |q_{e,cal} - q_{e,exp}|_i \quad (12)$$

3. The hybrid fractional error function (*HYBRID*) (26):

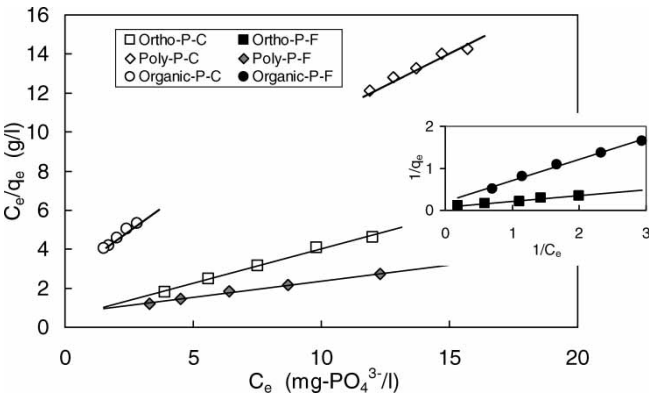
$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \quad (13)$$

4. Normalized percentage standard deviation (*NPSD*) (31):

$$NPSD(\%) = 100 \sqrt{\frac{1}{n-1} \sum_{i=1}^n \left( \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)_i^2} \quad (14)$$

where  $q_{e,exp}$  and  $q_{e,cal}$  are respectively the experimental values and calculated values by the adsorption isotherm;  $n$  and  $p$  refer to the number of data points and the number of isotherm parameter, respectively.

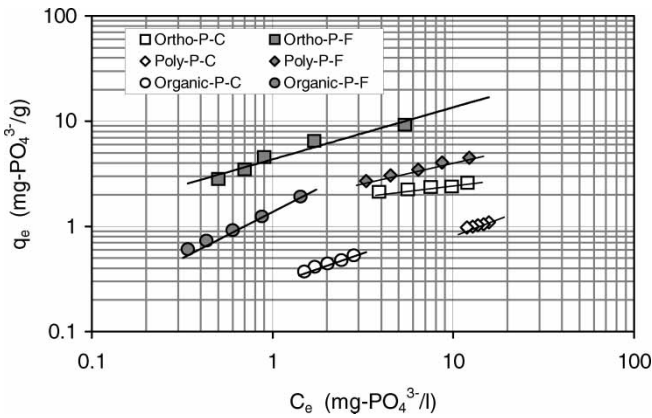




**Figure 1.** Langmuir isotherm (Eq. (2)) of three model P species sorbed on coarse and fine Al-WTS at pH 7.0.

**RESULTS**

The equilibrium adsorption data according to the linear plotting of Langmuir model (Eq. (2)), Freundlich model (Eq. (4)), Temkin model (Eq. (6)), and the Dubinin-Radushkevich model (Eq. (8)) are shown in Figs. 1 to 4, respectively. The fitting parameters and the magnitude of the correlation coefficient ( $R^2$ ) values as well as the error analysis results for both coarse and fine Al-WTS in adsorption of three P species used in this study are summarized in Table 1.



**Figure 2.** Freundlich isotherm (Eq. (4)) of three model P species sorbed on coarse and fine Al-WTS at pH 7.0.

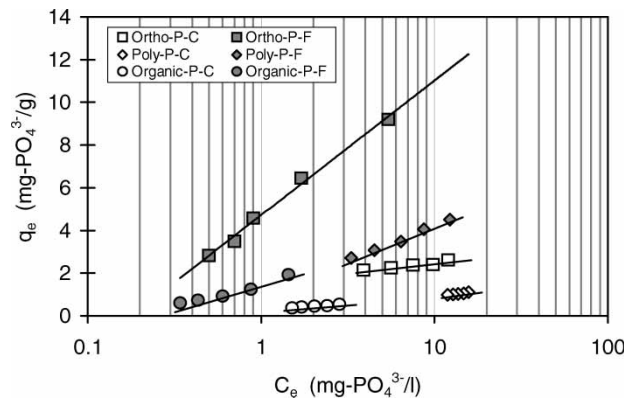


Figure 3. Temkin isotherm (Eq. (6)) of three model P species sorbed on coarse and fine Al-WTS at pH 7.0.

