

# **Batch Experiment and Adsorption Isotherm of Phosphate Removal by Using Drinking Water Treatment Sludge and Red Mud**

Asst. Prof. Dr. Alaa Hussein Al-Fatlawi , Mena Muwafaq Neamah

Department of Civil Engineering, Babylon University, Iraq

**ABSTRACT:** This study examine the efficiency of phosphate removal from the activated sludge effluent channel of Almuamirah wastewater treatment plant by using Drinking Water Treatment Sludge (DWTS), taken from the sedimentation tanks of Al-Tayara drinking water treatment plant, in Al-Hilla city, Iraq, and Red Mud (RM) sorbent. Series of laboratory batch and continuous tests, were conducted in order to assess the potential application of Drinking Water Treatment Sludge (DWTS) and Red Mud (RM) as filter to reduce the concentration of phosphate from contaminated effluent wastewater.

Batch experiment was carried out to study the adsorption isotherm of phosphorus at  $25 \pm 1^\circ\text{C}$  and solution of different pH and adsorbent dosages. The effects of (DWTS) dose, contact time (T), agitation speed (S), hydrogen ion concentration (pH), (DWTS –RM) ratio, were studied.

The phosphate removal efficiencies improved with increasing sorbent dosage from 5 g to 50 g for both (DWTS) and (RM), and they are remained approximately constant afterwards, and were significantly increased with an increase in contact time.

The sorption of phosphate on the (DWTS) was examined at different pH ranging from 4 to 8.4 with an initial concentration of 4 mg/L. It is seen that the maximum efficiency (95%) and (98%), are observed at pH=4, and dosages =50 g/L for (DWTS) and (RM) respectively. Results indicate that the effectiveness of (DWTS) in removing phosphate is highly dependent on initial pH. About 4% of phosphate was removed by (DWTS), and 15% by (RM) before shaking and the uptake increases with the increase in shaking rate. However, there was an increase in contaminants uptake when agitation speed was increased from zero to 250 rpm at which about 82% and 93 % of phosphate have been removed by (DWTS), and (RM) respectively.

To find the most appropriate model for the phosphate ions adsorption; data were fitted to Langmuir and Freundlich isotherm models. Results revealed that Langmuir adsorption isotherm was the best model for the phosphate ions adsorption onto (RM) with correlation coefficients ( $R^2$ ) of 0.977. The equilibrium parameter ( $R_L$ ) value in the present investigation was found to be 0.022– 0.806, indicating that the adsorption of the phosphate ion onto (DWTS) and (RM) are favorable.

## **I. INTRODUCTION**

Surface waters contain certain level of phosphorus in various compounds, which is an important constituent of living organisms. In natural conditions the phosphorus concentration in water is balanced i.e. accessible mass of this constituent is close to the requirements of the ecological system. When the input of phosphorus to waters is higher than it can be assimilated by a population of living organisms the problem of excess phosphorus content occurs. The excess content of phosphorus in receiving waters leads to extensive algae growth (eutrophication). The phenomenon of eutrophication usually decreases the water quality and as a result it may increase significantly the cost of water treatment (Plaza E., et al., 1997).

Phosphorus can be present in wastewater in the form of organic phosphate, orthophosphate or polyphosphate, (Caravelli, 2010). In municipal wastewater, phosphorus is present in dissolved and particulate forms, but most occurs as dissolved phosphate and consists of about 50% orthophosphate, 35% condensed phosphates and 15% organic phosphates, (Parsons and Smith, 2008). Human and kitchen wastes are the leading sources of phosphorus and account

# International Journal of Advanced Research in Science, Engineering and Technology

Vol. 2, Issue 3 , March 2015

for 30% to 50% of the phosphorus in domestic wastewater, (Cheremisinoff, 1994). Industrial wastes and agricultural runoff are other significant contributors of phosphorus in wastewater. As effluent discharge limits become more stringent, there is continued interest in removing phosphorus from wastewater. A typical municipal wastewater in the United States has a total phosphorus concentration of about 4 to 12 mg/L, (Metcalf and Eddy, 2003) and needs to be adequately treated before being discharged to receiving waters. Otherwise, the excess bioavailability of phosphorus can lead to eutrophication of water bodies and result in algal blooms.

The most common phosphorus removal treatment technologies are chemical precipitation (CP), enhanced biological phosphorus removal (EBPR), or a combination of the two, (Caravelli et al., 2010). Phosphate removal was initially achieved by chemical precipitation, which remains the leading technology today, (Morse et al., 1998). Chemical removal techniques, using metal salts (iron, alum and lime) are reliable and well-established processes, (Morse et al., 1998; Yeoman et al., 1988; Bashan et al., 2004). Chemical precipitation of phosphorus from wastewater is generally accomplished using metal salt coagulants, such as iron or aluminum, and can be performed at different stages within the treatment process. CP produces an insoluble metal phosphate that can be settled out and removed from water with sedimentation followed by sludge wasting or filtration.

## II. MATERIAL AND METHODS

### A. Adsorbate

Phosphate was selected as a representative of a contaminant because the discharge of phosphate loaded wastewater is one of the major sources of phosphorus in water bodies, causing environmental problems such as eutrophication and algae bloom.

Grab samples of final effluent from the activated sludge part of the secondary effluent channel of Almuamirah wastewater treatment plant in Al-Hilla city was collected. These samples were immediately transported to the laboratory for processing. The total amount of plant nutrients and other pollutants present in a sewage plant effluent is subjected to seasonal, daily, and hourly variation. Table 1 summarizes the composition and variability of the effluent under study. The wastewater sample was used as stock solution to provide the specific value of phosphate concentration. Where necessary, pH adjustment was made on each sample by addition of 0.1 M HNO<sub>3</sub> and NaOH solutions using a HACH-pH meter.

**Table 1: Physico-chemical analysis of secondary wastewater effluent sample, (Almuamirah wastewater treatment plant, 2014)**

parameters	Quantitative composition
E.C, $\mu\text{s/cm}$	3.5
T.D.S, mg/L	1288
Salinity, mg/L	2.18
Total hardness, as CaCO <sub>3</sub> , mg/L	1200
pH	7.9
Mg, mg/L	232.8
Ca, mg/L	160.3
So <sub>4</sub> , mg/L	769.4
Cl, mg/L	289.9
Po <sub>4</sub> , mg/L	2.7
No <sub>3</sub> , mg/L	0.46
T.S.S, mg/L	40
BOD <sub>5</sub> , mg/L	32
COD, mg/L	54
DO, mg/L	2.3
Fecal coliform, mpn/100 ml	120000
Total coliform, mpn/100 ml	128000

### B. Adsorbent

Two types of adsorbent were used in the present study for adsorption of phosphate from secondary effluents of wastewater treatment plant they are:

- I. Drinking Water Treatment Sludge (DWTS),
- II. Red Mud (RM).

#### a. Drinking Water Treatment Sludge(DWTS):

The (DWTS) used in this study was chosen as a promising treatment medium. (DWTS) has advantages over other media, due to its low cost as well as environmental benefits in terms of reuse of solid wastes. Furthermore, (DWTS) has been successfully implemented as a fixed-bed barrier for an on-site remediation system. This reactive material has been shown to be environmentally safe, possess stability and sufficient permeability.

