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Reuse of Aluminium-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 aluminium-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 optimise 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 polluted aqueous environment with adsorption ability in the order of KH_2PO_4 (ortho-P) > $\text{Na}(\text{PO}_3)_6$ (poly-P) > $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P H}_2\text{O}$ (organic-P). More importantly, this study provides an entire comparison of the four isotherms in describing the P adsorption behaviour. 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 Dubinin-Radushkevich isotherm poorly described the adsorption behaviour. The error analysis in this study provides vital evidence to reflect its role in facilitating the optimisation in adsorption isotherm study. Obviously, R^2 seems inadequate in optimising multi-isotherm models due to its inherent bias resulting from the least-squares linearisation.

Keywords; Adsorption, aluminium, disposal, drinking water treatment sludge, phosphorus removal, reuse, wastewater treatment

1. INTRODUCTION

The generation of coagulant residual sludge may remain unavoidable with the current water treatment technologies. Aluminium based water treatment sludge (Al-WTS) is generated at those water treatment plants where aluminium sulphate is used as the primary coagulant together with organic polymer as co-coagulant. Such sludge contains removed colour, turbidity and humic substances from source water, plus added aluminium 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 Irish Environmental Protection Agency (Water Quality Standards for Phosphorus, 1998 (SI 258 of 1998); 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, aluminium hydroxides become the important composition of the sludge once it has been dewatered. This makes a possibility of reusing such kind of sludge as a valuable material for P control since aluminium ion in Al-WTS has shown a strong affinity 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 of 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 large portion of insoluble aluminium 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 behaviour 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 to study 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. 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.

2. MATERIALS AND METHODS

2.1 Al-based WTS

An aluminium-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 aluminium sulphate as coagulant to treat reservoir water via the traditional processes of flocculation, sedimentation, filtration and disinfection, to produce about 230,000 m³/d of potable water for Dublin city. The raw water with a colour 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 aluminium sulphate is ranged 42-60mg/l. Water treatment sludges from sedimentation tank together with back washing stream from filtration tank were thickened and then conditioned with organic polymer and finally dewatered by 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% Al₂O₃, 1.2% Fe₂O₃, 1.2% CaO and 10% humic acids classified as TOC (10). The collected chunk Al-WTS cakes (with moisture content of 72-75%) were air-dried and then ground and sieved of 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 0.06-0.13mm (regarded as fine Al-WTS) and 0.25-0.45mm (regarded as coarse Al-WTS), respectively. The moisture content of the prepared sludge samples (air-dried) was 23.4-23.7%.

2.2 Phosphorus Aqueous Solutions

The phosphorus aqueous solutions used for batch adsorption tests were prepared by dissolving carefully weighed out phosphorus salts in distilled water. Three types of phosphate suspensions were prepared separately; orthophosphate (potassium dihydrogen phosphate: Riedel De Haen KH_2PO_4 , AnalaR grade), polyphosphate (sodium hexametaphosphate: BDH $(\text{NaPO}_3)_6$, no grade) and organic phosphate (adenosine monophosphate: Fluka $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P H}_2\text{O}$, AnalaR grade). The concentrations of the prepared solutions, which tend to simulate the similar concentrations of phosphates in typical municipal wastewater (21), are as follow, orthophosphate at $14.6 \text{ mg-PO}_4^{3-}/\text{l}$, polyphosphate at $10.8 \text{ mg-PO}_4^{3-}/\text{l}$ and organic phosphate at $3.4 \text{ mg-PO}_4^{3-}/\text{l}$.

2.3 Batch Adsorption Tests

Adsorption isotherms were studied by a series of batch adsorption tests. Different weight of prepared Al-WTS ranging between 0.1g to 0.5 g and 100 ml of each P aqueous suspensions were poured into 100ml 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 0.1M sulphuric acid and 0.01M 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.

2.4 Phosphorus Species Analysis

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

3 ADSORPTION ISOTHERMS

3.1 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 to solve the isotherm parameters.

3.2 Freundlich Isotherm

Although 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 unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; and if the value is above to 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 $1/n$.

3.3 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 (8.31J/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 .

3.4 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:

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

A linear form of Dubinin-Radushkevich isotherm is:

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

where q_m is the Dubinin-Radushkevich monolayer capacity (mg/g), β a constant related to sorption energy, and ε 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 β 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):

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

3.5 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 adsorption isotherm; n and p refer to the number of data points and the number of isotherm parameter, respectively.

4 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 Fig. 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 summarised in Table 1.

