Adsorption of Phosphate in Aqueous Solutions Using Manganese Dioxide

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Abstract. **Effort to remove phosphate from aquatic ecosystem is of great interest, not only for preventing algae bloom problem but also for recovering phosphate, as this is an essential material. Adsorption is considered as an effective method especially because the nutrient loaded adsorbent can be directly used for fertilizer. Therefore, this study investigated the potential use of manganese dioxide in natural form (pyrolusite) to adsorb phosphate in aqueous solutions. A series of batch experiments were done to elaborate the adsorption process of phosphate onto manganese dioxide. Several environmental conditions such as pH, temperature and ionic strength were applied in order to get a better understanding of the process mechanism. The results indicated that pH was obviously affected the adsorption process, meanwhile ionic strength did not play significant role. The adsorption of phosphate was higher at a lower pH and getting reduced as the pH increased. Similar to that, the percentage removal of phosphate was declined significantly in higher ionic strength, indicated that the interaction between phosphate and manganese dioxide was mainly controlled by electrostatic force. The adsorption isotherm data correlated better with Langmuir model rather than Freundlich model. The maximum adsorption capacity of manganese dioxide was 11.40 mg P/g. The kinetic data was very well fitted to pseudo second order equation suggested that chemical reaction involved in the adsorption process. Moreover, thermodynamic data confirmed that phosphate adsorption onto manganese dioxide was an endothermic process.**

Keywords— **adsorption; phosphate; manganese dioxide; isotherm; kinetic; thermodynamic.**

I. INTRODUCTION

Phosphate is an essential material for many applications in industrial sector such as paint and coating, a cleaning agent (detergent), pharmaceutical, water treatment and agriculture. However, besides its positive function, the accumulation of phosphate in the aquatic system creates serious problems. Phosphate may naturally occur in water body, but anthropogenic sources from domestic wastewater, industrial wastewater and runoff water from agriculture/feedlot area increase the concentration significantly [1]. It has been reported that 1.3 Mt of phosphate every year discharged into aquatic systems all over the world [2]. This oversupply condition will stimulate eutrophication condition. More than 38% of water bodies in many regions of the world were considered to have eutrophication problem [3]. Eutrophication will lead to algae bloom, abnormal growth of aquatic plants and algae. It is reported that once the concentration of phosphate in lakes or sea is over 0.03 mg/L, algae bloom will occur. The further effect will then arise since algae bloom potentially shifts the water system into anaerobic condition result in aesthetical

(e.g., odor, turbidity) and health problem by producing cyanotoxins. Considering the tremendous effect of phosphate in the water system, some countries applied strict regulation. Environmental Protection Agency (EPA) stated that the maximum permissible concentration and the stringent discharge limit of phosphate ions are 0.1 mg/L and less than 0.05 mg/L respectively [4]. In Australia, the total phosphorus contaminant level in rivers and streams is controlled in the range of 0.01 – 0.1 mg/L, while the requirement for lakes and reservoirs is more stringent as 0.005 – 0.05 mg/L [5].

Based on that condition, strategic effort to eliminate phosphate has been continually developed. Several techniques have been proposed to remove phosphates such as chemical precipitation, biological process, ion exchange, membrane technology and adsorption. Chemical precipitation (by adding ferric or aluminum salts) is a relatively easy method, but the excessive sludge as by-product requires post-treatment. The biological process is an effective method to remove phosphate from water. However stability is another issue since the performance of microorganism is strongly depend on nutrients (e.g., carbon,

nitrogen, iron) availability and operational condition (e.g., pH, temperature). Meanwhile, ion exchange and membrane technology only work well for phosphate elimination if there is no other contaminant exist [6]. Therefore, among those methods, adsorption is considered the most economical, effective and reliable method [7]. Adsorption is a simple technology that requires a relatively low-cost facility, yet has been proved to be able to reduce contaminant in a high percentage. Regards to phosphate, adsorption can be applied not only for removal but also to recover it from the water system. This is important since the demand for phosphate still growing, especially for fertilizer production and detergent manufacturing, but at the same time, the phosphate reserves are gradually diminishing. Another interesting feature from this technique is that nutrient loaded filter can be used directly as phosphate fertilizer and soil conditioner [8], [9].