The (DWTS) used in this study was taken from the sedimentation tanks of Al-Tayara drinking water treatment plant, in Al-Hilla city, Iraq. This sludge was dried at atmospheric temperature for 5 days, and then sieved on 2 mm mesh to achieve satisfactory uniformity. The sludge had a particle size distribution ranged from 150  $\mu\text{m}$  to 10 mm (Fig. 1) with an effective grain size,  $d_{10}$ , of 250  $\mu\text{m}$ , a median grain size,  $d_{50}$ , of 460  $\mu\text{m}$  and a uniformity coefficient,  $C_u = d_{60}/d_{10}$ , of 2.24.

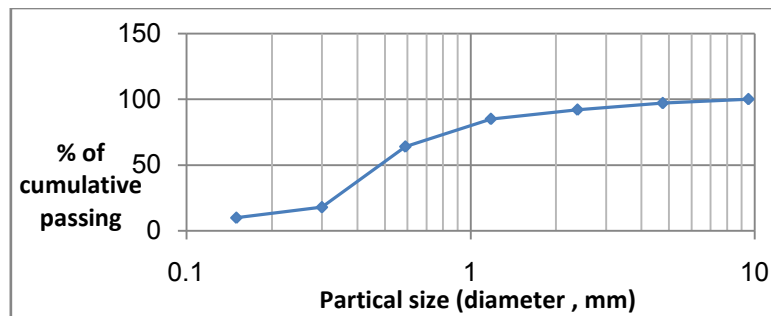


Fig. 1: Gradation curve for (DWTS) used in the present study.

The geometric mean diameter (1.19) is given by  $d_{gm} = (d_1 d_2)^{1/2}$  where  $d_1$  is the diameter of lower sieve on which the particles are retained and  $d_2$  is the diameter of the upper sieve through which the particles pass (**Alexander and Zayas, 1989**). Table 2 presents the physical and chemical characteristics of this (DWTS).

**Table 2: Physical and chemical characteristics of DWTS**

Element	Quantitative composition
T.O.C, mg/L	4.29
E.C, $\mu\text{s}/\text{cm}$	620
T.D.S, mg/L	312
Salinity, mg/L	0.2
pH	8.1
L.O.I, mg/L	15.76
$\text{Fe}_2\text{O}_3$ , mg/L	3.6
CaO, mg/L	15.32
$\text{SO}_3$ , mg/L	0.63
MgO, mg/L	3.66
$\text{Al}_2\text{O}_3$ , mg/L	11.56
$\text{R}_2\text{O}_3$ , mg/L	15.16
$\text{SiO}_2$ , mg/L	45

## b. Red Mud (RM):

The Red Mud (RM) used in this study was supplied by the Iraqi commercial markets. It is the industrial waste generated during the production of alumina. According to the grade of raw material bauxite and the production process of alumina. There are different aluminum production processes to different bauxites. Red mud is mainly composed of coarse sand and fine particle. The mesh size of red mud used in the study was of 1mm. This size was obtained by sieving analysis using the American Sieve Standards in the building of Materials Engineering laboratory at the University of Babylon. Its composition, property and phase vary with the type of the bauxite and the alumina production process, and also change over time. The chemical composition of the red mud is given in Table 3.

As a pre-treatment, (RM) was crushed and sieved to get granular (RM) with particle size of 1mm to be used in present experiments as shown in Fig. 3. The granular (RM) was firstly washed with distilled water and then dried in an electric oven at 120°C, overnight. This time was usually enough to remove any undesired moisture within the particles. It was then placed in desiccators for cooling.



Fig. 2: The raw red mud (RM) used in the present

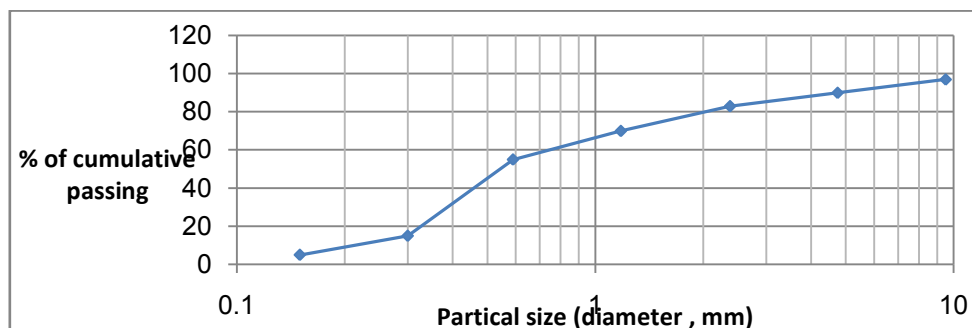


Fig. 3: Gradation curve for (RM) used in the present study.

**Table 3: The main chemical constituents of (RM), (Ping and Dong, 2012)**

Chemical constituent	Quantitative composition, %
Fe <sub>2</sub> O <sub>3</sub>	26.41
Al <sub>2</sub> O <sub>3</sub>	18.94
SiO <sub>2</sub>	8.52
CaO	21.84
Na <sub>2</sub> O	4.75
TiO <sub>2</sub>	7.40
K <sub>2</sub> O	0.068
Sc <sub>2</sub> O <sub>3</sub>	0.76
V <sub>2</sub> O <sub>5</sub>	0.34
Nb <sub>2</sub> O <sub>5</sub>	0.008
TREO	0.012
Loss	9.71

# International Journal of Advanced Research in Science, Engineering and Technology

Vol. 2, Issue 3, March 2015

## III. EXPERIMENTAL PROCEDURES

### A. Batch Experiments and Adsorption Isotherms

Sorption studies were conducted by the batch technique and column test using wastewater from the secondary effluent of Almuamirah wastewater treatment plant in Al-Hilla city, Iraq. Batch experiments were carried out to determine the adsorption isotherms of phosphate ions onto the adsorbents in 500mL glass flask. The study was performed at room temperature ( $25 \pm 1^\circ\text{C}$ ) to be representative of environmentally relevant condition. All experiments were carried out in duplicate and the average value was used for further calculation. The pH of the solution was measured with a HACH-pH meter. The flasks were plugged and kept closed to avoid the fluctuation of pH due to the exchange of gases during the experiment. The effects of various parameters on the rate of adsorption process were observed by varying adsorbent dose, contact time, adsorbate concentration, (DWTS – RM) ratios, agitation speed, and pH of the solution.

Batch studies are used to obtain the majority of single equilibrium data and to specify the best conditions for treatment process. This means that these tests are suited to identify the activity of the reactive material and the sorption isotherm.

The measurements were carried out using HPLC. However, the adsorbed concentration of contaminant on the reactive material was obtained by a mass balance.

Kinetic studies were investigated with different values of pH (4, 6 and 8.4), different values of initial concentration of contaminant (2.7 and 4 mg/L), different amounts (DWTS and RM) dosages (5, 10, 15, 30, and 50 g/L) and finally different values of shaking speed (0, 50, 100, 150, 200 and 250 rpm).

