

## Phosphate removal by using activated red mud from Seydisehir Aluminium Factory in Turkey

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**Abstract:** Phosphorus is one of the main elements for living and developing organisms. But this property increases the biological productivity in the water basin and causes eutrophication. Classical wastewater treatment processes are not effective enough in removal of the phosphate. For this reason, some chemical phosphate removal systems are developed with precipitation. In this study, adsorption method was used to remove the phosphate from the wastewater. Red-mud waste of the aluminium factories was used as an adsorbent after activation processes. The substance, produced by activating adsorbent, was used in different doses, at the different pH values *etc.* So, productivity of the red-mud in removal of the phosphate ion was investigated. In the experiments, the drinking water of Selcuk University in Turkey was used by adding phosphate synthetic samples. Removal productivity of phosphate was about 85% in the situation of suitable dose of red-mud and pH value.

**Keywords:** Phosphate, eutrophication, adsorption, orthophosphate, red mud, aluminium factory.

### Introduction

Bauxite is composed primarily of fine particles of silica, aluminium, iron, calcium and titanium oxides and hydroxide, which are responsible for its high surface reactivity. It contains aluminium hydroxides in large percentage and is therefore largely used for the production of alumina ( $\text{Al}_2\text{O}_3$ ) through the Bayer chemical process, which is based on the reaction with sodium hydroxide under heat and pressure (Brunori *et al.* 2005). Its main constituents are iron (giving the red colour), aluminium, sodium and silica, and their amounts vary according to the bauxite location. The disposal of large quantities of waste red-mud is a serious ecological problem. Many investigations for its application have been done. Because of its high content of iron and aluminium, red mud has been also studied as a coagulant for wastewater treatment (Koumanova *et al.*, 1997; Brunori *et al.*, 2005).

Red mud, bauxite wastes of alumina manufacture, emerges as an unwanted by-product during alkaline leaching of bauxite in the Bayer process. For every tonne of alumina produced, between 1 and 2 tonnes (dry weight) of red mud residues are produced. About 500,000 m<sup>3</sup> of strongly alkaline (pH about 12-13) red mud water is dumped annually into specially constructed dams near the Seydisehir Aluminium Plant. Since the plant began to process, red mud has accumulated over time, therefore causing serious environmental problems. Today, then disposal and utilization of red mud are problems for all aluminium industries in the world. Red-mud has been used in absorbents, building materials, catalysts, fillers and pigments (Lopez *et al.*, 1998; Chvedov *et al.*, 2001; Santona *et al.*, 2006; Çengelöglu *et al.* 2001).

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Adsorption is the most popular method for wastewater treatment due to its easy and inexpensive operation, but there are certain problems using activated carbon as adsorbents due to the high cost of use and regeneration. The adsorption process will provide an attractive technology if the sorbent is inexpensive and ready for use (Wang *et al.*, 2005). In order to minimize processing costs for these effluents, recent investigations have focused on the use of a low-cost-adsorbent (Bailey *et al.*, 1999; Kocaoba *et al.*, 2005). Many industrial wastes are also the potentially low-cost adsorbent. It requires little processing to increase its sorption capacity. Generally industrial wastes are generated as by-products such as red-mud. Since these materials are locally available in large quantities and obtained inexpensively (Babel *et al.*, 2003). Red mud, due to high aluminium, iron and calcium, has been suggested as an economic adsorbent for removal of toxic metals as well as for water or wastewater treatment. The basic advantage of red mud is its versatility in application. Because of these characteristics red-mud has been the subject of many investigations including some on the removal of toxic heavy metals from wastewater in recent years. However, little research has been conducted to utilise red mud for phosphate removal (Pradhan *et al.*, 1998).

Phosphorus is an important element, making a major contribution to agricultural and industrial development. However, its release to surface waters in agricultural runoff and wastewaters has led to legislation, such as the European Union Urban Wastewater Directive Commission of the European Communities, 1991, designed to remove phosphorus from domestic and industrial wastewater. Wastes containing phosphate create eutrophication in the receiving bodies of water. In order to eliminate the possible dangers to receiving water sources, it is necessary to treat before discharge. Adsorption of the phosphate from aqueous solution has been studied in the past few decades by several authors using different adsorbents (Pradhan *et al.*, 1998).

