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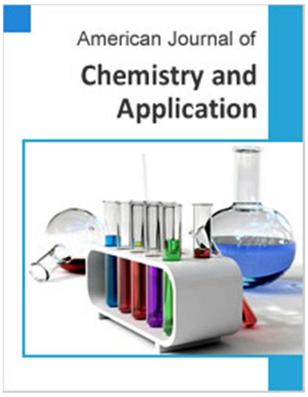

# Adsorptive Removal of Phosphorous from Wastewater Using Drinking Water Treatment-Alum Sludge (DWT-AS) as Low Cost Adsorbent

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## Abstract

Developing a low-cost effective phosphate absorbent is crucial for the control of water eutrophication. Drinking-water treatment alum sludge (DWT-AS) produced at water treatment plants is an unavoidable by-product. DWT-AS can be used for the effective removal and recovery of phosphate from wastewater. Adsorption of phosphate from wastewater by DWT-AS has been studied. The influence of various factors, such as initial pH, initial phosphate concentration, contact time and adsorbent dose on the removal efficiency was also studied in batch equilibration technique. Solution pH significantly influenced the sorption. Each sample achieved the maximal removal of phosphate at pH 5.0. Results showed that the removal percentages increased as the weight of sorbent increased. The study of the effect of contact time indicated that the removal percentages increase with increasing contact time. By increasing initial concentration of phosphate, the removal efficiency was decreased. The Freundlich and Langmuir models were used to simulate the sorption equilibrium. From the experimental data, the results indicate that both models are clearly best fitting isotherms with correlation coefficients greater than expected. The objective of this study is to demonstrate that DWT-AS can be employed as a highly effective natural adsorbent for phosphorus removal from wastewater and aqueous solutions.

## 1. Introduction

Phosphorus in the form of phosphate is essential for all living organisms as an essential component of RNA and DNA and its expected role in cellular metabolism. Each year, approximately 38.0 million tones of phosphorus are extracted from rock. The production of fertilizers relies on the extracted phosphorus to replace the phosphates that plants remove from the soil. However, scarce natural resources and current estimations suggest that reserves of phosphate rock may only continue for the next 45-100 years Phosphate in wastewater is a pollutant that supports increased growth of algae and other plants and reducing the oxygen available for aquatic vegetation and organisms. However, excessive levels of phosphate can cause eutrophication, which poses the single biggest threat to water quality. In spite of phosphate is not toxic and is very essential in processes related to water contamination but it became widely recognized as the source of fresh water eutrophication problems of fresh water bodies [1]. Therefore, efforts began to reduce phosphorus inputs to aquatic ecosystems by removing phosphate ion from water which could be an effective method for controling the eutrophication in sources of waters. Typical removal methods for high concentration phosphate ion consist of biological treatments such as chemical treatments, the conventional activated-sludge process, or combination of both treatments [2, 3]. However, in the case of a lower concentration of phosphate, phosphate removal is tricky and more sludge is produced [4-6]. For this reason, it is necessary to find ways to evaluate the capacities of some low-cost adsorbents to eliminate phosphate ion from water.

It is well known that phosphate ion has a relatively strong affinity for mineral surface [7]. Therefore, great attention has been paid in recent years to investigate different types of low-cost adsorbents such as alum sludge [8], red mud [9], goethite [10] and other waste materials [11].

Alum sludge consists mostly of aluminum hydroxide [12]. According to the literature survay, it was found that the soil science has revealed that $Al(OH)_3$ is capable of binding orthophosphate [13-15]. Aluminum hydroxide polymerization occurs through the transformation of non-structural hydroxyl groups into structural binding components [15]. These structural groups are strongly bound and as aging occurs. This means that more hydroxyl groups become fixed. Therefore, less adsorption of phosphorous takes place. Such a decrease in P adsorption with hydroxide age has been well documented in the literature [14, 15].

The overall goal of this study is to discuss and to evaluate the effectiveness of low-cost adsorbent materials for removing phosphate from wastewater.

## 2. Materials and Methods

### 2.1. Drinking Water Treatment Alum Sludge (DWT-AS)

The DWT-AS used as adsorbent in this study was obtained from the discharged sludge of Meet Khames station which discharged an amount of 1.7 million $m^3$/ year. The sludge washed several times with distilled water. Because it is important to make sure that there is no soluble salt which could be dissolved during the batch adsorption experiments and to remove the surface adhered particle. The (DWT-AS) was first dried, sieved and the particles smaller than 24 mesh were kept for further consideration in the trials without any further treatment. The major elemental components of oven-dried DWT-AS used in this study as determined by ICP analysis were 41.2% aluminum (as $Al_2O_3$), 1.1% iron (as $Fe_2O_3$), 1.2% calcium (as CaO), and 0.73% (as MgO).