The adsorption of phosphate onto (DWTS) and (RM) was studied by batch technique. Series of 500 mL flasks are employed and each flask is filled with 100 mL of wastewater which have an initial concentration of phosphate of 2.7 and 4 mg/L. A known weight of adsorbent (5, 10, 15, 30, and 50 g/L) was equilibrated with 100 mL of wastewater into different flasks. The solution in the each flask was kept stirred in the different speed orbital shaker at (0, 50, 100, 150, 200, and 250 rpm) at a room temperature of  $25 \pm 1^\circ\text{C}$ , for a known period of time. The flasks were shaken at a constant rate, allowing sufficient time for adsorption equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with phosphate ions over the course of the experiments. A fixed volume (20 mL) of the solution was withdrawn from each flask at different periods. The withdrawn solution was filtered, using Whatman No. 1 filter paper. Blank experiments were conducted to ensure that no adsorption was taking place on the walls of the glass beakers used. The concentration of phosphate remaining in solution was measured by spectrophotometer using molybdate blue method. All experiments were conducted in triplicate and mean values were used. A fixed volume (10 mL) of the clear solution was pipetted out for determination the concentration of contaminant still present in solution. The solution volume ( $V$ ) was kept constant. The amount of phosphate adsorbed per unit mass is calculated as:

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

Where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $C_o$  and  $C_e$  are the initial and equilibrium concentration (mg/L),  $V$  is the volume of aqueous solution (L) and,  $m$  is the dry weight of the adsorbent (g).

Percent phosphate ion removal was calculated using the equation:

$$\text{removal (\%)} = [C_o - C_e] \times 100 / C_o \quad \dots\dots\dots (2)$$

In order to estimate equilibrium isotherms of the (RM), the same experiment mentioned above was repeated.

## IV. RESULTS AND DISCUSSIONS

### A. Sorption Studies

#### a. Effect of Mass of (DWTS) and (RM) on the Adsorption Process

To investigate the effect of adsorbent dose on the phosphate adsorption onto various adsorbent surfaces, experiments were carried out with initial phosphate concentration of 4 mg/L, pH=4, 6, and 8.4, agitation speed=250 rpm and varying the amount of (DWTS) and (RM) from 5 to 50 g added to 100 mL of contaminated solution for batch tests at  $25^\circ\text{C}$ .

Figs. 4 to 9, show the effect of adsorbent dosage on the sorption capacity of various contact time and different pH solution. These Figs. presents the phosphate removal efficiencies as a function of different amounts of (DWTS). It is clear that these efficiencies improved with increasing sorbent dosage from 5 g to 50 g and they are remained approximately constant afterwards. This was expected due to the fact that the higher dose of sorbents in the solution, the greater availability of sorption sites. This means that the more (DWTS) particles are able to provide more surface-active sites for collision with phosphate molecules to accelerate the removal efficiencies (Rahmani et al., 2010). This also suggests that after a certain dose of sorbent, the maximum sorption sets in and hence the amount of phosphate bound to the sorbent and the amount of these sorbate in solution remains constant even with further addition of the dose of sorbent.

different pH values. These Figs. demonstrate that removal percentage of this contaminant significantly increased with an increase in contact time. It is clear that the sorption rate was rapid at the initial stage and gradually slowed down afterwards. The slower sorption was likely due to the decrease in sorption sites on the surface of the (DWTS) and (RM).

## b. Effect of Contact Time on Adsorption

For batch experiments, the contact time should be fixed at value ensure reaching equilibrium concentrations. Figs. 10 to 15 show the effect of contact time on phosphate removal using 5, 10, 15, 30, and 50 g of (DWTS) and (RM) added to 100 mL of contaminated solution for batch tests at  $25 \pm 1^\circ\text{C}$  and different pH values.

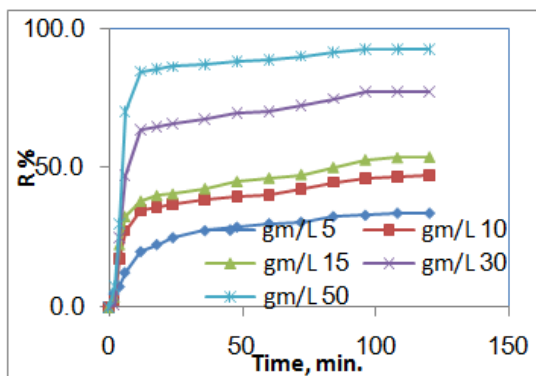


Fig. 4: Removal efficiency of phosphate on (DWTS) as a function of contact time, (pH=4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).

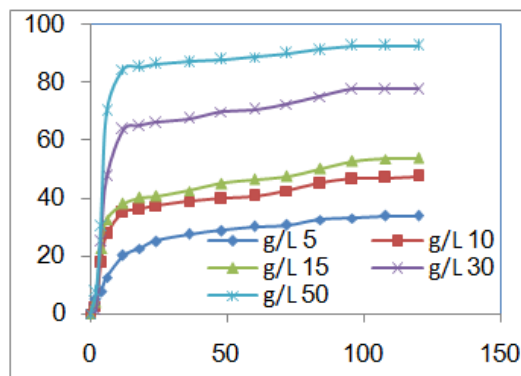


Fig. 5: Removal efficiency of phosphate on (RM) as a function of contact time, (pH=4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).

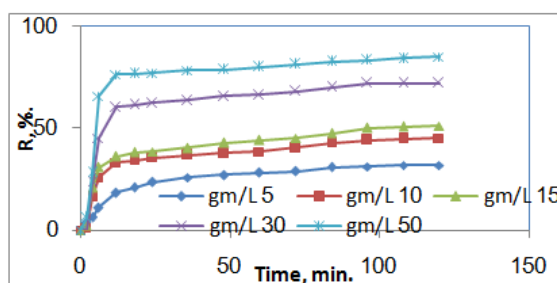


Fig. 6: Removal efficiency of phosphate on (DWTS) as a function of contact time, (pH=6,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).

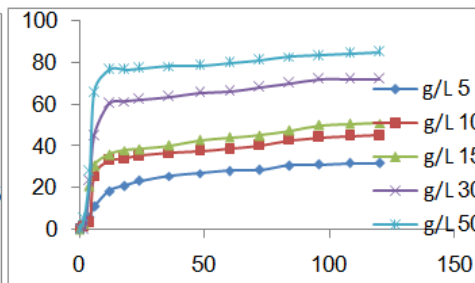
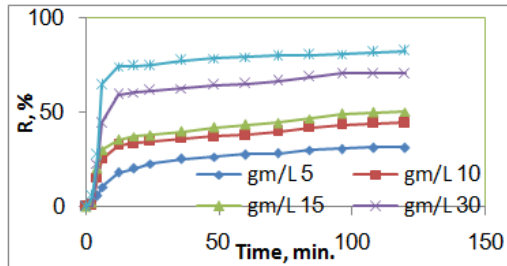
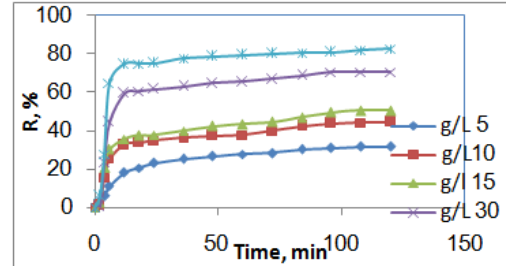


Fig. 7: Removal efficiency of phosphate on (RM) as a function of contact time, (pH=6,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).