Utilisation of industrial solid wastes for the treatment of wastewater from another industry could be helpful not only to environment in solving the solid waste disposal problem, but also the economy. Due to its high calcium and sodium hydroxide content, red mud is relatively toxic and can pose a serious pollution hazard. In recent years, a great deal of research has been undertaken to utilise red mud for wastewater treatment, such as removal of toxic heavy metals (Apak *et al.*, 1998; Gupta *et al.*, 2001; Pradhan *et al.*, 1999; Zouboulis *et al.*, 1993) and dyes (Namasivayam *et al.*, 1997; Namasivayam *et al.*, 2002; Wang *et al.*, 2005). Among them, the possibility of using red mud or activated red mud for phosphate removal from water is important. It is necessary to treat before discharge. There is therefore a strong need to develop cost effective adsorbents (Genç-Fuhrmann *et al.*, 2004).

In the present study, the adsorption of phosphate on activated red-mud was evaluated under various conditions such as pH, phosphate concentrations and red-mud dosages. This study provided some information on the possibility of increasing the phosphate sorption capacity of red-mud, and the possibility of using these substances as an unconventional means of removing phosphate from water. To determine the optimum conditions of adsorption capacity was also aimed.

## Material and Methods

### Red Mud

Red mud used in the present experiments was supplied from Seydisehir Aluminium Plant in Turkey. It has the following average chemical composition (%):  $\text{Al}_2\text{O}_3$ , 19.88;  $\text{Fe}_2\text{O}_3$ , 36.47;  $\text{CaO}$ , 2.33;  $\text{SiO}_2$ , 15.95;  $\text{Na}_2\text{O}$ , 10.03;  $\text{TiO}_2$ , 4.97;  $\text{CO}_2$ , 2.48; S, 0.09;  $\text{V}_2\text{O}_5$ , 0.074;  $\text{P}_2\text{O}_5$ , 0.041 and loss on ignition, % 8.04. After arrival in the laboratory, red mud was air dried and sieved by 250 mesh steel sieve. The studies were carried out with the red mud of particle size of 0.1-1.0 mm diameter. Sieved red-mud was stored at laboratory conditions until activation processes.

***Activation of red mud***

Red mud was activated through acid treatment with concentrated HCl acid. For this purpose, 25 grams of oven-dry- weight red-mud were prepared in 1 L capacity baker and suspended in 50 mL distilled water (2 mL distilled water per gram red-mud) by adding 0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 8.0 mL concentrate HCl (Merck Co. Germany) and the suspensions were stirred for 30 min. Then, they were washed twice with 100 mL of distilled water to remove the residual acid and soluble compounds. The treated red-mud was filtrated by using Whatman No. 1 filter to remove the solution content. Mud cakes were dried at 105 °C overnight and stored in vacuum desiccators until using in the experiments.

***Adsorption experiments***

In the adsorption study, phosphate adsorption characteristics of activated red-mud were investigated. Adsorption experiments were performed by Jar Test Method (Armfield W1-A, UK) at room temperature. A preliminary jar-test procedure was used to select activation conditions, coagulant dosage range and the optimal pH value ranging from 4 to 8. The pH of the solutions was adjusted with either an acid (HCl) or a base (NaOH) solution to achieve the desired pH.

***Preparation of phosphate solutions***

All experiments were run at a 30 mg L<sup>-1</sup> constant phosphate concentration. Phosphate stock solutions were prepared by dissolving 55 mg K<sub>2</sub>HPO<sub>4</sub> in 100 ml distilled water. Then 10 ml of previously prepared solution were made up to 1 liter using tap water as a final volume to achieve a concentration of 30 mg L<sup>-1</sup>.