Various materials have been tested to be an effective adsorbent for phosphate; it was including natural minerals, industrial by-products (steel slag, fly ash, and red mud) and synthetic compound. Focus on the usage of natural minerals such as iron (hydr)oxides including amorphous hydrous ferric oxide, poorly crystalline hydrous ferric oxide goethite and akaganeite has increased as these materials have high affinity to phosphate, low cost and environmentally friendly [10]. Manganese oxides are another natural mineral with poor crystalline oxides, like a ferric oxide, which generally found in manganese-rich coatings. This mineral is considered as a potent scavenger of trace metals in soil, sediment, and rocks [11]. There was much research has been done to test the ability of manganese oxides as an adsorbent for various metals in aqueous solutions. However, there was a limited study to investigate the usage of manganese oxides for phosphate removal.

Therefore, a set of experiments was done to get further information on phosphate removal by using manganese oxides. In this work manganese oxides, ore was used as an adsorbent for phosphate in aqueous solutions. The experiments were done in a batch system with several environmental conditions, such as pH, ionic strength and temperature to elucidate the processing mechanism. The kinetic data, as well as adsorption isotherm, were also determined.

II. MATERIAL AND METHOD

A. Material

All chemicals including KH_2PO_4, $KMnO_4$, H_2SO_4, Sodium oxalate, HNO_3, NaOH, HCl were purchased in analytical grade and used directly without any further treatment. A private company in Surabaya supplied pyrolusite as the manganese oxide ore for this research. This material was sieved to get a size of 100 mesh and washed with demineralized water before the usage. To determine the manganese oxides content in the minerals, a simple titration was performed by weighing out 1 g of pyrolusite and put it into a conical flask with 40 mL of 0.5N Sodium oxalate. 50 mL of diluted H_2SO_4 was added before heating process. After black colored of particles disappeared, the solution was titrated against 0.3N $KMnO_4$ until the colorless turn into pink. The result indicated that the content of manganese oxides (MnO_2) was 84.76% (w/w). Also, the characterization

of surface functional groups of pyrolusite was done by Fourier Transform Infra Red (FTIR, Shimadzu).
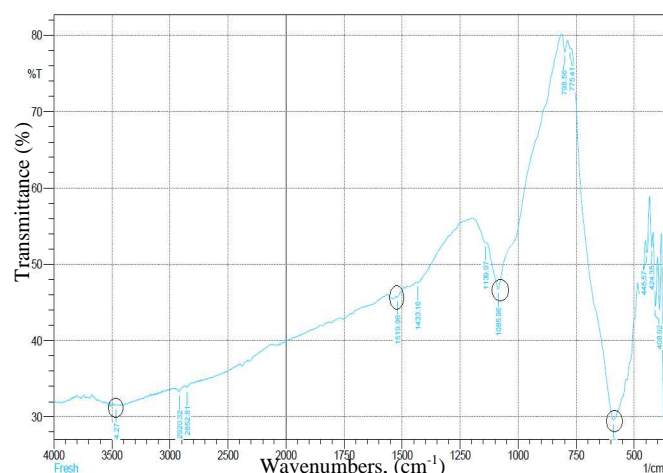

Fig.1. FTIR spectrum of MnO2 (Pyrolusite)

Refers to the Figure 1, the peak at about 590 cm^{-1} is a result of stretching vibration of the Mn-O and Mn-O-Mn bonds. The peak at 1085 cm^{-1} indicates a vibration of hydroxyl groups that are joined to Mn atoms. As for peak at 1519 cm^{-1} arises from bending vibration of O-H and H_2O, which implies that water molecule exists in nanostructures. Meanwhile, peak at about 3464 cm^{-1} describes the stretching vibration on O-H bond and bending vibration of the absorbed water molecule in the lattice [12].

B. Method

1) Effect of pH and Ionic Strength: Adsorption batch experiments to investigate the effect of pH and ionic strength was done by preparing 200 mL of phosphate solution with an initial concentration of 10 mg/L into a conical flask. 2.5 g/L of MnO_2 (pyrolusite) was added into the flask before mixing process on thermoshaker at 160 rpm. A variation on pH was set at 2, 4, 6 and 8. pH adjustment was done by using either 0.1 M HCl or NaOH. Sampling was done in a certain interval until the phosphate concentration reached an equilibrium condition. Solution samples were filtered using membrane filter 0.45 µm (Agilent) before phosphate analysis with UV-Spectrometer (Agilent). Ionic strength variation was arranged by using NaCl at 0.01 M, 0.1 M and 1 M. All tests were conducted at temperature 25.5^{o}C.