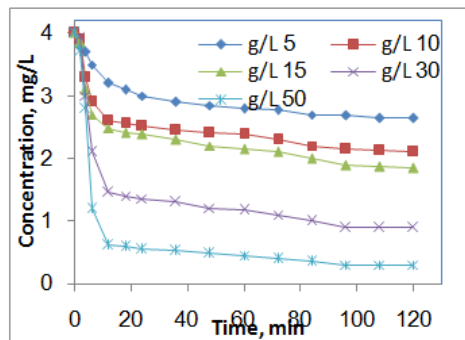




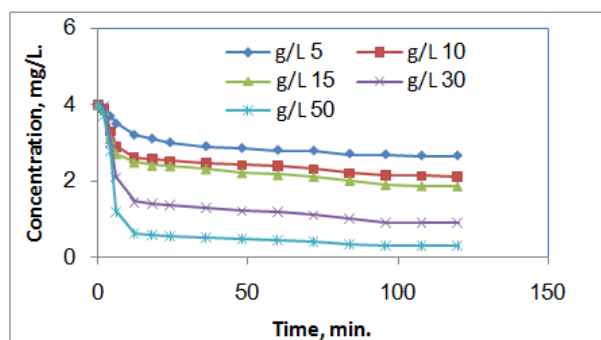
**Fig. 8: Removal efficiency of phosphate on (DWTs) as a function of contact time, (pH=8.4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).**



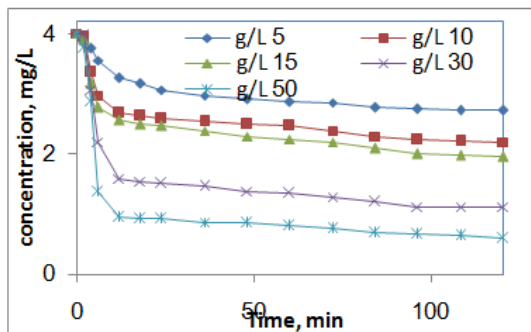
**Fig. 9: Removal efficiency of phosphate on (RM) as a function of contact time, (pH=8.4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).**



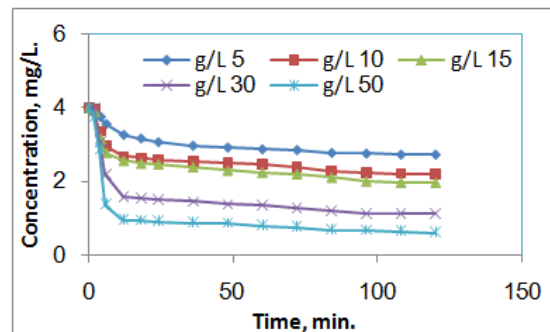
**Fig. 10: Residual phosphorus concentration with adsorption period at varied sludge dosages, (pH=4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).**



**Fig. 11: Residual phosphorus concentration with adsorption period at varied red mud dosages, (pH=4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).**



**Fig. 12: Residual phosphorus concentration with adsorption period at varied sludge dosages, (pH=6,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).**



**Fig. 13: Residual phosphorus concentration with adsorption period at varied red mud dosages, (pH=6,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).**

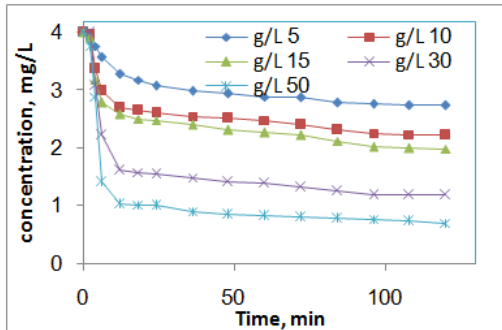


Fig. 4.14: Residual phosphorus concentration with adsorption period at varied sludge dosages, (pH=8.4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).

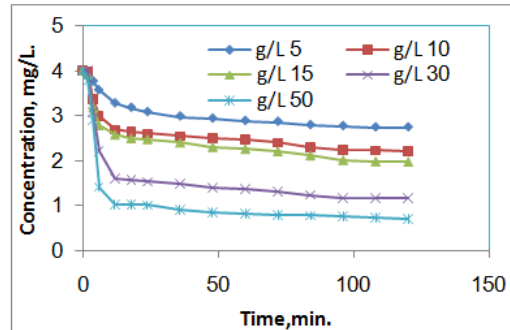


Fig. 4.15: Residual phosphorus concentration with adsorption period at varied red mud dosages, (pH=8.4,  $C_0=4\text{mg/L}$ , Temp.=25 °C, agitation speed=250 rpm).

Contact time is one of the most effective factors in batch adsorption process. Adsorption rate initially increased rapidly, and the optimal removal efficiency was reached (Fig. 16). Further increase in contact time did not show significant change in equilibrium concentration; that is, the adsorption phase reached equilibrium. Increasing (RM) ratio increasing the removal efficiency and decreasing the equilibrium time in about 57% and 38% for 50% and 33% (RM) ratio respectively.

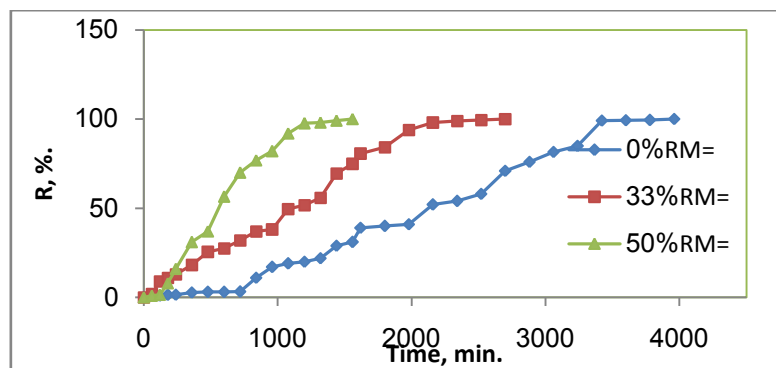


Fig.16: Removal efficiency of phosphate at different RM ratios as a function of time ,(pH=4,  $C_0=4\text{mg/L}$ , Temp.=25, agitation speed=250 rpm).

## c. Effect of pH of the Solution

The pH of the aqueous solution is an important variable, which influences the sorption of both anions and cations at the solid-liquid interface. The anion exchange capacity is strongly governed by the pH of the solution and by the surface chemistry of the solids. It is most important single parameter influencing the sorption capacity which is related to the sorption mechanisms onto the sorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the sorption sites of sorbent.

The sorption of phosphate on the (DWTS) and (RM) were examined at different pH ranging from 4 to 8.4 with an initial concentration of 4 mg/L and different values of contact time, (Figs 17 to 26). The pH of the solutions was adjusted to the required value with 0.1 M  $\text{HNO}_3$  and NaOH solutions. It is clear that the best initial pH of the sorption was found to be 4. An increase or decrease in the pH from this best pH resulted in a reduction in the sorption of these contaminants. This may be due to competition for binding sites between cations and protons at low pH values. While at higher pH, solubility of complexes decreases sufficiently allowing precipitation which may complicate the sorption process and do not bind to the sorption sites on the surface of the (DWTS) and (RM), (Kurnaz and Buyukgungor, 2009; Sulaymon et al., 2011).