It is seen from Fig. 1 that the Langmuir equation fits the experimental data well for both the coarse and the fine Al-WTS. By inspecting Table 1, the  $R^2$  of Langmuir fitting shows the highest of all the different isotherms employed in this study. The values of  $Q_0$ , which represents the maximum adsorption capacity, were in decreasing order of ortho-P > poly-P > organic-P with higher values for fine Al-WTS. As  $b$  values reflect the affinity property of the adsorption process, it is known from Table 1 that ortho-P has maximum affinity while poly-P has minimum affinity for both coarse and fine Al-WTS tested.

As can be seen from Fig. 2 the Freundlich isotherm is also a good model along with the Langmuir isotherm for P adsorption process by Al-WTS. Among the three P species tested, the  $R^2$  values in Table 1 indicate that the

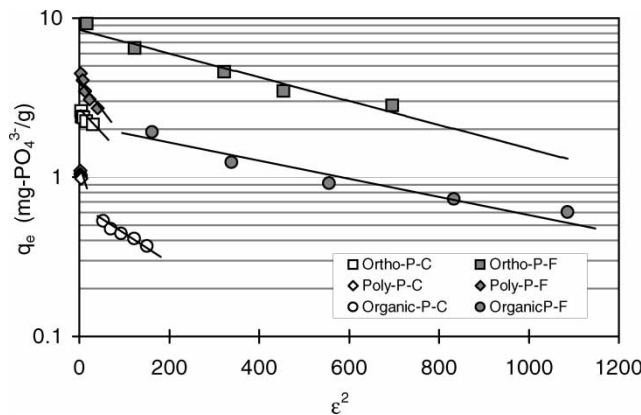


Figure 4. Dubinin-Radushkevich isotherm (Eq. (8)) of three model P species sorbed on coarse and fine Al-WTS at pH 7.0.

**Table 1.** Isotherm parameters with error analysis for P species adsorption on coarse and fine Al-WTS at pH 7.0

Parameter	Coarse Al-WTS (0.25–0.45 mm)			Fine Al-WTS (0.06–0.13 mm)		
	Ortho-P	Poly-P	Organic-P	Ortho-P	Poly-P	Organic-P
Langmuir isotherm						
Q <sub>0</sub>	2.845	1.744	0.975	12.195	6.050	4.699
b	0.692	0.106	0.413	0.605	0.230	0.426
R <sup>2</sup>	0.994	0.981	0.984	0.990	0.994	0.994
SSE	0.0145	0.0003	0.0002	0.1854	0.0268	0.0225
SAE	0.2311	0.0369	0.0256	0.8350	0.2711	0.2213
HYBRID	0.2043	0.0107	0.0135	1.1825	0.2766	0.4312
NPSD (%)	2.5535	0.8761	1.4925	4.2641	2.5587	4.4835
Freundlich isotherm						
K <sub>F</sub>	1.715	0.359	0.302	4.361	1.695	1.414
1/n	0.159	0.403	0.539	0.493	0.393	0.800
R <sup>2</sup>	0.944	0.969	0.983	0.950	0.996	0.998
SSE	0.0073	0.0003	0.0002	1.5661	0.0115	0.0027
SAE	0.1430	0.0320	0.0265	2.4820	0.2033	0.1011
HYBRID	0.0996	0.0087	0.0127	8.1365	0.0974	0.0664
NPSD (%)	1.7407	0.7857	1.4877	10.4723	1.3675	2.0450
Temkin isotherm						
B	0.374	0.418	0.240	2.736	1.388	0.923
A	75.105	1.156	3.145	5.619	2.054	5.161
R <sup>2</sup>	0.932	0.964	0.988	0.993	0.993	0.958
SSE	0.0081	0.0736	0.0002	0.1842	0.0158	0.0465
SAE	0.1520	0.6054	0.0255	0.8211	0.2227	0.4394
HYBRID	0.1102	2.3837	0.0133	1.2765	0.1527	1.4794
NPSD (%)	1.8341	13.1866	1.4673	4.6932	1.8372	11.1617
Dubinin-Radushkevich isotherm						
q <sub>m</sub>	2.541	1.267	0.6204	8.430	4.385	2.0146
β	0.0062	0.0706	0.0035	0.0017	0.0131	0.0012
R <sup>2</sup>	0.828	0.943	0.979	0.954	0.909	0.938
SSE	0.0221	0.0005	0.0004	1.4787	0.2096	0.0961
SAE	0.2940	0.0468	0.0395	2.3466	0.8945	0.5479
HYBRID	0.2969	0.0160	0.0274	7.4158	1.8634	2.1484
NPSD (%)	3.0042	1.0680	2.0578	10.1599	6.1983	11.2228