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

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

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

[Fig. 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]

It is seen from Fig. 1 that 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.

Freundlich isotherm was illustrated in Fig. 2 and the regression parameters are also listed in Table 1. As can be seen from Fig. 2 Freundlich isotherm is also a good model along with 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 Freundlich isotherm is more suitable to describe the adsorption behaviour of poly- and organic-P in case of fine Al-WTS adsorption although it gives a comparatively lower R^2 as compared with the Langmuir model in all the cases of P adsorption. The values of K_F 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 small than 1, indicating adsorption being favourable. Yang et al., (10) has 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 not in the cases of both Langmuir and 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, Dubinin-Radushkevich equation represents the poorest fit of experimental data than 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 Langmuir equation for both coarse and fine Al-WTS of P species adsorption, but with considerably decreased magnitude.

5 DISCUSSION

Adsorption equilibrium data are important to determine the adsorption parameters using adsorption isotherms. These fundamental data should be useful in designing and predicting 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 linearisation, R^2 is not the unique criterion to evaluate the best fit. Studying cadmium sorption on tree fern, Ho (24) pointed out that the commonly used R^2 is not appreciate 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 to participate the evaluation of data fit of four isotherms and the results are presented in Table 1. 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 (return to 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 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 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).

[Fig. 5 Comparison of isotherms in the data fitting from error analysis]

[Fig. 6 Comparison of isotherms in the data fitting from correlation coefficient (R^2)]

By considering both the R^2 and the error function analysis shown in Fig. 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 behaviour, 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 Fig. 5 and 6, it appears that the Dubinin-Radushkevich model would be inappropriate to describe the adsorption behaviour 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 adsorption process in future and large scale application.

[Fig. 7 Plot of measured and calculated results of coarse Al-WTS adsorption of ortho-P at pH 7.0]

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 favour in the acidic environment, compared to the basic. This is confirmed in this study from equilibrium data computed by 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.

[Table 2 Maximum adsorption capacities (Q_0) of three model P at varied pH conditions]

6 CONCLUSIONS

This study focused on the adsorption equilibrium of a wide range of phosphorus species adsorbed by an aluminium-based water treatment sludge. Four kinds of adsorption-isotherm models were used to fit the adsorption equilibrium data. In order to optimise 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, KH_2PO_4), followed by polyphosphate (say $(\text{NaPO}_3)_6$) and finally organic phosphate (say $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P H}_2\text{O}$). 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. P adsorption process favours 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 behaviour by Al-WTS. However, each isotherm has its own accuracy to describe such adsorption process. 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 behaviour.
- It has been demonstrated in this study that error analysis is useful tool to facilitate the optimisation in adsorption isotherm study. Due to the inherent bias resulting from the least-squares linearisation, R^2 seems inadequate in optimising analysis when multi-isotherms are applied to the experimental data.

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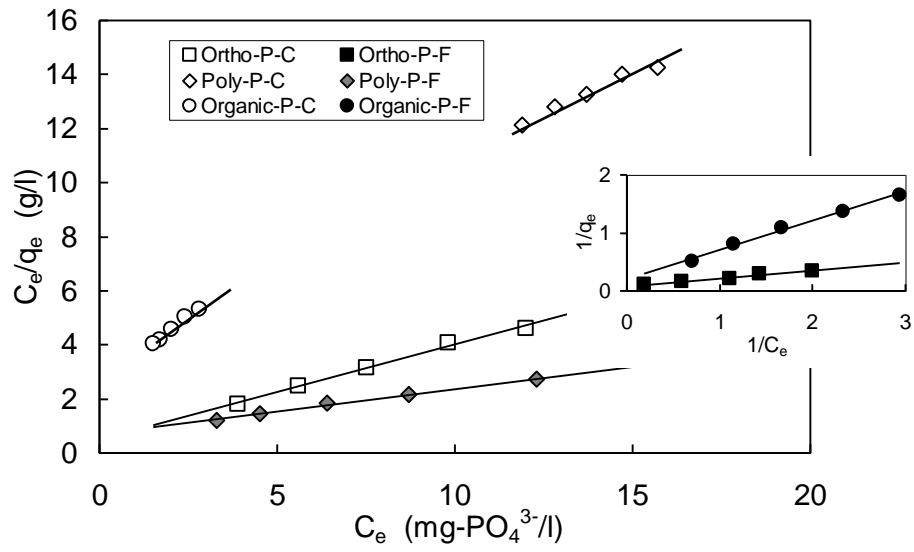