The efficiency performance under various initial pH are presented in Figs. 11 to 15. As it is shown, the phosphate removal yield by (DWTS) and (RM) increased with decreasing initial pH in the solution. It is seen that the maximum efficiency (95%) is observed at pH=4, and (DWTS) dosage =50 g/L. Results indicate that the effectiveness of (DWTS) in removing phosphate is highly dependent on initial pH. This is due to the fact that phosphate adsorption onto the (DWTS) and (RM) are coupled with the release of  $\text{OH}^-$  ions (Yang et al, 2009). So (DWTS) and (RM) are very beneficial for the use in the removing of phosphate from the secondary wastewater treatment plants effluents. The removals of phosphorus on (DWTS) and (RM) for all the pHs values were more than (60)% and (30)% respectively.

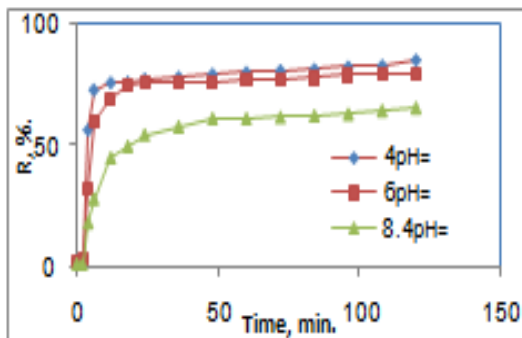


Fig. 17: Effect of pH on adsorption of phosphate by DWTS, ( $C_0=4 \text{ mg/L}$ , DWTS= 5 g/L, Temp. =25 °C, Agitation speed = 250 rpm).

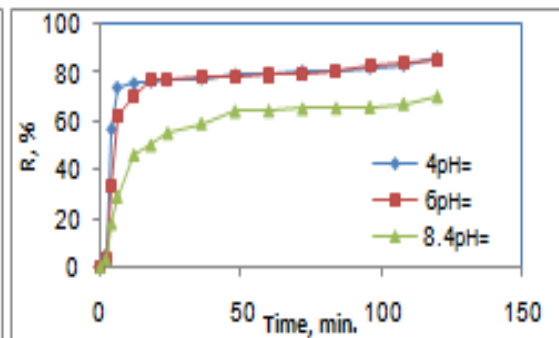


Fig. 18: Effect of pH on adsorption of phosphate by RM, ( $C_0=4 \text{ mg/L}$ , DWTS= 5 g/L, Temp. =25 °C, Agitation speed = 250 rpm).

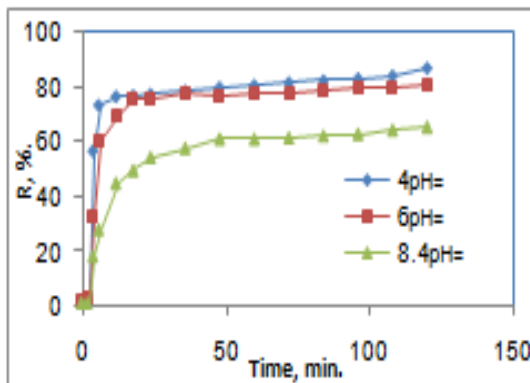


Fig. 19: Effect of pH on adsorption of phosphate by DWTS, ( $C_0=4 \text{ mg/L}$ , DWTS= 10 g/L, Temp. =25 °C, Agitation speed = 250 rpm).

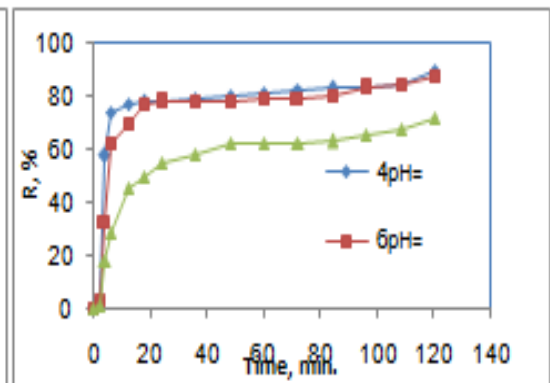


Fig. 20: Effect of pH on adsorption of phosphate by RM, ( $C_0=4 \text{ mg/L}$ , DWTS= 10 g/L, Temp. =25 °C, Agitation speed = 250 rpm).

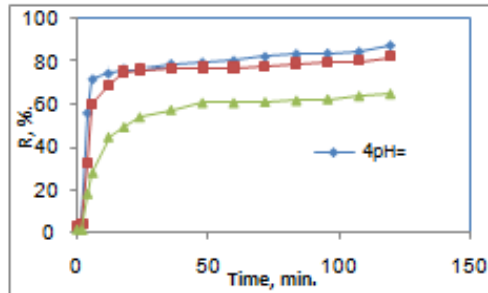


Fig. 21: Effect of pH on adsorption of phosphate by DWTS, ( $C_0=4$  mg/L, DWTS= 15 g/L, Temp. =25 °C, S = 250 rpm).

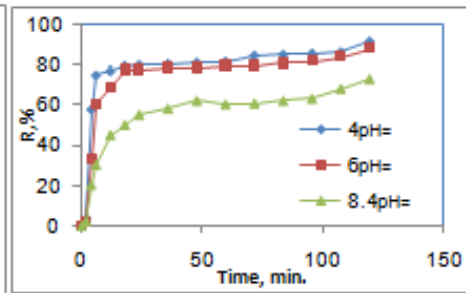


Fig. 22: Effect of pH on adsorption of phosphate by RM, ( $C_0=4$  mg/L, DWTS= 15 g/L, Temp. =25 °C, S = 250 rpm).

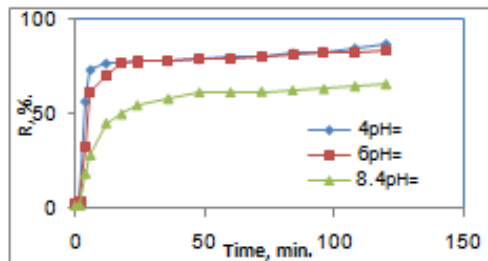


Fig. 23: Effect of pH on adsorption of phosphate by DWTS, ( $C_0=4$  mg/L, DWTS= 30 g/L, Temp. =25 °C, S = 250 rpm).

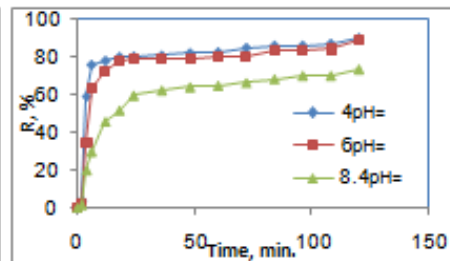


Fig. 24: Effect of pH on adsorption of phosphate by RM, ( $C_0=4$  mg/L, DWTS= 30 g/L, Temp. =25 °C, S = 250 rpm).

