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Kinetic Study of the Recovery of Phosphorus from Wastewater by Calcium Hydroxide Solution

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ABSTRACT

This research presents a study for precipitating phosphorus (as phosphate ion) from simulated wastewater (5ppm initial concentration of phosphorus) using calcium hydroxide $Ca(OH)_2$ solution. The removal of phosphorus by $Ca (OH)_2$ solution is expected to be very effective since the chemical reaction is of acid-base type but $Ca(OH)_2$ forms complex compound with phosphate ions called. Hydroxyapatite $Ca_5 (PO_4)_3OH$. hydroxyapatite is slightly soluble in water. This research was directed towards sustainable elements as phosphorus. Kinetics of the dissolution reaction of hydroxyapatite was investigated to find the best factors to recover phosphorus. The effect of concentration of $Ca(OH)_2$ (180- 380 ppm) on phosphorus precipitation on the outputs like the residual phosphorus concentration in the simulated solution, the percentage removal of phosphorus and the weight of the precipitate was also studied. The residual phosphorus decreased with increasing $Ca(OH)_2$ concentration while the percentage removal, as well as the weight of the precipitate, increased with increasing $Ca(OH)_2$ concentration at constant temperature and mixing speed. The best $Ca(OH)_2$ concentration was obtained depending on the lowest amount of the residual phosphorus concentration. The best value obtained was 230 ppm at a fixed mixing speed of 400 rpm and a temperature of 20°C. The best value for $Ca(OH)_2$ concentration under fixed stirring speed and temperature was applied on a real wastewater taken from the detergent factory. The percentage removal was 30. 69% due to the complexity of the real sample. Oxalic acid was chosen to dissolve hydroxyapatite because it is an organic acid, less hazardous than mineral acids and of less cost. Kinetics of the dissolution reaction of hydroxyapatite in (160 ppm) concentration oxalic acid under ambient conditions (20°C and 1 atm) and mild stirring (200 rpm) was studied using the differential method for determining the order of the reaction which was 0.4296 and the rate constant 0.0743 $(L/mg)^{-0.5704}$. min^{-1}. The reaction was considered as a rate-controlled reaction.

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دراسة حركية تفاعل الاسترجاع للفسفور من المياه الصناعية باستخدام محلول هيدروكسيد الكالسيوم

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الخلاصة

هذا البحث يقدم دراسة لإزالة الفسفور (كأيونات الفسفور) من مياه مطروحة محاكاة بتركيز ابتدائي للفسفور 5 جزء بالمليون باستخدام محلول هيدروكسيد الكالسيوم. ان ازالة الفسفور باستخدام محلول هيدروكسيد الكالسيوم يتوقع ان تكون فعالة جدا لان التفاعل الكيميائي هو من نوع حامض – قاعدة لكن هيدروكسيد الكالسيوم يكون مركب معقد مع ايونات الفوسفات يسمى هيدروكسي ابتايت $Ca_5(PO_4)_3\ OH$. هذا المركب قليل الذوبان في الماء. هذا البحث وجه لدراسة العناصر المستدامة مثل الفسفور. درست حركية تفاعل اذابة الهيدروكسي ابتايت في الماء لإيجاد أفضل الطرق لاسترجاع الفسفور. ايضا درس تأثير تركيز $Ca(OH)_2$(180-380 ملغرام/لتر) على ترسيب الفسفور مضافا الى الماء في دورق على مخرجات مثل: تركيز الفسفور المتبقي، النسبة المئوية لإزالة الفسفور ووزن الراسب. تبين ان تركيز الفسفور المتبقي يقل بزيادة تركيز هيدروكسيد الكالسيوم لكن النسبة المئوية للإزالة بالإضافة الى وزن الراسب يزداد بزيادة تركيز هيدروكسيد الكالسيوم بثبوت درجة الحرارة وسرعة المزج. تم الحصول على أفضل قيمة لتركيز هيدروكسيد الكالسيوم بالاعتماد على اقل قيمة لتركيز الفسفور المتبقي. أفضل قيمه كانت 230 ملغرام/لتر بثبوت سرعة المزج على 400 د/ثانيه ودرجه الحرارة 20 درجه مئوية. طبقت أفضل قيمة لتركيز هيدروكسيد الكالسيوم بثبوت سرعة الخلط ودرجة الحرارة على ماء مطروح حقيقي مأخوذ من معمل المنظفات.