Fig. 1 Langmuir isotherm (Eq. (2)) of three model P species sorbed on coarse and fine Al-WTS at pH 7.0

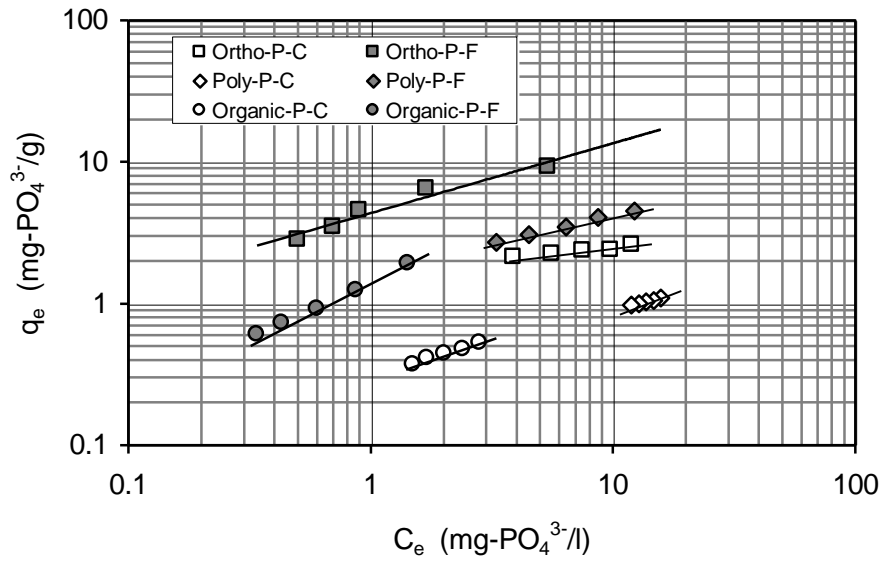


Fig. 2 Freundlich isotherm (Eq. (4)) of three model P species sorbed on coarse and fine Al-WTS at
pH 7.0

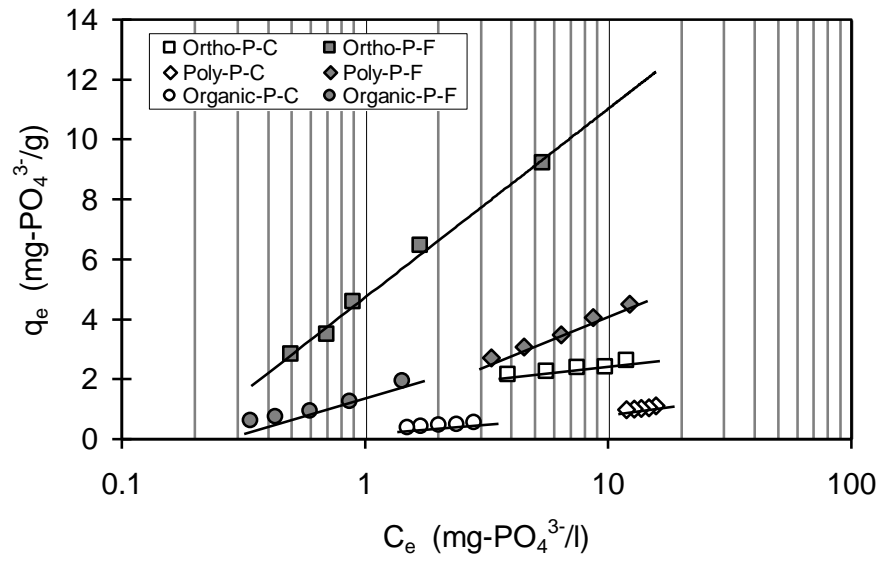


Fig. 3 Temkin isotherm (Eq. (6)) of three model P species sorbed on coarse and fine Al-WTS at pH