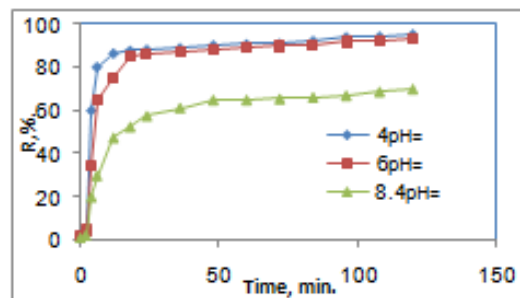


Fig. 25: Effect of pH on adsorption of phosphate by DWTS, ( $C_0=4$  mg/L, DWTS= 50 g/L, Temp. =25 °C, S = 250 rpm).

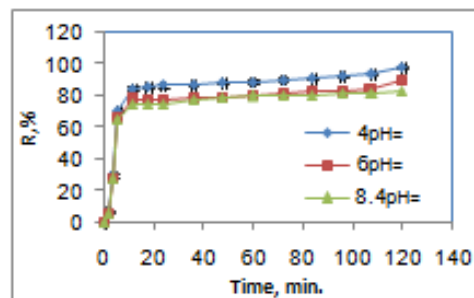


Fig. 26: Effect of pH on adsorption of phosphate by RM, ( $C_0=4$  mg/L, DWTS= 50 g/L, Temp. =25 °C, S = 250 rpm).

Fig. 27 and 28 illustrate the effect of dosage of (DWTS) and (RM) on phosphorus removal, at best conditions, ( $H=25$  cm,  $C_0=4$  mg/L, Temp.=25,  $t=30$  min.). It appears from this Fig. that the pH removal efficiency increased as (DWTS) and (RM) dose increased for all pH values, and get maximum efficiency at pH=4 and dose =50 mg/L.

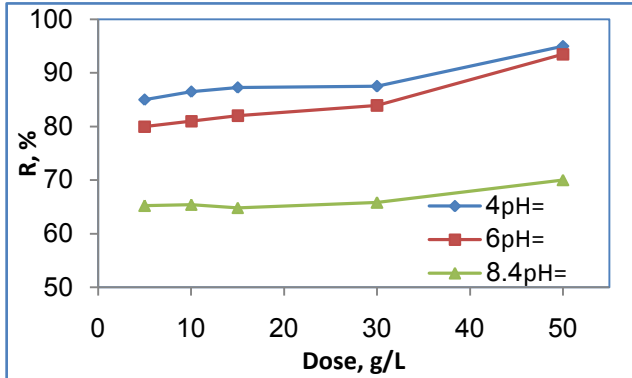


Fig. 27: Effect of dosage of DWTS on phosphorus removal, (H=25 cm,  $C_0=4$  mg/L, Temp.=25°C).

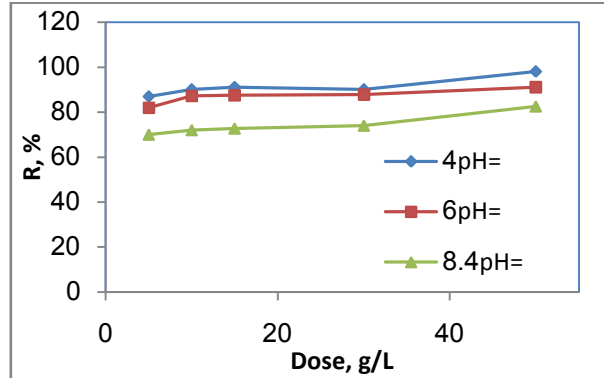


Fig. 28: Effect of dosage of RM on phosphorus removal, (H=25 cm,  $C_0=4$  mg/L, Temp.=25°C).

Effect of pH, on the adsorption density is illustrated in Fig. 29 and 30. pH had little effect on the adsorption capacity. However, solution pH of 4 appeared to produce maximum adsorption capacity in many of the experimental results. The effluent pH was understandably dependent on the influent pH. An influent pH 4 produced effluent pH of (3.7–4.6). Similarly an influent pH 6 generated an effluent pH range (5.8–6.5), and an influent pH 8.4 generated an effluent pH range of (7.5–8.5). It was due to the adsorption and desorption of  $H^+$  ions during the adsorption of phosphorus ion. An effluent pH below 4.5 is not suitable for disposal in surface water. The effluent pH can be increased prior to disposal in surface water. However, the cost of chemicals to reduce initial pH and to increase final pH and hazards of dealing with increased amount of sludge would pose negative interest for pH control. In general, a pH value in the range of (6–9) is reasonable for wastewaters before disposal into surface water.

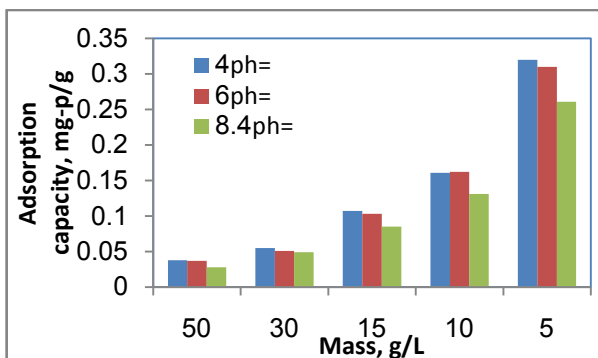


Fig. 29: The adsorption capacity of (DWTS) at different pHs.

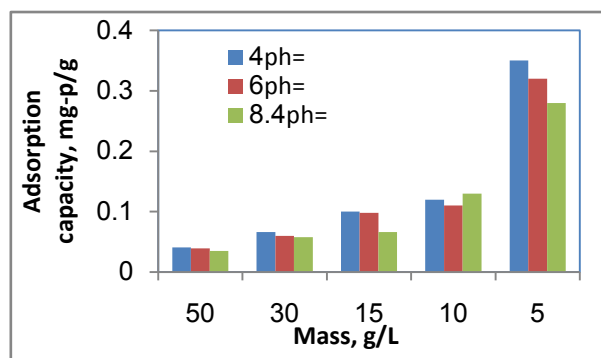
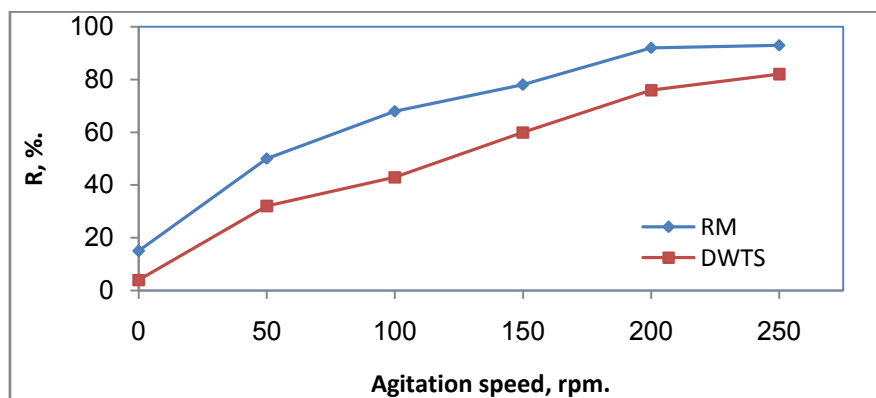


Fig. 30: The adsorption capacity of (RM) at different pHs.