2) Adsorption Isotherms: Experiments for isotherms study were performed with initial concentrations of 10 – 100 mg/L. All processes were the same with the previous explanation, except for sampling time, which was set 24 hours to make sure equilibrium condition was reached. The collected data of adsorbed phosphate onto MnO_2 at equilibrium condition were then analyzed with two adsorption models, Langmuir and Freundlich.

Langmuir model :
$$q_e = \frac{bq_{max}C_e}{1+b.C_e} \tag{1}$$

Freundlich model :
$$q_e = k_f C_e^n \qquad (2)$$

where C_e is the phosphate concentration in the solution at equilibrium (mgP/L), b is Langmuir constant related to the affinity of binding sites (L/mg), q_{max} is the maximum adsorption capacity (mg/g), k_f is a Freundlich constant related to roughly adsorption capacity (mgP/L), n is the constant related to adsorption density.

3) Adsorption Kinetics: Adsorption kinetics was defined from an experiment with one initial concentration of phosphate (10 mg/L) at 25.5°C. Phosphate concentration was analysed until an equilibrium condition achieved. Two equations were applied to define whether the process fit to pseodo-first order or pseodo-second order.

Pseudo first order :
$$\log(q_e - q_t) = \frac{K_1 t}{2,303} + \log q_e \qquad (3)$$

Pseudo-second order :
$$\frac{t}{q_t} = \frac{1}{2 K q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Where q_t is phosphate concentration over the sampling time (mgP/L), q_e is phosphate concentration at equilibrium condition (mgP/L), K_1 is pseudo first order constant (L/min) and K is a pseudo second order constant ($\frac{g}{mg.min}$)

4) Thermodynamic Data: Thermodynamic data were collected from experiments with different temperature applied (25.5°C, 35°C and 45°C). T, e values of standard enthalpy change (ΔH°) , standard entropy change (ΔS°) moreover, Gibb's free energy (ΔG^0) were determined to ascertain the nature of adsorption process under different temperature condition. Those three parameters can be calculated by applying the following equations :

$$K_d = \frac{C_s}{C_e} \qquad (5)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

where C_s and C_e are the removed and remaining concentrations of phosphate, respectively. R (8.314 Jmol⁻¹K⁻¹) is the ideal gas constant, T is the temparature in Kelvin. While free energy changes (ΔG°) is defined from :

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \qquad (7)$$

The values of ΔH^0 and ΔS^0 were determined from the slope and y-intercept of the plot between $\ln K_d$ versus $\frac{1}{T}$ [2].

III. RESULTS AND DISCUSSION

Results of adsorption experiment in different conditions are presented below.

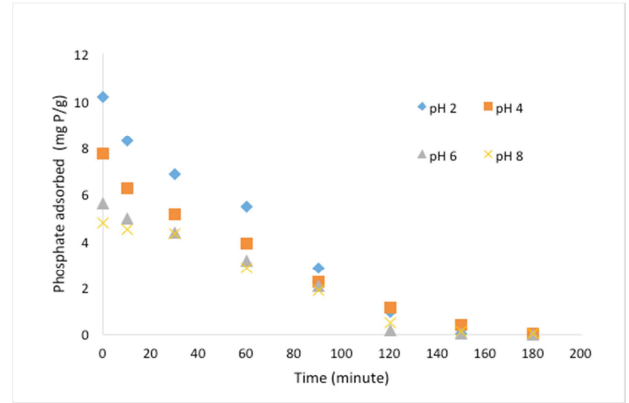## A. Effect of pH and Ionic Strength

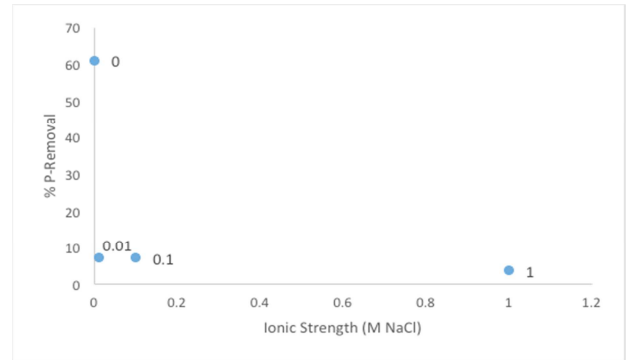Fig.2. Phosphate adsorbed in different pH