7.0

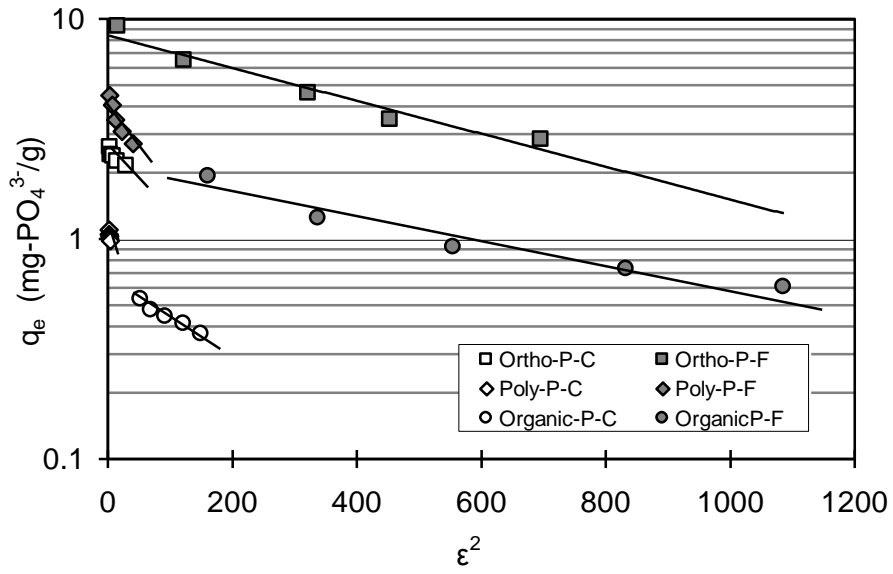


Fig. 4 Dubinin-Radushkevich isotherm (Eq. (8)) of three model P species sorbed on coarse and fine Al-WTS at pH 7.0

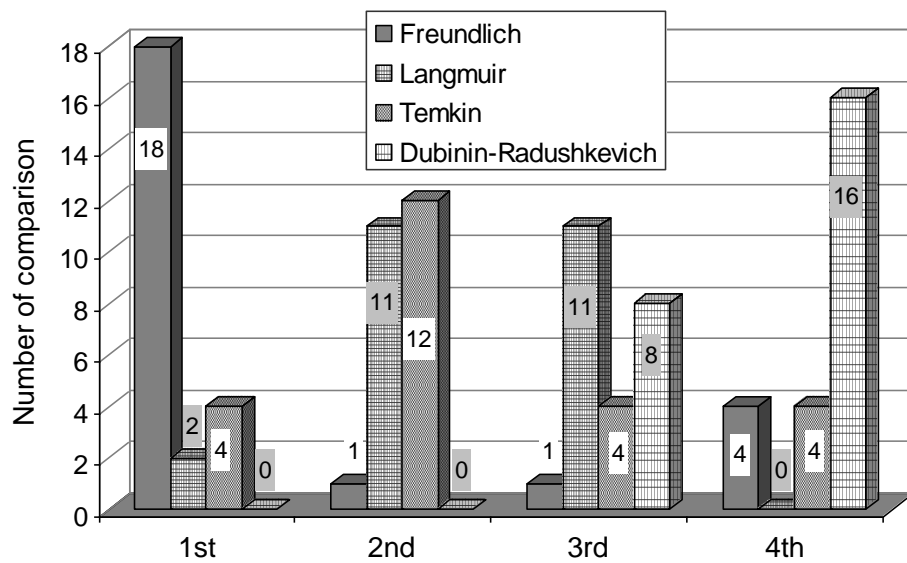


Fig. 5 Comparison of isotherms in the data fitting from error analysis

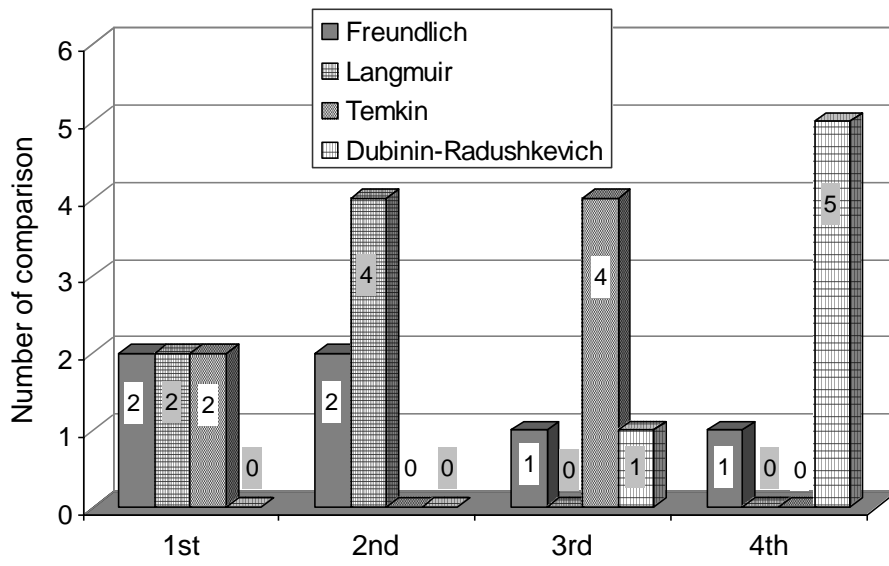


Fig. 6 Comparison of isotherms in the data fitting from correlation coefficient (R^2)