### 2.2. Phosphate Solutions

All chemicals used in this study were analytical grade (A.R.) and were obtained from Fisher Scientific. Standard solution (1000 mg/l) of phosphate was prepared by dissolving required amount of potassium dihydrogen phosphate ($KH_2PO_4$) in double distilled water. Finally, the solutions were further diluted to the required concentrations before use.

### 2.3. Batch Adsorption Studies

Batch adsorption experiments were performed by shaking the predetermined amount of DW-AS adsorbent with 50 ml of phosphate solution. pH of the solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution as per required pH value. The contents in all adsorption experiments were shaken at 400 rpm using a Velp Scientifica magnetic stirrer in 120 ml capped flask and then filtered through Whattman 42 filter paper. In this study, the contact time was varied from 5 to 60 min, the pH of the solution from 2 to 11, the initial concentration from 10 to 250 mg/L and the adsorbent dosage from 5 to 40 mg/l.

### 2.4. Analytical Procedures

Using spectrophotometric technique, phosphate concentration as phosphorus was determined at 470 nm, following the vanadomolybdophosphoric acid method [16] with unico/4802 UV/Vis double beam spectrophotometer. The results are expressed in terms of removal efficiency (%) and adsorption capacity (mg/g) of DW-SA, according to the following relationships:

$$\textbf{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$\textbf{Adsorption capacity} \left(\frac{mg}{l}\right) = \frac{C_0 - C_e}{m} \times V \tag{2}$$

Where, $C_o$ and $C_e$ are the initial and final $PO_4$-P concentrations, respectively, m is the mass of adsorbent (g) and V is the volume of phosphate solution (L). In this study, each analysis point reported was an average of three independent parallel sample solutions. Triplicate tests showed that the standard deviation of the results ±3 %.

## 3. Result and Discussion

### 3.1. Effect of pH on the Adsorption Process

pH is considered as one of the most important parameters controlling the adsorption process at water adsorbent interfaces. Using a series of experiments by varying pH between 2 and 11, the effect of pH on phosphorus adsorption was examined. The amount of phosphorus adsorbed onto DWT-AS as function of the pH is illustrated in Fig.1. From the results, it is clear that the amount of phosphorus adsorbed slightly increases with increasing the pH value reaching the maximum removal at pH 5 and then decreases with increasing of pH values. The various decreases of the amount of phosphorus adsorbed may be due to the phosphorous structures or hydroxyl group as functional groups [17]. Phosphorous is mainly adsorbed by ligand exchange between phosphorous (P) and hydroxyl ($OH^-$). This study conducted by Yang et al. [18]. pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So, an increase in pH would lead to a rise in $OH^-$ ions. It may be occupy more active sites on the surfaces of DWT-AS and enhance the competitive strength with P. At the same time, the increasing amount of $OH^-$ ions would induce the formation of electrostatic repulsion and a new charged counter-ion layer, which would reject P adsorption. It is obvious that apart from these factors, at the point of zero charge ($pH_{PZC}$), the pH played a significant role in the adsorption processes [19], since the surface charge of DWT-AS would be positive at a pH less than the $pH_{PZC}$. Consequently, at lower pHs, phosphorous adsorption would be facilitated by electrostatic and chemical attraction onto the abundantly positive charged surface. However, as pH rose above the $pH_{PZC}$ and beyond 9 the surface charge became predominantly negative and phosphorous adsorption reduced. Therefore, we can conclude that the DWT-AS may work well in acidic solutions but not in basic conditions. These results were in agreement with previous results reported by other authors using slag and palygorskite ash adsorbent [20-22].