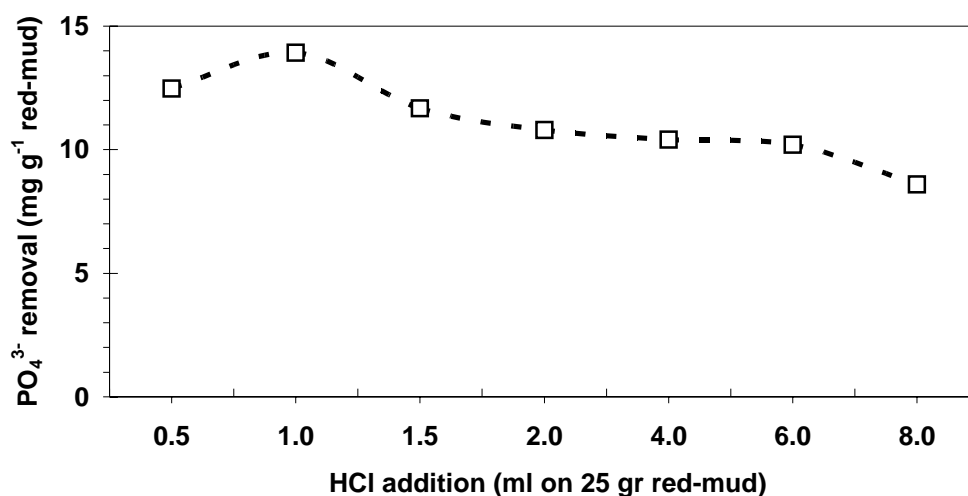
***Determination of phosphate concentration***

Ortho-phosphate was analyzed with spectrophotometric method using cuvette test by the CADAS 200 UV-VIS spectrophotometer (Dr Bruno Lange GmbH & Co. KG, Düsseldorf, Germany). Each experiment runs, initial and final concentrations were determined at each experiment run.

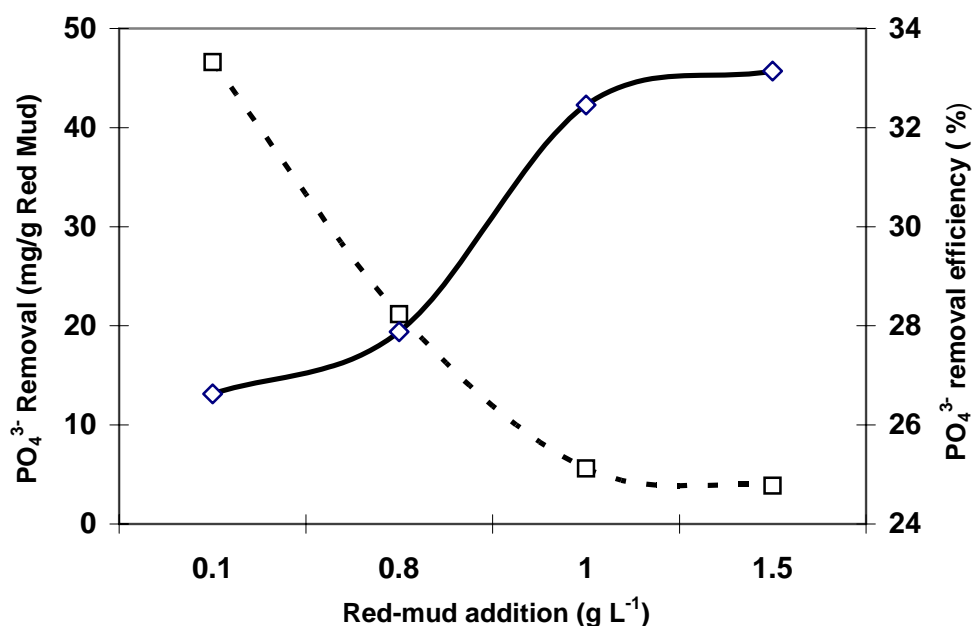
**Result and Discussion**

Before the adsorption experiment, activation conditions were tested treating red-mud with aside solution. For this processes, each separate 25 g over dry weight (odw). Red-mud was put in the 50 ml distilled water into the 1 L glass-baker, then concentrated HCl acid in 0.5 to 8 ml volume was added separately red-mud suspensions in the each baker. These activated red-mud were filtered, dried and then used to test effect of activation conditions. Results of activation conditions tests given in Figure 1 that optimum activation condition was with addition of 1 ml concentrate HCl onto 25 g red-mud in 50 ml distilled water.