Freundlich isotherm is more suitable to describe the adsorption behavior of poly- and organic-P in case of fine Al-WTS adsorption although it gives a comparatively lower R<sup>2</sup> as compared with the Langmuir model in all the cases of P adsorption. The values of K<sub>F</sub> increase with the decrease of sludge particle size for all the P species tested while 1/n shows an irregular increase. It is noted that the 1/n values in Table 1 are all smaller than 1, indicating adsorption being favorable. Yang et al. (10) have claimed that the

dewatered alum sludge takes up P species on a heterogeneous surface by ligand-exchange process.

The constants  $A$  and  $B$  of Temkin equation are listed in Table 1 and the theoretical plot of this isotherm is shown in Fig. 3. The  $R^2$  is also listed in Table 1 and is more or less lower than the Langmuir and Freundlich values but higher than Dubinin-Radushkevich values. Therefore, the Temkin equation only represents a better fit of experimental data than the Dubinin-Radushkevich equation but is not better than either the Langmuir or Freundlich equations.

The results plotted in Fig. 4 tend to suggest that the Dubinin-Radushkevich equation also provide a reasonable description and analysis of experimental data. However, by comparison of  $R^2$  values with that from all other three isotherms, it is fair to say that, in all cases, the Dubinin-Radushkevich equation represents the poorest fit of experimental data compared to the other three isotherm equations. The values of adsorption capacity,  $q_m$ , in Dubinin-Radushkevich equation exhibit the same trend (see Table 1) as obtained from the Langmuir equation for both coarse and fine Al-WTS of P species adsorption, but with considerably decreased magnitude.

## DISCUSSION

Adsorption equilibrium data are important to determine the adsorption parameters using adsorption isotherms. These fundamental data should be useful in designing and predicting the adsorption process in practice. Generally, the most widely used approach to determine the isotherm parameters is by linear regression with  $R^2$  value nearer to unity being deemed to provide the best fit. This method appears to give an acceptable fit to the experimental data in this study. However, due to the inherent bias resulting from linearization,  $R^2$  is not the only criterion to evaluate the best fit. Studying cadmium sorption on tree fern, Ho (24) pointed out that the commonly used  $R^2$  is not appreciated to compare the best fit between Langmuir and Freundlich isotherms. Some error functions are often used to integrated evaluate the fit (23, 24, 26). In this study, four different error functions are used in all cases of adsorption. By comparing each error function in four adsorption isotherms' fitting for a phosphorus type, a rank of the four adsorption isotherms for the adsorption of P can be made in the order of the best (corresponding to the lowest value of error function) to the poorest (highest value of error function), which is in turn marked as 1st, 2nd, 3rd, and the 4th position in the rank among the four isotherms tested. By considering all the P species of the coarse and fine Al-WTS adsorption, 24 comparisons could be made in each error function, thus 96 comparisons were done in total for the four error functions. Accordingly, the individual isotherm in the rank can be accounted for. This leads to the plotting of each isotherm in the rank in numbers, as shown in Fig. 5. By carefully inspecting Fig. 5, it is clear that

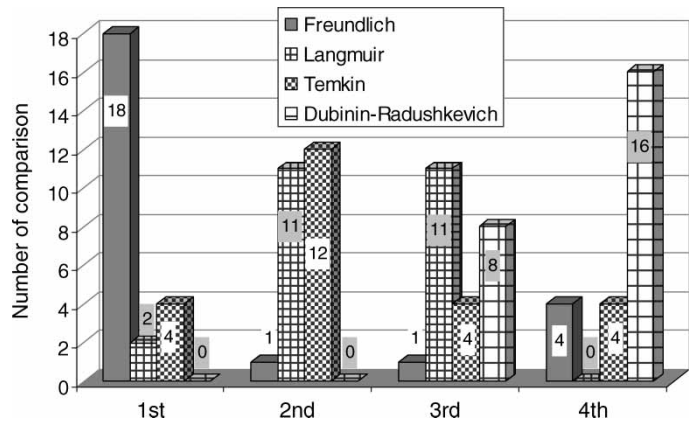


Figure 5. Comparison of isotherms in the data fitting from error analysis.

the Freundlich model appears to be the best fitting (18 in 1st place, 1 in 2nd place, 1 in 3rd place, and 4 in 4th place). It is followed by the Temkin model (4 in 1st place, 12 in 2nd place, 4 in 3rd place, and 4 in 4th place), the Langmuir model (2 in 1st place, 11 in 2nd place, 11 in 3rd place, and none in 4th place), and the Dubinin-Radushkevich model (none in 1st and 2nd place, 8 in 3rd place, and 16 in 4th place).