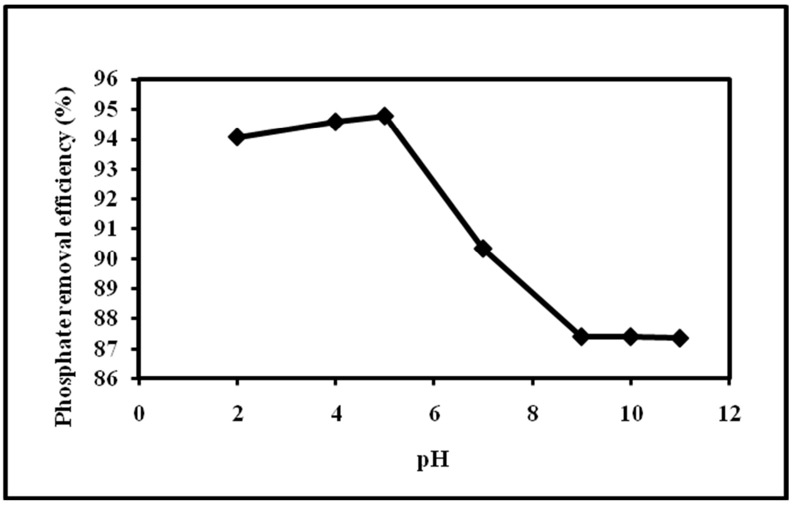

***Fig. 1.*** *Effect of pH on phosphate uptake by DWT-AS (initial phosphate concentration = 20 mg/l, adsorbent dose = 40 g/l and contact time = 30 min.).*

### 3.2. Effect of Temperature

The influence of changing the temperature on phosphorus adsorption was studied at temperature ranged from 25-75°C. As shown in Fig. 2, an increase in temperature is favorable for the phosphate removal by DWT-AS. This suggests that adsorption reaction is of endothermic nature and the ion-exchange mechanism is favored at higher temperature. This increase may be caused by the enlargement of pore size and or activation of the adsorbent surface [23]. Likewise, decreased adsorption capacity at lower temperature, may be caused by decrease in pore size. It is well known that increasing temperature accelerates the rate of diffusion of the adsorbent molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to decrease in viscosity of the solution [24].

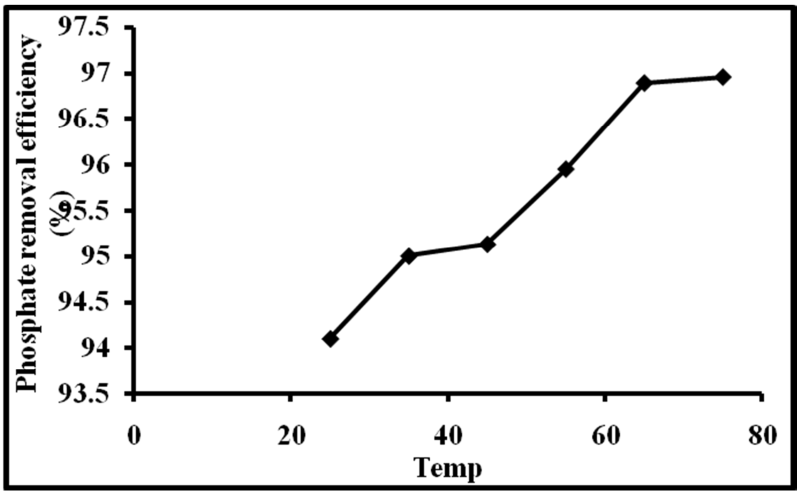

***Fig. 2.*** *Effect of temperature on phosphate uptake by DWT-AS (initial phosphate concentration = 20 mg/L, adsorbent dosage = 40/L, and contact time = 30 min.).*

## 3.3. Effect of Contact Time

The effect of time on the removal of phosphate was made on the basis of the phosphate removal depending on contact time. The influence of contact time on adsorption of phosphate ion on DWT-AS has been studied by varying it in the ranges of 5-60 min. as shown in Fig. 3. From the figure, it is clear that most phosphate is captured during the first 20 min. of adsorption. Also, as contact time increased the removal rate decreased considerably and was almost negligible at 30 min. It is noticed that at the beginning of the experiment, the high adsorption rates observed were caused by the rapid filling of the active sites (boundary layer diffusion). While, it's gradual decrease is connected with intra particle diffusion processes.