After designation of the activation condition, red-mud samples were prepared activating with addition of 1 ml concentrate HCl onto 25 g red-mud in 50 ml distilled water and used following experiments. Second experiment was determination of red-mud amounts given the results in the Figure 2. Figure 2 shows that removal efficiencies were strongly increased up to 1mg L<sup>-1</sup> red-mud and similarly, mg phosphate removal per gram red-mud was very low after addition of 1 g red-mud in 1 L 30 mg L<sup>-1</sup> phosphate sample. One g red-mud additions were preferred in 1 L sample at the following experiments.

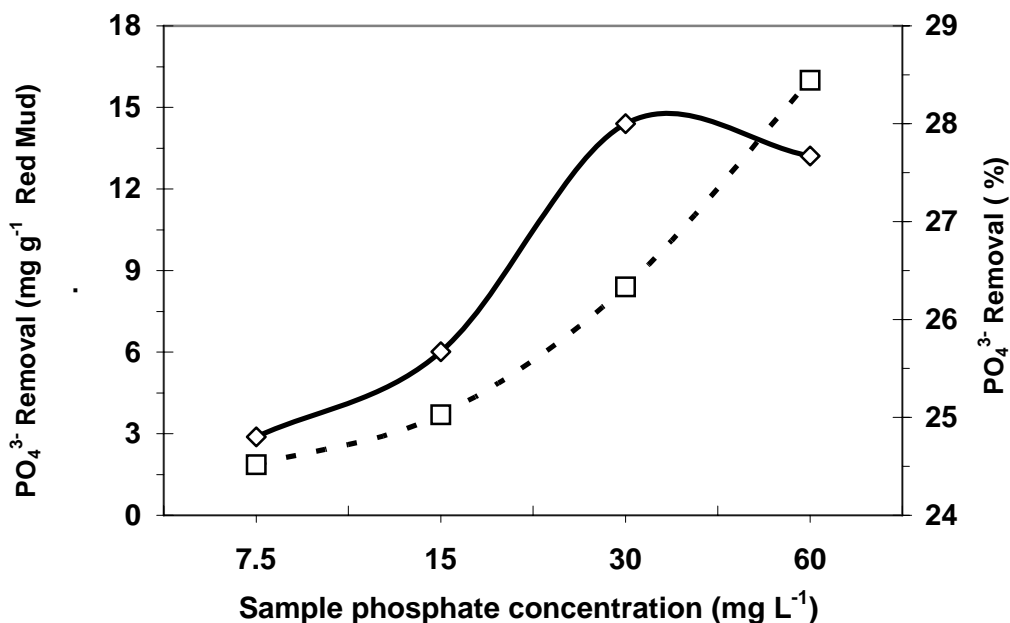


**Figure 1.** Effect of 0.5 g activated red-mud with 0.5, 1, 1.5, 2, 4, 6 and 8 ml concentrated HCl on phosphate removal from synthetic polluted water containing 30 mg phosphate L<sup>-1</sup> tap water



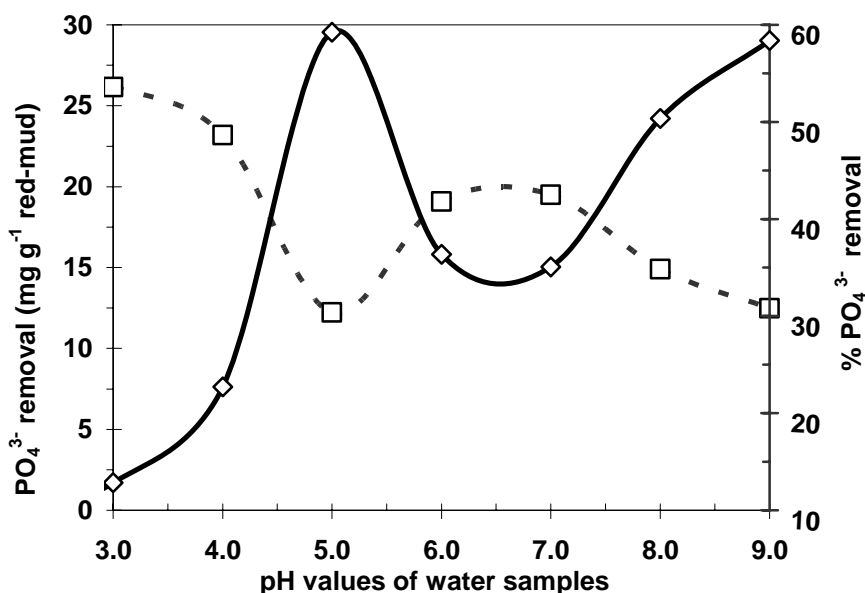
**Figure 2.** Phosphate adsorption from synthetic polluted water containing 30 mg l<sup>-1</sup> phosphate by the different amounts of red-mud addition activated by 1 ml concentrated HCl. Symbols in the figure are □, phosphate removal (mg/g red-mud) and ◇, phosphate removal efficiency (%).