Fig.3. % Phosphate removal in different ionic strength ("0" mean there was no NaCl addition)

In all pH condition, the amount of adsorbed phosphate onto manganese dioxide was high at the beginning, indicating a spontaneous reaction, and gradually decreased until an equilibrium stage (after 2.5 hours). Fig. 2 portrays that pH is a significant factor in determining sorption process of phosphate onto manganese dioxide. The higher the pH value, the amount of absorbed phosphate reduced. In this experiment, the most suitable pH for the adsorption of phosphate onto manganese dioxide was 2. The effect of pH can be explained, related to the pH_pzc (point of zero charges) of manganese dioxide. pH_pzc is a pH in which the net charge of chemical substances in the aqueous solution is zero. At pH < pH_pzc the adsorbent's surface will positively charge, while at pH > pH_pzc the surface charge will be negative. The manganese dioxide has a low pH_pzc (1.4<pH_pzc<4.5) [8], later on, it was reconfirmed that the pH_pzc is about 4.2 [11], [12]. Thus, if the pH solution above 4.2 the surface site of adsorbent will have more negative charges because of deprotonation, in which more hydrogen ions leave the sites. Since the domination species of phosphate are negatively charged ($H_2PO_4^-$, HPO_4^{2-}), the interaction with adsorbent will be unlikely. More favorable interaction exists at pH below 4.2 due to protonation at the surface site of manganese dioxide results in more positively charged. In addition to that, at lower pH value the presence of phosphate hydrate ions is ampler than its anhydrate. Thus interaction with the active sites of adsorbent will be much more comfortable. A pH-dependent process indicates that the adsorption of phosphate onto manganese dioxide is driven

by different charges interaction or so-called surface complexation. Phosphate adsorption onto metal oxides has been reported as a dependent process. The amount of adsorbed phosphate tended to increase by decreasing solution pH [5].

Application of ionic strength in different level was intended to explain the sorption mechanism. The increase of ionic strength will reduce the adsorption capacity if electrostatic interaction applies between adsorbate and adsorbent. In contrary, the adsorption capacity will increase along with the increase of ionic strength if different mechanism pertains. The result, as can be seen in Fig. 3., shows a higher level of ionic strength (indicated by the higher concentration of NaCl) the removal of phosphate decreased significantly (about six times lower). The additional concentration of NaCl produces more ions speciation that inhibits the interaction between phosphate and manganese dioxide. This is in another way, indicates that the sorption mechanism of phosphate onto manganese dioxide is driven by electrostatic interaction or surface complexation rather than ligand exchange.

B. Adsorption Isotherms

Adsorption isotherm was used to explain the distribution of adsorbate in liquid and solid phase. Two models, Langmuir and Freundlich, were applied to identify the adsorption isotherm. Data analysis for adsorption isotherms (as can be seen in Fig.4a and 4b) suggested that the adsorbent performance fit better to Langmuir model than Freundlich model, indicated by the higher value of R^2 (0.9955 compared to 0.9397) assuming:

- Manganese dioxide has homogeneous active sites
- A monolayer adsorption process between manganese dioxide and phosphate
- There is no further interaction among adsorbed phosphate

Thus, based on the preferred model, maximum adsorption capacity of manganese dioxide was 11.40 mgP/g (Table I).
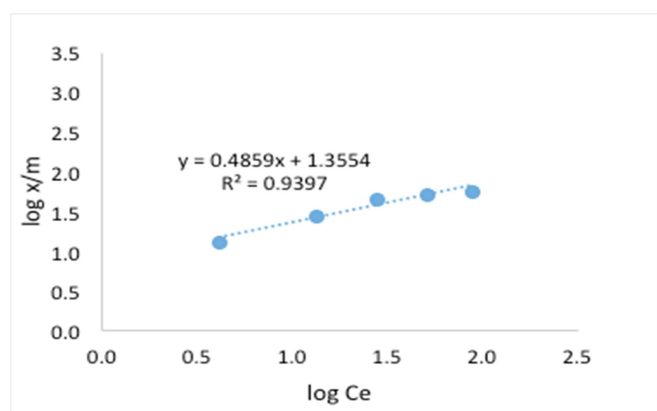