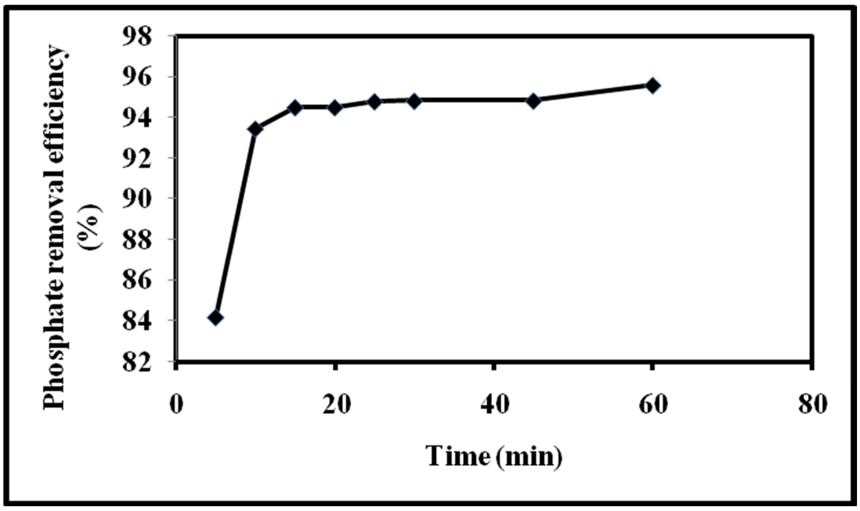

***Fig. 3.*** *Effect of time on phosphate uptake by DWT–AS (initial phosphate concentration = 20 mg/l adsorbent dosage 2 gm.*

## 3.4. Effect of Adsorbent Dose

The impact of DWT-AS dose on phosphorus removal from the prepared aqueous solutions was studied by varying the quantity of DWT-AS from 0.25 to 2.5 g/l under the optimum conditions of phosphate concentration, pH and contact time. The results obtained are presented in Fig. 4. It noticed that the removal efficiency of phosphorus ions by DWT-AS increased rapidly with the increase of the amount of the DWT-AS adsorbent. When the adsorbent content is 1.00 g/L, the percentage of adsorbed phosphate reaches 96.97 %. Also, the removal efficiency of phosphorus ions increases from 41.5 % to 96.97 % in the range of adsorbent doses 0.25 - 2 g/l, respectively. As expected, the amount of phosphate adsorption increases with the increase of adsorbent dosage, which indicates that the adsorption depends upon the availability of binding sites for phosphate. The results show that the percent removal increased with increasing absorbent dose due to the increase in the total available surface area and the active sites of the absorbent particles. Therefore, the adsorption occurs easily and fast [25].

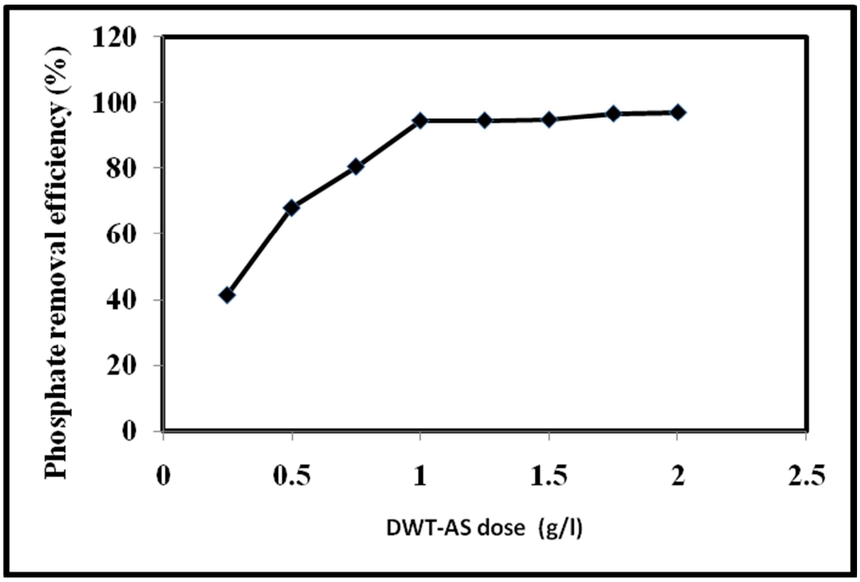

***Fig. 4.*** *Effect of adsorbent dosage on phosphate uptake by DWT-AS (phosphate concentration 20 mg/l, contact time 30 min.).*

### 3.5. Effect of Initial Phosphorus Concentration

To investigate the effect of the initial phosphorus concentration on phosphate adsorption, experiments were carried out with initial phosphate concentration. Figure 5 indicates that the phosphorus uptake increased with increasing initial phosphorus concentration. In fact, raising the initial phosphate concentration from 10 to 250 mg/l allows the DWT-AS to increase their adsorption capacities. It is clear that the number of ions adsorbed from a solution of higher concentrations is more than that removed from less concentrated solutions and at lower phosphate concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of phosphate became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. At a higher concentration of phosphate, the ratio of initial number of moles of phosphate to the adsorption sites available was higher, resulting in lower adsorption percentage. These results also suggested that the higher concentration is the initial aqueous phosphate concentrations. The higher is the concentration gradient between aqueous solution and the solid phase which result in more important diffusion rates. Eventually, in case of high initial aqueous concentrations, the contact probability between the DWT-AS adsorbent and phosphates species contained in the aqueous phase might be more privileged [25-29].