## d. Effect of Agitation Speed

The effect of agitation speed on removal efficiency of phosphate was studied by varying the speed of agitation from 0 (without shaking) to 250 rpm and keeping other parameters equal to best ones obtained in the previous steps. Fig. 31 shows that about 4% of phosphate was removed by (DWTS), and 15% by (RM) before shaking and the uptake increases with the increase in shaking rate. However, there was an increase in contaminants uptake when agitation speed was increased from zero to 250 rpm at which about 82% and 93 % of phosphate have been removed by (DWTS), and (RM) respectively. These results can be associated to the fact that the increase in the agitation speed improves the

diffusion of contaminant towards the surface of the reactive media. Thus, proper contact is developed between sorbate in solution and the binding sites, which promotes effective transfer of sorbate to the sorbent sites.



**Fig. 31: Effect of agitation speed on percentage removal of phosphate ( $C_0=4$  mg/L; pH=4, Temp.=25**

### B. Equilibrium Isotherm Experiments a. Estimation of the Adsorption Isotherm Constants

The isotherm is represented by the linear plot of specific adsorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ). Fig. 19 shows that the adsorption obeys the Langmuir model. The constants  $b$  and  $q_{\max}$  relate to the energy of adsorption and maximum adsorption capacity, and their values are obtained from the slope and interception of the plot and are presented in Table 4. The Freundlich isotherm Fig. 20 is introduced as an empirical model, where  $q_e$  represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g),  $C_e$  represents the equilibrium concentration (mg/L), and  $K_f$  and  $n$  are parameters that depend on the adsorbate and adsorbent.

Freundlich equilibrium constants were determined from the plot of  $\ln q_e$  versus  $\ln C_e$ . From Fig. 20, on the basis of the linear form of Freundlich equation, the  $n$  value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if  $n=1$ , then adsorption is linear; if  $n<1$ , then adsorption is a chemical process; if  $n>1$ , then adsorption is a physical process. The situation  $n>1$  is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density (Reed and Matsumoto, 1993) and the values of  $n$  within the range of 1–10 represent good adsorption (McKay et al., 1980; Ozer and Pirinc, 2006). In the present study, since  $n$  lies between 1 and 10 it indicates the physical adsorption of phosphate ions onto (DWTS). In both cases, linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process. Figs. 21 and 22 exhibit Langmuir and Freundlich plots, respectively, for the adsorption of phosphate ions onto (RM), and different Langmuir and Freundlich constants and correlation coefficients ( $R^2$ ) derived from these plots are presented in Table 4. Nearly similar results have been reported in the literature (Mittal et al., 2007; Malakootian et al., 2009; Liu et al., 2010) for Langmuir and Freundlich models. To find the most appropriate model for the phosphate ions adsorption; data were fitted to Langmuir and Freundlich isotherm models. Results revealed that Langmuir adsorption isotherm was the best model for the phosphate ions adsorption onto (RM) with  $R^2$  of 0.977.

# International Journal of Advanced Research in Science, Engineering and Technology

Vol. 2, Issue 3, March 2015

**Table 4: Langmuir and Freundlich Isotherms Parameters for phosphate Adsorption onto Different Adsorbents used in the Study.**

Model	Adsorbent			
	(DWTS)		(RM)	
	Parameters	value	Parameters	value
Langmuir	$Q_0$ , mg/g	0.094	$Q_0$ , mg/g	0.163
	$b$ , l/mg	0.958	$b$ , l/mg	11.04
	$R_L$	0.806	$R_L$	0.022
	$R^2$	0.8238	$R^2$	0.977
Freundlich	$K$ , mg/g(l/mg) <sup>1/n</sup>	-0.435	$K$ , mg/g(l/mg) <sup>1/n</sup>	0.749
	$1/n$	0.5185	$1/n$	0.2525
	$R^2$	0.7838	$R^2$	0.8431

The essential features of Langmuir adsorption isotherm parameter can be used to predict the affinity between the sorbate and sorbent using a dimensionless constant called separation factor or equilibrium parameter ( $R_L$ ), which is expressed by the following relationship (Malik et al., 2004):

$$R_L = \frac{1}{1 + bC_i}$$

where  $b$  is the Langmuir constant and  $C_i$  is the initial concentration. The value of  $R_L$  indicated the type of Langmuir isotherm to be irreversible ( $R_L = 0$ ), linear ( $R_L = 1$ ), unfavorable ( $R_L > 1$ ), or favorable ( $0 < R_L < 1$ ) (McKay et al., 1982). The  $R_L$  values between 0 and 1 indicate favorable adsorption. The  $R_L$  value in the present investigation was found to be 0.022–0.806, indicating that the adsorption of the phosphate ion onto (DWTS) and (RM) are favorable.

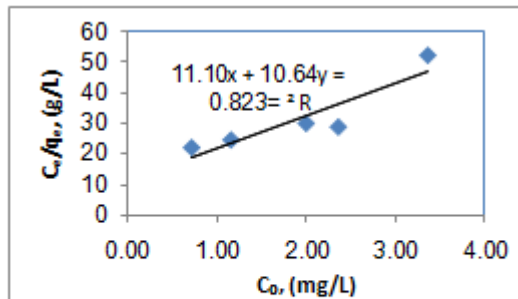


Fig. 22: Langmuir adsorption isotherm of phosphate onto (DWTS) at 25 ± 1 °C,  $C_e$ =4 mg/L, pH=4, agitation speed=250rpm, contact time=2 hr.

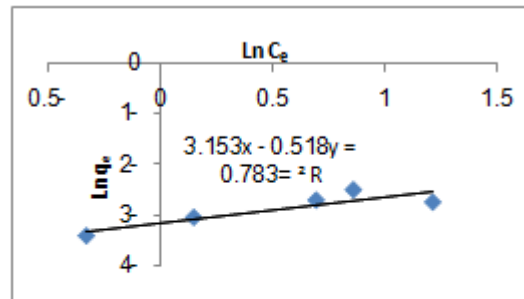


Fig. 23: Freundlich adsorption isotherm of phosphate onto (DWTS) at 25 ± 1 °C,  $C_e$ =4 mg/L, pH=4, agitation speed=250rpm, contact time=2 hr.

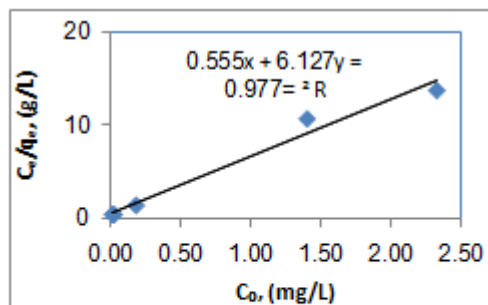


Fig. 24: Langmuir adsorption isotherm of phosphate onto (RM) at 25 ± 1 °C,  $C_e$ =4 mg/L, pH=4, agitation speed=250rpm, contact time=2 hr.