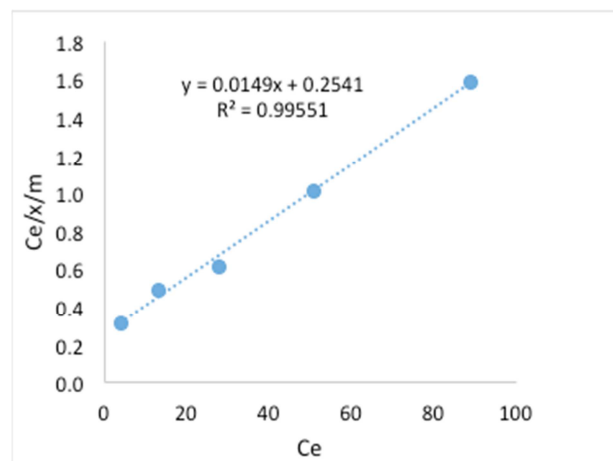Fig. 4(a). The linear plot of Freundlich isotherm

Fig. 4(b). The linear plot of Langmuir isotherm

TABLE I
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS

Langmuir	b	0.02 (L/mg)
	q_{max}	11.40 (mg/g)
Freundlich	K_f	22.67 (mg/g)
	n	2.06

Comparison of the performance of manganese dioxide for adsorbing phosphate in aqueous solution to other natural materials or industrial by-products as reported from previous works can be seen in Table II. The maximum adsorption capacity of manganese dioxide is similar to magnetite, about 1.4 times of iron oxide tailings, almost two times higher than vesuvianite and fly ash and 2.4 times of dolomite. This result is promising for further development.

TABLE II
COMPARISON OF ADSORBED PHOSPHATE IN SEVERAL NATURAL MATERIALS

Adsorbent	Adsorption Capacity (mgP/g)	Reference
La-doped vesuvianite	6.70	[7]
Magnetite	11.20	[13]
Iron oxide tailings	8.20	[14]
Class F fly ash	6.60	[15]
Natural palygorskite	4.00	[16]
Dolomite	4.76	[17]
Manganese dioxide	11.40	This study

C. Adsorption Kinetics

Adsorption kinetics was applied as one of the most important factors to identify the adsorption efficiency and working mechanism of adsorbent. The removal of phosphate from aqueous solutions was occurred relatively fast, in 2.5 hours the adsorption process reached an equilibrium condition. A rapid adsorption rate could be ascribed to the high driving force provided by the concentration gradient of phosphate in aqueous solutions and the large number availability of active sites on the surface of manganese dioxide [4]. Measurement on phosphate concentration at 24 and 48 hours was done, and there was no indication of

further reaction (no additional removal) or desorption confirming that effective process was found at the initial phase (Fig.5.)
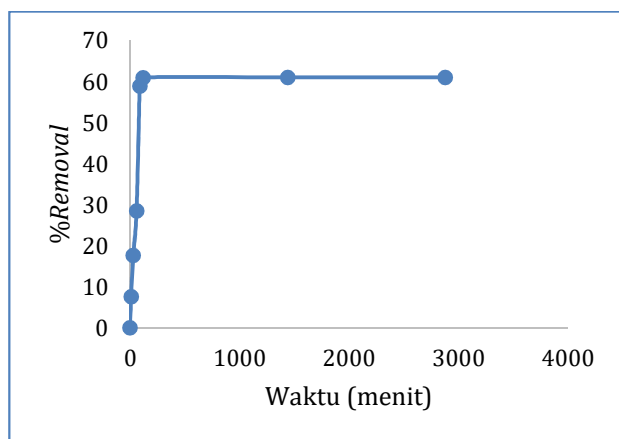

Fig. 5. % Removal of Phosphate as a Function of Time, pH = 2, T = 25.5°C, initial concentration = 10 mg/L

To further evaluate the adsorption mechanism of phosphate onto manganese dioxide, two model equations, pseudo first order, and pseudo second order were employed. Experimental data, the concentration of phosphate over the time periods of monitoring (q_t) and concentration of phosphate at equilibrium condition (q_e) were fitted to both models (Fig. 6a and 6b).