Similarly, a comparison of  $R^2$  was made and the position of each isotherm in the rank (among the 1st to 4th) was accounted. Six comparisons could be made in each error function and 24 comparisons were conducted in total for the four error functions. The results are illustrated in Fig. 6. It is seen that the order of best fitting is the Langmuir model (2 in 1st place, 4 in 2nd place, none in 3rd and 4th place) > the Freundlich model (2 in 1st place, 2 in 2nd

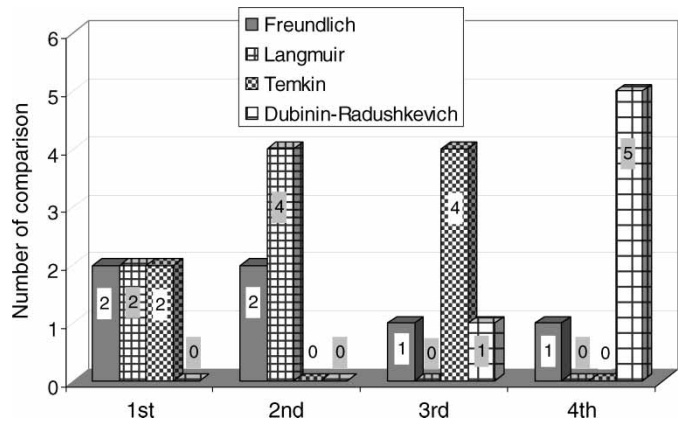
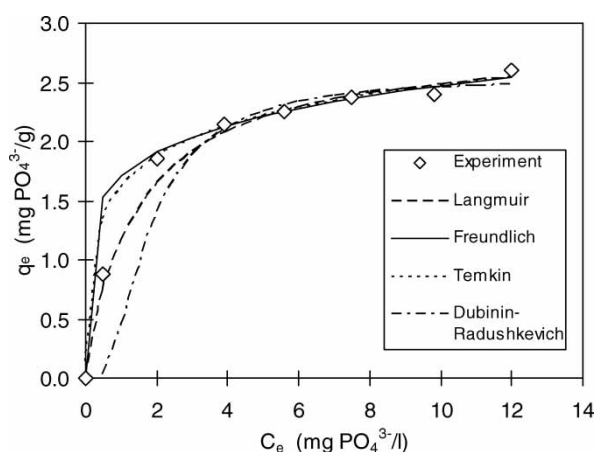


Figure 6. Comparison of isotherms in the data fitting from correlation coefficient ( $R^2$ ).



**Figure 7.** Plot of measured and calculated results of coarse Al-WTS adsorption of ortho-P at pH 7.0.

place, 1 in 3rd, and 1 in 4th place) > the Temkin model (2 in 1st place, none in 2nd place, 4 in 3rd and none in 4th place) > the Dubinin-Radushkevich model (none in 1st and 2nd place, 1 in 3rd place and 5 in 4th place).

By considering both the  $R^2$  and the error function analysis shown in Figs. 5 and 6, it becomes clear that the Freundlich model seems to provide the best description of the adsorption process for all the P species tested. However, it should be pointed out that the Freundlich model is not the best for the description of the adsorption process of fine Al-WTS adsorption of ortho-P, as can be seen from Table 1. The reason remains unclear. A typical plotting of measured and calculated results of coarse Al-WTS adsorption of ortho-P is illustrated in Fig. 7. It is noted from the literature that, for phosphorus adsorption by Al-WTS, Makris et al. (2) claimed that Langmuir-based P sorption capacity were not determined since isotherms exhibited Freundlich behavior, no obvious adsorption plateau being observed when equilibrium data were plotted. Studying P adsorption by sand, Rodgers et al. (32) reported that the Freundlich model often fits data better. However, the Langmuir model was reported as the more useful model to describe the adsorption processes of phosphorus adsorption by 13 kinds of sands when precipitation of phosphates did not occur (20). By combining the information from Figs. 5 and 6, it appears that the Dubinin-Radushkevich model would be inappropriate to describe the adsorption behavior in the current study. Overall, this study provides a comparison of the four commonly used adsorption isotherms models to best describe P adsorption onto Al-WTS. It should be noted that past studies have extensively demonstrated the effectiveness of Al-WTS for P immobilization (1, 7–11). Therefore, the input of this study lies in exploring the best isotherm which could be employed in designing and predicting the adsorption process in future and large-scale application.