نسبة الإزالة كانت 30.69% بسبب تعقيد النموذج الحقيقي. اختير حامض الاوكزاليك لإذابة الهيدروكسي ابتايت لأنه حامض عضوي، اقل خطورة من الحوامض المعدنية، اقل كلفة. تم دراسة حركية تفاعل الاذابة لهيدروكسي ابتايت في (160 ملغرام/لتر) تركيز حامض الاوكزاليك تحت ظروف المحيط (20 درجة مئويه، ضغط 1 جو) و سرعة خلط معتدلة (200 د/دقيقه) باستخدام الطريقة التفاضلية لتحديد مرتبة التفاعل والتي كانت 0.496 وثابت سرعة التفاعل 0.0743 (لتر/ملغرام)$^{-0.5704}$ دقيقة$^{-1}$. لذألك اعتبر التفاعل من التفاعلات المسيطر عليها من النسبة التفاعلية.

الكلمات الرئيسية: ازالة الفسفور، معالجة المياه المطروحة، الترسيب الكيميائي، هيدروكسيد الكالسيوم، هيدروكسي ابتايت ، استرجاع الفسفور.

1. INTRODUCTION

The main reason for wastewater treatment is to keep rivers, lakes and streams pure and healthy. If contaminants in wastewater are not eliminated, they go straight into waterways. This will affect negatively on human health, wildlife and fisheries. Phosphorus in wastewater is a necessary nutrient for growing living creatures and plants. Flowing these nutrients into collecting sources will increase in growing algae and causes eutrophication in lakes and rivers **Banu, et al., 2008**. This will disperse the balance of these micro creatures that present in water and will affect water purity, especially when oxygen is disappeared at algae decomposition. When oxygen content is decreased, this can make serious effects on fish and the mini living creatures which will have side effect on biodiversity to be depleted. There are many sources of phosphorus in water. The major sources are domestic and industrial wastewater, agricultural because of using fertilizers, and deposition, **Plaza, et al., 1997.** Wastewater treatment is classified into three major groups; biological, chemical, and physical, **Tchobanoglous, 1991**. The treatment by chemical processes involves changing the contaminants by using chemicals. Chemicals used in this treatment to treat (remove) phosphorus are basically alum, calcium hydroxide, calcium oxide, and many other chemicals that purify water, **Moniwa, 2010**. Chemical precipitation, biological phosphorus recovery, crystallization, advanced chemical precipitation, and ion exchange techniques are the most common and advanced for phosphorus removal and recovery from wastewater, **Strom, 2006**. Chemical precipitation removes phosphorus bound as a metal salt with waste sludge, and because of its flexibility, it's applied at any step through wastewater treatment.