Based on regression coefficients, adsorption process of phosphate onto manganese dioxide was much better represented by pseudo-second-order model (R^2 = 0.9999) compared to the pseudo-first-order model (R^2 = 0.8341). This indicates that chemisorption rather than physisorption drives adsorption mechanism and only induces a monolayer system. This finding inline with isotherm model that follow Langmuir equation, which is also, assume a monolayer adsorption process. A similar finding was reported by previous work, suggesting that the adsorption process of phosphate onto manganese dioxide involves valency forces through sharing or exchanging electrons between adsorbate and adsorbent [2], [9], [17].
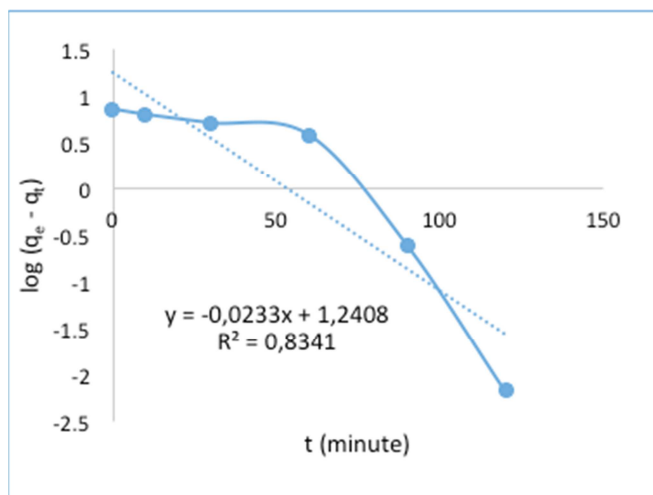

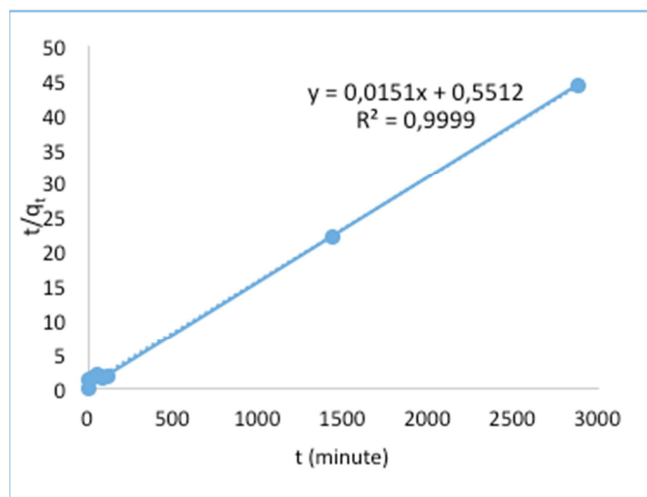Fig. 6(a). pseudo-first-order model for phosphate adsorption

Fig. 6(b). pseudo-second-order model for phosphate adsorption

D. Thermodynamic Data

Temperature is a significant factor in determining the adsorption process. The result of adsorption experiment in different temperature conditions showed that the removal of phosphate from aqueous solutions slightly increased with the increase of temperature. The highest removal, 62.63%, was achieved at the highest temperature applied, 45°C (Fig.7.).
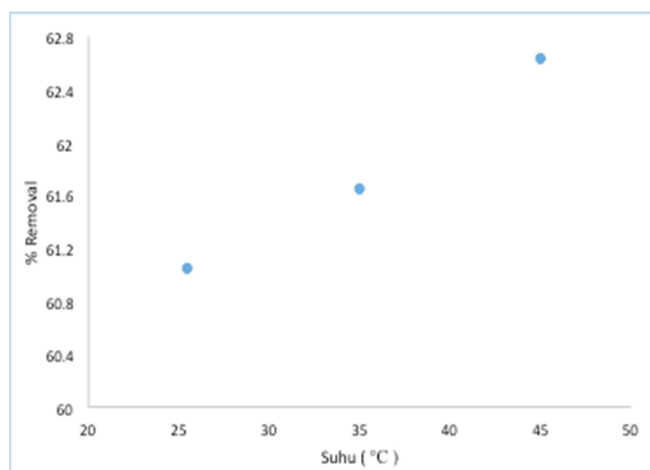

Fig.7. % removal of Phosphate in Different Temperature Conditions

This phenomenon can be explained as the increase in temperature there will be dehydration on phosphate ions, results in unstable binding between the ions. The more unstable the binding will make the adsorption of phosphate onto manganese dioxide sites easier. It seems more energy needed to enhance the adsorption process. By increasing temperature, more energy will be provided thus the interaction between phosphate ions and active sites of manganese dioxide will be more intense, results in more adsorbed phosphate.