Figure 3 shows that removal efficiencies were increased with increasing phosphate concentration up to 30 mg L<sup>-1</sup> phosphate then decreased. On the other hand mg phosphate removal per gram red-mud was also increased with increasing phosphate concentration addition of 1 g activated red-mud addition. For this reason, 30 mg L<sup>-1</sup> phosphate concentration was used at the following experiments. Removal efficiencies were still lower and not enough to use at this conditions.



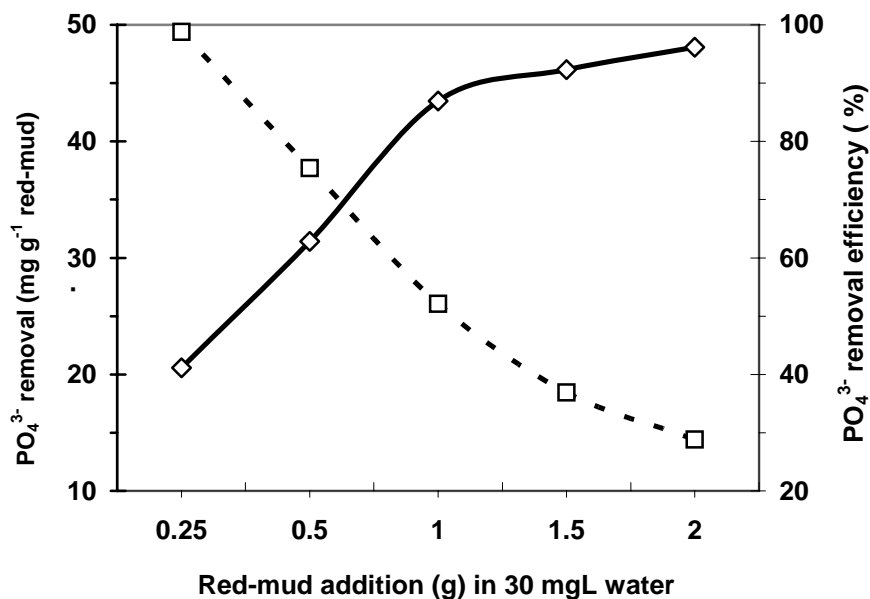
**Figure 3.** Effects of phosphate concentrations on phosphate removals by 1.0 g L<sup>-1</sup> activated red-mud in water. Symbols in the figure are □, phosphate removal (mg/g red-mud) and ◇, phosphate removal efficiency (%).

The effects of pH on adsorption capacity of activated red-mud were at different pH values between 3.0 to 9.0. The pH of the 30 mg L<sup>-1</sup> phosphate working solutions were adjusted from 3.0 to 9.0 separately and 1 g activated red-mud additions were made. Phosphate removal efficiencies were increased from 3.0 to 5.0, were decreased until 7.0 and then were increased again with increasing pH at 8.0 and 9.0 (Figure 4).



**Figure 4.** Effects of pH values (3.0 - 9.0) on phosphate removal from 30 mg L<sup>-1</sup> phosphate containing polluted water added 1 g activated red-mud. Symbols in the figure are □, phosphate removal (mg/g red-mud) and ◇, phosphate removal efficiency (%).

In the last step of the experiments, usage of adsorbent dosage between 0.25 to 2 g L<sup>-1</sup> activated red-mud was tested. % phosphate removal efficiency strongly increased with increasing red-mud dosage up to 1 g L<sup>-1</sup> that removal efficiency was about 87% (Figure 5). After that removal efficiency was increased about 5 % with addition of 50 % more red-mud addition and 9 % with addition of 100 % extra red-mud (2 g L<sup>-1</sup>). Other hand, mg phosphate removals per g red-mud were decreased with increasing red-mud dosage.