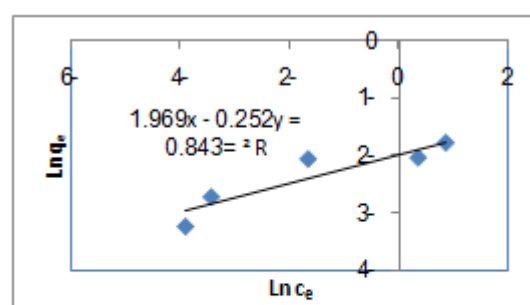


Fig. 25: Freundlich adsorption isotherm of phosphate onto (RM) at 25 ± 1 °C,  $C_e$ =4 mg/L, pH=4, agitation speed=250rpm, contact time=2 hr.

# International Journal of Advanced Research in Science, Engineering and Technology

Vol. 2, Issue 3 , March 2015

It is clear that the Langmuir isotherm model provided the best correlation in compared with Freundlich isotherm model for phosphate sorption on the (DWTS) and (RM).

One of the important aspects of the present study is represented by considering the (DWTS) as reactive medium, i.e. not inert. Accordingly, sorption tests for single component system of phosphate onto (DWTS) were conducted with best conditions specified previously. The utilization of these conditions is logic because the (DWTS) and (RM) may be worked together under the same field conditions of the continuous flow.

## V. CONCLUSIONS

The following Conclusions were obtain from this study:-

- (DWTS) seems suitable for use as filler for remediation of wastewater contaminated by phosphate.
- The use of (DWTS) as a reactive medium for the treatment of wastewater ensures that significant rates of reduction of phosphate are achieved, particularly in cases in which there is initially a high concentration.
- It is clear that the Langmuir isotherm model provided the best correlation in compared with Freundlich model for phosphate sorption on the (DWTS).
- It is clear that the removal efficiencies improved with increasing sorbent dosage from 5 g to 50 g for both (DWTS) and (RM), and they are remained approximately constant afterwards.
- the removal percentage of this contaminant significantly increased with an increase in contact time. It is clear that the sorption rate was rapid at the initial stage and gradually slowed down afterwards. The slower sorption was likely due to the decrease in sorption sites on the surface of the (DWTS).
- In batch studies, pH of 4 and dosage of 50gm/L was found to be optimized condition for the phosphate removal by (DWTS). Increase in adsorbent dosage increased the percentage removal of phosphate.
- (DWTS) is environment friendly, cost- effective, and locally available adsorbent for the adsorption of phosphate ions from secondary wastewater effluents.
- The equilibrium isotherms for the (DWTS) used in the study are of favorable type. These isotherms rise slightly at the initial stages for low  $C_e$  and  $q_e$  values.
- One of the important aspects of the present study is represented by considering the (DWTS) as reactive medium, i.e. not inert. The utilization of these conditions is logic because the (DWTS) and (RM) may be worked together under the same field conditions of the continuous flow.

## REFERENCES

1. Almuamirah wastewater treatment plant, 2014.
2. Caravelli, A.H., Contreras, E.M. and Zaritzky, N.E., "Phosphorus removal in batch systems using ferric chloride in the presence of activated sludges", Journal of Hazardous Materials, Vol. 177(1-3), pp.199-208, 2010.
3. Cheremisinoff, P. N., "Biomangement of Wastewater and Wastes". Water and Wastewater Treatment Guidebooks. PTR Prentice Hall, New Jersey, 1994.
4. Bashan, L.E., Bashan, Y., "Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003) ". Water Research 38, 4222-4246, 2004.
5. Morse, G.K., Brett, S.W., Guy, J.A. and Lester, J.N., Review: "phosphorus removal and recovery technologies". Science of the Total Environment, Vol. 212(1), pp.69-81, 1998.
6. Yeoman, S., Stephenson, T., Lester, J.N., Perry, R., "The removal of phosphorus during wastewater treatment". A review. Environmental Pollution 49, 183-233, 1988.
7. Alexander, P.M., Zayas, I., "Particle size and shape effects on adsorption rate parameters". Environ. Eng., 115(1), 41-55, 1989.
8. Rahmani, A.R., Ghaffari, H.R., Samadi, M.T., "Removal of arsenic (iii) from contaminated water by synthetic nano size zero valent iron". World Academy of Science, Engineering and Technology, 38, 737-740, 2010.
9. Sulaymon, A.H., Abbood, D.W., Ali, A.H., "Competitive adsorption of phenol and lead from synthetic wastewater onto granular activated carbon". Journal of Environmental Science and Engineering, 5, 1389-1399, 2011.
10. Reed, B.E., Matsumoto, M.R., "Modeling cadmium adsorption by activated carbon using the Langmuir and Freundlich isotherm expressions," Separation Science and Technology, vol.28, no. 13-14, pp. 2179-2195, 1993.
11. Kurnaz, S.U., Buyukgungor, H., "Assessment of various biomasses in the removal of phenol from aqueous solutions". Journal of Microbial & Biochemical Technology, 1, 047-050, 2009.
12. Liu, H., Dong, Y., Wang, H., Liu, Y., "Adsorption behavior of ammonium by a bioadsorbent—Boston ivy leaf powder", Journal of Environmental Sciences, vol.22, no.10, pp.1513-1518, 2010,
13. Ozer, A., Pirinc, H.B., "The adsorption of Cd (II) ions on sulphuric acid-treated wheat bran," Journal of Hazardous Materials, vol.137, no.2, pp.849-855, 2006.
14. McKay, G., Otterburn, M.S., Sweeney A.G., "The removal of colour from eluent using various adsorbents. III. Silica: rate processes," Water Research, vol.14, no.1, pp.15-20, 1980.





ISSN: 2350-0328

# International Journal of Advanced Research in Science, Engineering and Technology

Vol. 2, Issue 3 , March 2015

15. Mittal, A., Kurup, L., Mittal, J., "Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers," Journal of Hazardous Materials, vol.146,no.1-2,pp.243–248, 2007.
16. Malakootian, M., Nouri, J., Hossaini, H., "Removal of heavy metals from paint industry's wastewater using Leca as an available adsorbent," International Journal of Environmental Science and Technology, vol.6,no.2, pp.183–190, 2009,
17. Malik, P.K., "Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics," Journal of Hazardous Materials, vol. 113, no. 1–3, pp.81–88, 2004.
18. Metcalf and Eddy, Inc., "Wastewater Engineering: Treatment and Reuse". Fourth Edition. New Delhi: Tata McGraw-Hill, 2003.
19. McKay, G., Blair, H.S., Gardner, J.R., "Adsorption of dyes on chitin," Journal of Applied Polymer Science, vol.27,no.8, pp.3043–3057, 1982.
20. Plaza, E., Levlin, E., Hultman, B., "Advanced wastewater treatment". Report No 1., phosphorus removal from wastewater Stockholm, 1997.
21. Ping Wang, Dong-Yan Liu, "Physical and Chemical Properties of Sintering Red Mud and Bayer Red Mud and the Implications for Beneficial Utilization", China, 2012.
22. Yang, Y., Zhao, Y.Q., Babatunde, A.O., Kearney, P., "Two strategies for removal of reject water of municipal waste water treatment plant using alum sludge". water science and technology, volume 60, Issue 12, Page No. 3181-3188, 2009,