To evaluate the adsorption mechanism of phosphate onto manganese dioxide, the thermodynamic parameters ($\Delta G^o, \Delta H^0, \Delta S^0$) were determined in various temperatures (298.65 ; 308.15 and 318.15 K). A plot of ln K_d versus 1/T was found to be linier, as can be seen in Fig.8. From that plot, the values of ΔH^0 and ΔS^0 were ascertained. Then, from both parameters the value of ΔG^0 could be calculated.
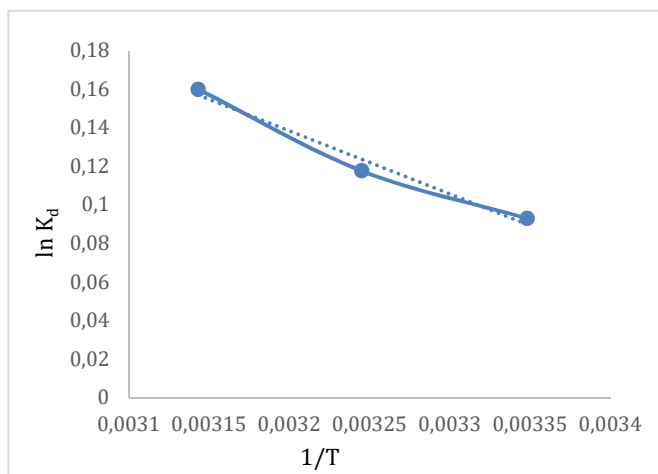
Fig.8. Van't Hoff plot of adsorption equilibrium constant, K_d

TABLE III
Thermodynamic Parameters of Phosphate Adsorption

T (K)	C_0 (ppm)	$\Delta S°$ (J/mol.K)	$\Delta H°$ (J/mol)	$\Delta G°$ (J/mol)
298.65	106.80	10.81	2710.63	-517.26
308.15	106.40	10.81	2710.63	-619.93
318.15	106.55	10.81	2710.63	-728.02

The analysis of thermodynamic data revealed several essential pieces of information (Tabel III) that explain the adsorption mechanism. The decrease in ΔG^0 value with the increase of temperature suggests that the adsorption process is more favour at high than at low temperature. This is an indication that the nature of phosphate adsorption by manganese dioxide was not spontaneous. Or, it can be said that the spontaneity of adsorption is driven by the temperature. The negative value of ΔG^0 confirms that energy is needed to enhance the reaction, the energy requirement is bigger at lower temperature. The positive value of $\Delta H°$ denotes that the adsorption process is endothermic and irreversible, probably due to non polar interactions [2]. However, the low value of $\Delta H°$ the point to the adsorption of phosphate onto manganese dioxide is weak. Meanwhile, the positive value of ΔS^0 indicates that randomness at the solid-liquid interface increases during the adsorption process of phosphate onto manganese dioxide. It also reflects the affinity of the adsorbent for phosphate and suggests some structural changes in adsorbate and adsorbent [3].

Many scientific reports have mentioned that endothermic reaction drives the adsorption process of phosphate for most adsorbents, for example, iron oxide tailings, bentonite, red mud, [3], [14], [18]. Referring to the low values of standard Gibbs free energy that have been obtained in this study, the use of manganese dioxide as an adsorbent for phosphate will save energy consumption.

IV. CONCLUSIONS

Manganese dioxide in natural form (Pyrolusite) can be used as an adsorbent to remove phosphate from aqueous solutions. The adsorption process was pH dependent. In this study, the most effective process was at pH = 2. Adsorption isotherm was fitted to Langmuir better compared to Freundlich model. The maximum adsorption capacity of manganese dioxide following the Langmuir is 11.40 mg Phosphate/g. Pseudo-second order model best represented the adsorption kinetics characteristic. Indicating that adsorption process is mainly driven by chemical reaction (chemisorption). Thermodynamic data demonstrated that the adsorption process of phosphate onto manganese dioxide is endothermic and at high affinity. Compared to several natural materials, manganese dioxide (Pyrolusite) presented a considerably higher adsorption capacity for phosphate removal. However, modification to enlarge its capacity needs to be investigated to find the optimum condition of the adsorbent utilization.

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