**Figure 5.** Effects of different amount of red-mud addition (0.25-2 g L<sup>-1</sup>) to phosphate removal from 30 mg/ L<sup>-1</sup> phosphate containing water at pH 5.0. Symbols in the figure are □, phosphate removal (mg/g red-mud) and ◇, phosphate removal efficiency (%).

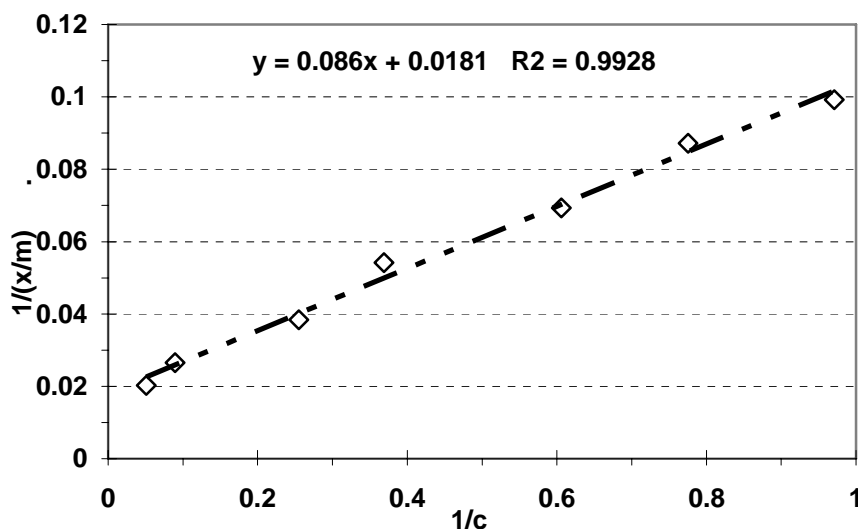
The equilibrium adsorption isotherm for phosphate on activated red-mud was plotted for varying adsorbent dose changing from 0.25 to 3.0 g L<sup>-1</sup>) and fixed initial phosphate concentration (30 mg L<sup>-1</sup>) at pH 5. The percentage of phosphate adsorption decreased with increasing adsorbate amount, which indicates that the adsorption depends upon the availability of the binding sites for phosphate. In order to determine the adsorption capacity of the activated red-mud, the equilibrium data for the adsorption of phosphate were analyzed in the light of adsorption isotherm models. Mostly used adsorption isotherms are Langmuir and Freundlich equations which were given below respectively (Eqs. 1 & 2):

$$\frac{1}{x/m} = \frac{1}{a} + \frac{1}{ab} \frac{1}{c} \quad (1)$$

$$\ln \frac{x}{m} = \ln k + \frac{1}{n} \ln c \quad (2)$$

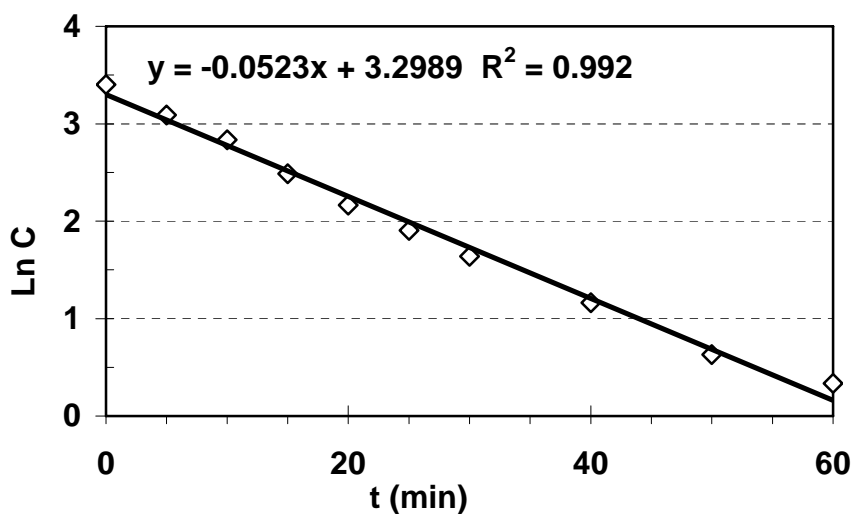
where  $x/m$  is the amount of phosphate adsorbed from per unit weight of adsorbent (mg g<sup>-1</sup>),  $c$  is the concentration of phosphate at equilibrium (mg L<sup>-1</sup>),  $1/ab$  is slope for plot with  $1/a$  contact

point on y axis for Lanmuir adsorption isotherm, and  $1/n$  is slope for plot with contact point of  $\ln k$  constant on crossing point of y axis for Freundlich adsorption isotherm. The straight line nature of the graph indicates that the adsorption confirms the Langmuir model (Figure 6). The experimental data points were fitted to the Langmuir equation, but it was not fit well to the Freundlich equation.