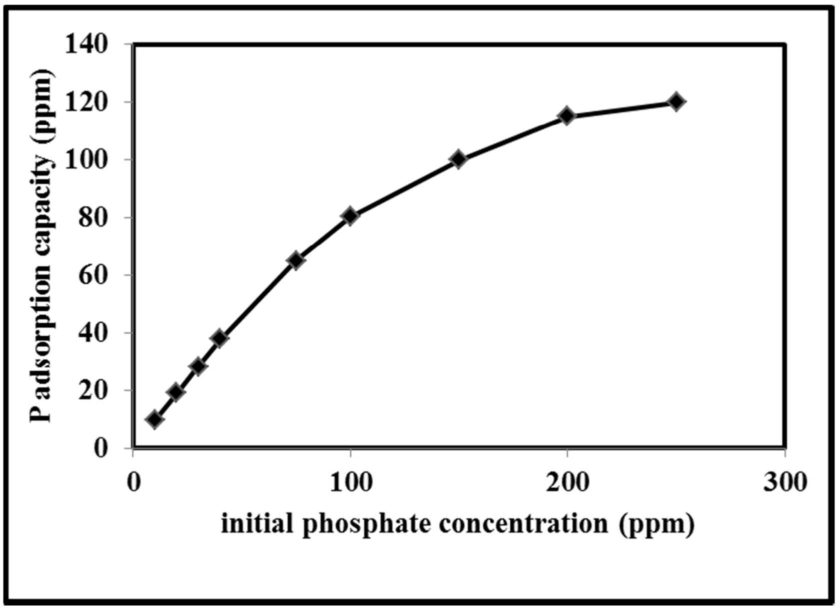

***Fig. 5.*** *Effect of initial phosphate concentration on phosphate uptake by DWT-AS (adsorbent dosage 40 g/l and contact time 30 min.).*

### 3.6. Adsorption Isotherm

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems and are used for the mathematical description since they indicate how phosphate ions are partitioned between the adsorbent and liquid phases at equilibrium. When an adsorbent comes into contact with phosphate ion solution, the concentration of phosphate ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached. The results obtained on the adsorption of phosphate were analyzed by Langmuir or Freundlich isotherms to discribe the experimental data. The correlation of equilibrium data using an equation is essential for practical adsorption operation. The Langmuir isotherm assumes a homogeneous surface and a constant sorption potential. The maximum monolayer adsorption capacity was calculated from Langmuir model. It is represented by the following equation:

$$1/q_e = 1/Q_o + (1/b\ Q_o)\ (1/C)$$

where $Q_o$ and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively, $q_e$ is the amount of solute adsorbed per unit weight of solid adsorbent equilibrium time (mg/g) and C is the concentration of solute remaining in solution at equilibrium (mg/l). The Freundlich sorption isotherm also gave an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherm was applied for the adsorption of phosphorous on DWT-AS. The linearized form can be represented as:

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C$$

Where $K_f$ is the adsorption capacity and n is the adsorption intensity.

Figs. 6, 7 show the adsorption isotherm curves for phosphorus adsorption onto DWT–AS. The obtained data was correlated with Langmuir and Freundlich models. All parameters with their correlation coefficients ($R^2$) are summarized in Table 1 with the values of linear regression coefficient. In the view of the values of linear regression coefficient, Langmuir model fits well to the sorption data in the studied concentration range.

As seen from the above figures and table, the correlation coefficient value $R^2$ was higher (0.993 – 0.928) for Langmuir and Freundlich, respectively. This indicates that the isotherms are clearly best fitting isotherm to the experimental data. The maximum adsorption capacity ($Q_m$) determined from the Langmuir isotherm was estimated to be 6.21 mg/g at pH 5. This relatively high adsorption capacity shows the strong electrostatic force of attraction between the phosphorus molecules and the adsorbent binding sites [30].

The calculated value of Freundlich exponent n = 2.062 is in the range of 1-10, which indicates a favorable adsorption of phosphorus onto DWT–AS.