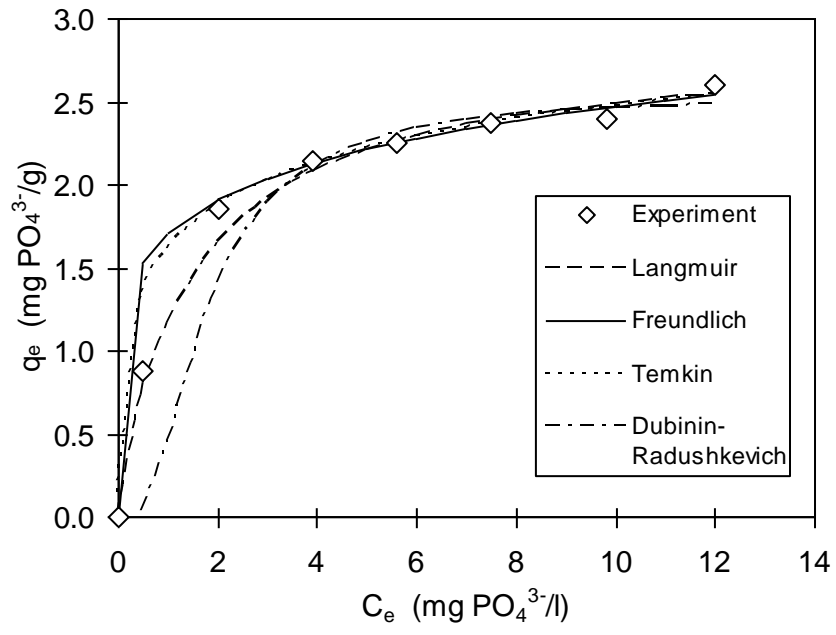


Fig. 7 Plot of measured and calculated results of coarse Al-WTS adsorption of ortho-P at pH 7.0

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 ₀	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 ²	0.994	0.981	0.984	0.990	0.994	0.994
SSE	0.01448	0.00034	0.00019	0.18536	0.02675	0.02248
SAE	0.23112	0.03687	0.02563	0.83495	0.27106	0.22130
HYBRID	0.20433	0.01074	0.01354	1.18248	0.27655	0.43121
NPSD (%)	2.55353	0.87606	1.49254	4.26406	2.55871	4.48350
Freundlich isotherm						
K _F	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 ²	0.944	0.969	0.983	0.950	0.996	0.998
SSE	0.00738	0.00028	0.00017	1.56610	0.01153	0.00270
SAE	0.14298	0.03197	0.02648	2.48204	0.20326	0.10109
HYBRID	0.09959	0.00870	0.01265	8.13649	0.09735	0.06635
NPSD (%)	1.74071	0.78569	1.48766	10.47226	1.36753	2.04499
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 ²	0.932	0.964	0.988	0.993	0.993	0.958
SSE	0.00814	0.07363	0.00019	0.18420	0.01575	0.04647
SAE	0.15196	0.60544	0.02545	0.82108	0.22267	0.43937
HYBRID	0.11021	2.38374	0.01325	1.27645	0.15265	1.47939
NPSD (%)	1.83411	13.18657	1.46732	4.69324	1.83720	11.16165
Dubinin-Radushkevich isotherm						
q _m	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 ²	0.828	0.943	0.979	0.954	0.909	0.938
SSE	0.02208	0.00051	0.00040	1.47865	0.20960	0.09610
SAE	0.29399	0.04679	0.03953	2.34656	0.89448	0.54792
HYBRID	0.29694	0.01604	0.02737	7.41575	1.86341	2.14843
NPSD (%)	3.00416	1.06796	2.05777	10.15985	6.19832	11.22284

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

Phosphate type	Chemical name & formula	pH	Q_0 (mg PO_4^{3-} /g Al-WTS)	
			Coarse (0.25-0.45mm)	Fine (0.06-0.13mm)
Ortho-phosphate	Potassium dihydrogen phosphate KH_2PO_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'-monophosphoric 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 Langumir model.

Figure legend

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

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

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

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

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

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

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