**Figure 6.** Langmuir adsorption isotherm plot for phosphate adsorption of activated red-mud

Chemical kinetics of phosphate removal was also investigated in batch reactor for 60 min. contact time that checked with  $^0$ ,  $^1$ ,  $^2$  and  $^3$  order reaction equations. Only our data is quite well fit to  $1^{\text{st}}$  order reaction kinetic (Figure 7). Square of correlation coefficient was  $R^2=0.992$  which confirms good relation between contact time and concentration change by experimental period. Figure 7 shows that reaction kinetic of phosphate removal from the aqueous environment by red-mud is  $1^{\text{st}}$  order that adsorption of red mud was physical character and it is suitable for reuse.



**Figure 7.** Reaction kinetic (1<sup>st</sup> order) plot for the phosphate adsorption of activated red-mud (30 mg L phosphate concentration and 60 min contact time period).

Studies using red mud residues from aluminium refineries as unconventional adsorbents for water and wastewater treatment purposes are motivated by the fact that red mud is a fine-grained mixture of oxides and hydroxides, capable of removing several contaminants, as well as being widely available. Thus, several studies have used red mud or activated red mud for adsorbing heavy metals and anionic pollutants from water, including phosphate, cadmium, lead, copper, and arsenic. Among them, the possibility of using red mud or activated red mud for phosphate removal from water is important, as elevated concentrations of phosphate have been detected in natural water in many parts of the developing world. There is therefore a strong need to develop cost effective adsorbents for removal of unwanted substance from the natural sources (Genç-Fuhrmann et al., 2004).

For this reason, their removal from the environment is more important. There are many treatment methods for chromium removal from the water. Scientists used natural and synthetic materials. Natural materials might be used directly or by its activation with some processes. For example Wood dust materials for heavy metal adsorption were used as a sorption material by Argun et al., 2005 with some activation processes. It has some filtration and precipitation problems in the water treatment usage. Red-mud was also used for the treatment after activation processes (Couillard, 1982). Alkaline red mud is a waste product of extracting alumina from bauxite and it is produced in large quantities. It is a by product and also undesirable materials for aluminium factories. For example, Seydisehir-Turkey Aluminium Factory has same red-mud disposal problem around the factory. Adsorption by activated red mud is investigated as a possible alternative to the conventional methods of phosphate removal from aqueous synthetic solutions and industrial effluents by Pradhan et al., 1999.

In this recent investigation showed that pH and  $\text{PO}_4^{3-}$  concentration of solution as well as red-mud dosage are the most important parameters for phosphate removal. Maximum removal efficiency was obtained at pH 5. Phosphate removal is strongly dependent on insoluble phosphate formation. In our study, high sorption capacities are obtained from the batch tests. Sorption capacities for adsorbents between 0.25 g to 3.0 g obtained from batch tests are between 19.7 and 1.03 mg g<sup>-1</sup> for red-mud (calculated using the Langmuir equation), respectively; similar behaviour has been reported elsewhere (Gupta et al., 2001). Adsorption capacity of red-mud was decreased with increasing dosage (Figure 6), for this reason lower adsorbent dosage may be preferred until suitable phosphate concentration of final sample.

## Conclusion

It has been found that red mud, wasted from aluminium factory, is, after treatment with concentrated hydrochloric acid, a highly effective reagent for the removal of phosphates from aqueous solutions. Red-mud usage will be an economical method for phosphate removal. This usage for water treatment would be given another change for disposal and reuse of the aluminium plants. This process can be extended to the removal of phosphate from industrial effluents. Phosphorus and other waste materials material will be further researched and would maximise its environmental benefits.

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