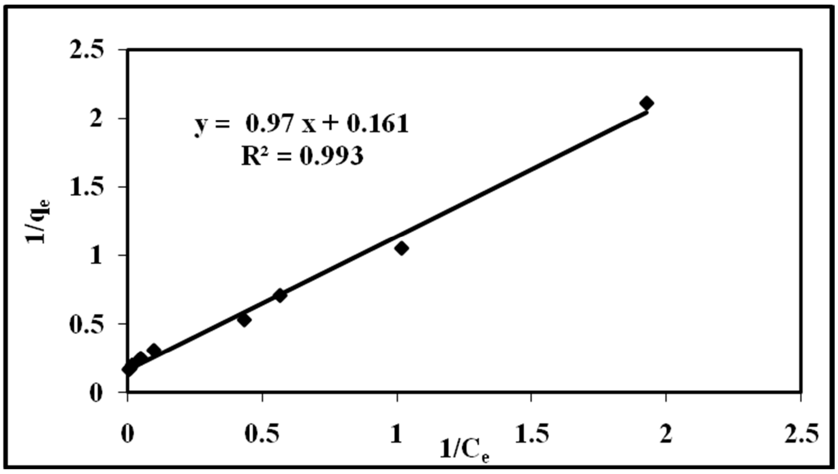

***Fig. 6.*** *Linear Langmuir isotherm of phosphate ion adsorption onto DWT-AS.*

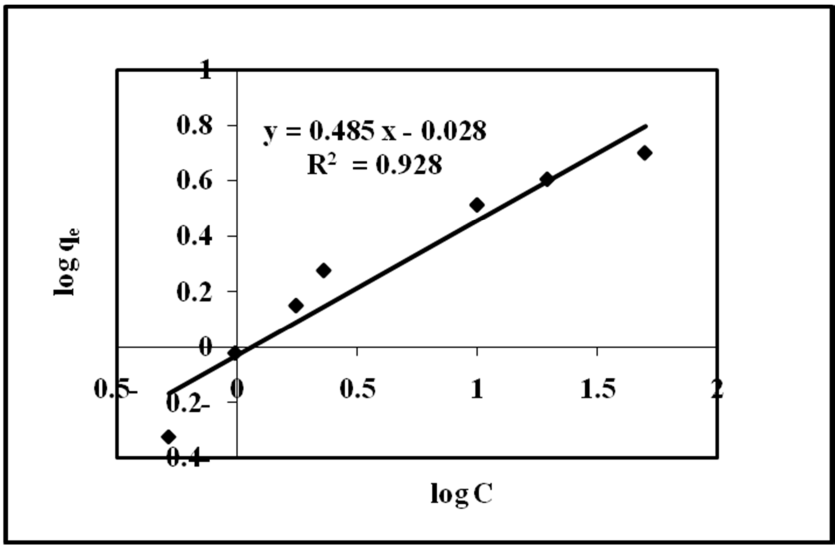

***Fig. 7.*** *Linear Freundlich isotherm of phosphate adsorption onto DWT-AS.*

***Table 1.*** *Isotherm parameters for the removal of phosphate by (DWT–AS).*

| Adsorbent | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $Q_o$ (mg $g^{-1}$) | b (l $mg^{-1}$) | $R^2$ | n | $K_F$ | $R^2$ |
| DWT-AS | 6.211 | 0.1649 | 0.993 | 2.06 | 1.06 | 0.928 |

## 4. Conclusions

This paper highlights the use of highly efficient low-cost DWT-AS absorbent as an available material for removal of phosphate. In batch studies, the optimum pH, effective dosage and reaction time were optimized. From the experimental data of adsorption of phosphate ions, the following points can be concluded, the adsorption capacity of phosphate was found dependent on initial pH, contact time, adsorbent amount. The analyses of the results were fitted very well to both Langmuir and Freundlich mathematical equations with correlation coefficients greater than expected. This work demonstrates that DWT-AS can be employed as a highly effective natural adsorbent for phosphorus removal from aqueous solutions. Therefore, the finding of this study quantifies the benefits of reusing such sludge to remove phosphorus from wastewater. Also, one of the benefits of the results might be in its application for agricultural purposes. On the other hand, the study also has an impact on drinking water treatment residual sludge from the treatment process in a cost-effective and sustainable way. Also this proves the potential of the DWT-AS as a filter material in various forms of phosphorous immobilization, thus converting it from a waste to a useful material in pollutant control and lead to less environmental problems.

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