**Table 2.** Maximum adsorption capacities ( $Q_0$ ) of three model P at varied pH conditions

Phosphate type	Chemical name and formula	pH	$Q_0$ (mg $\text{PO}_4^{3-}$ /g Al-WTS)	
			Coarse (0.25–0.45 mm)	Fine (0.06–0.13 mm)
Ortho-phosphate	Potassium dihydrogen phosphate $\text{KH}_2\text{PO}_4$	4.0	7.32	15.90
		5.5	4.58	14.62
		7.0	2.85	12.20
		9.0	3.23	12.23
Poly-phosphate	Sodium hexametaphosphate $\text{Na}(\text{PO}_3)_6$	4.0	3.23	8.99
		5.5	2.59	8.61
		7.0	1.74	6.05
		9.0	1.05	4.99
Organic Phosphate	Adenosine 5'-mono-phosphoric acid monhydrate $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P} \cdot \text{H}_2\text{O}$	4.0	1.88	6.23
		5.5	1.42	5.52
		7.0	0.98	4.70
		9.0	0.87	4.04

Note: Maximum adsorption capacities ( $Q_0$ ) were determined by Langmuir model.

It is also noted from the literature that a lot of studies have shown the P adsorption is affected by the pH of the P aqueous solution (8, 10, 33). The general trend is that the P adsorption is favor in the acidic environment, compared to the basic. This is confirmed in this study from equilibrium data computed by the Langmuir model. Table 2 shows the results of the maximum adsorption capacities ( $Q_0$ ) for the three P species adsorption at pH of 4.0, 5.5, 7.0 and 9.0, respectively. It is seen that the adsorption capacities varied for each phosphate type where orthophosphate has the highest adsorption capacities for all pH values tested while organic phosphate removal was the smallest. In addition, for each P type, higher adsorption capacities were obtained at lower pH ranges while the converse was also true. Overall the adsorption capacities are in the following order: orthophosphate > polyphosphate > organic phosphate.

CONCLUSIONS

This study focused on the adsorption equilibrium of a wide range of phosphorus species adsorbed by an aluminum-based water treatment sludge. Four kinds of adsorption-isotherm models were used to fit the adsorption equilibrium data. In order to optimize the adsorption-isotherm model, correlation coefficient ( $R^2$ ) and four error functions were adopted. The following conclusions can be drawn from the present study:

- Dewatered Al-WTS has exhibited an excellent P immobilization ability with wide range of P species simulated using typical concentrations found in municipal wastewater. Within the three kinds of P species tested, the highest P adsorption ability is obtained for orthophosphate (say,  $\text{KH}_2\text{PO}_4$ ), followed by polyphosphate (say  $(\text{NaPO}_3)_6$ ) and finally organic phosphate (say  $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P} \cdot \text{H}_2\text{O}$ ). Therefore, it is believed that such Al-WTS may be used as an adsorbent involving various P removal in environmental management. However, the adsorption abilities vary with the pH of the P suspension. The P adsorption process favors acidic suspensions rather than alkaline suspensions for all the three P species tested.
- Different adsorption isotherms, such as Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms can be used to describe the P adsorption behavior by Al-WTS. By means of the  $R^2$  and especially the error analysis using four different error functions, this study reveals that the Freundlich isotherm appears to be the best model to fit the experimental equilibrium data. Langmuir and Temkin isotherms are also good models in current experimental conditions while Dubinin-Radushkevich isotherm seems inappropriate to describe the adsorption behavior.
- It has been demonstrated in this study that error analysis is useful tool to facilitate the optimization in the adsorption isotherm study. Due to the inherent bias resulting from the least-squares linearization,  $R^2$  seems inadequate in optimizing analysis when multi-isotherms are applied to the experimental data.

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