Biological phosphorus removal happens when activated sludge takes up phosphorus in considerable raise without chemical usage and excess sludge production, **Sommarivan, 1996**. In the crystallization process, phosphorus removal produces a marketable end-product in the form of calcium phosphate, and the crystallization happens when adding either milk of lime or caustic soda. Advanced chemical precipitation is pointed to as HYPRO and happens when the crystallization of phosphorus organic matter and hydrolysis producing carbon and energy in an obtainable form. The ion exchange technique forms struvite. During the ion-exchange precipitation process, phosphorus and NH_3 ions form struvite when recovered from wastewater, **Adnan, 2003.** Many chemicals are used in precipitating phosphorus from wastewater such as metal salts, iron (either Fe^{+2} or Fe^{+3}), aluminum (either sodium aluminate, $NaAl_2O_4$, or alum, $Al_2(SO_4)_3.18H_2O$), or calcium (Ca^{+2}), **Droste, 1997**. Some processes focused on treating wastewater in order to remove phosphorus by adsorption onto natural and local materials limestone, bauxite, porcelanite, and burned kaolin. The efficiency of removal for limestone was 90%, bauxite 30 %, porcelanite 90% and burned kaolin showed the lowest adsorption capacities in these tests, **Abdul Wahab, et al., 2011**. Also, an experimental study used to evaluate phosphorus removal from wastewater by a moving bed biofilm process and the removal efficiency was76%, **Al-Zuhairy, et al., 2015**. Calcium hydroxide has a less solubility in water (1560 mg/L) at 20°C which is 220 less than alum and 550 less than ferric chloride solubility, this is the disadvantage of using calcium hydroxide. The pH of calcium hydroxide in a wastewater solution increases to more than 10, excess. The reaction between calcium ions and phosphate precipitates hydroxyapatite [$Ca_9(OH)(PO_4)_3$]. The hydroxyapatite formation reaction is:

$$5Ca^{+2} + 4OH^{-} + 3HPO_4^{-} \rightarrow Ca_5OH(PO_4)_3 + 3H_2O \qquad \ldots\ldots (1)$$

The reaction is first order, endothermic, and the activation energy is 95000 J/mole (22700 Cal/mole), **Changsheng, 2001**. This research was devoted to removing phosphorus from wastewater by using calcium hydroxide. Although calcium hydroxide was regarded as less promising than aluminum and ferric compounds because of its scarce solubility in water it was used because it is a strong base and it was expected to be efficient in removing phosphorus from aqueous solutions since it is of acidic nature. The kinetics of chemical dissolution reaction was studied in order to understand the complexity of the solubility process. There are eight models used to show the kinetics of the chemical reaction which describes basic reaction parameters (pH, saturation and hydrodynamics, and structure synthesis), the roof of the calcium phosphate (hydroxyapatite), and bulk solid properties (solubility, particle volume, chemical composition). Hydroxyapatite is considered as an essential source of phosphorus in nature and exists in bones and teeth. Therefore, calcium phosphate is the most common source for many usages like fertilizer production and medical things such as covering the synthetic bone graft), **Maurer, 1999.** The present research focuses on the criteria of sustainable elements recovery and recycling. Using chemical precipitation for phosphorus removal from wastewater by using calcium hydroxide with different concentrations to obtain the best removal of phosphorus. Then approaching to recover phosphorus from this complex, slightly soluble substance. Oxalic acid was chosen to dissolve hydroxyapatite because it is an organic acid, less hazardous than other mineral acids and of low cost, **Wilhelm, et al., 2002**. It was attempted to carry out the dissolution of hydroxyapatite under ambient conditions to achieve promising recovery.

2. EXPERIMENTAL WORK

Materials used in the research are shown in **Table 1.**

Table 1. Specifications of materials.

Name	Formula	Purity %	Source or (company)
Calcium hydroxide	$Ca(OH)_2$	95%	MAY and BAKER L (DAGENHAM)
Monopotassium phosphate	KH_2PO_4	commercial	CHINA
Deionized water	H_2O	Cond. ≤ 3	IRAQ
Oxalic acid	$C_2H_2O_4$	99.6%	CHINA

As a first step, simulated water was prepared with (5 ppm) of phosphorus concentration by dissolving (0.219 g) of KH_2PO_4 in (1L) of deionized water. The initial concentration of phosphorus was fixed at (5 ppm) for all of the experiments.

Different dose concentrations of $Ca(OH)_2$ were added to the simulated water of (5 ppm) phosphorus at constant mixing speed and temperature. $Ca(OH)_2$ concentration was changed to values (180 ppm, 230 ppm, 280 ppm, 330 ppm, and 380 ppm) while the mixing speed and temperature were fixed at (400 rpm) and (20 °C), respectively. Mixing speed at 400 rpm was continued for (10 min) then it was lowered to (80 rpm) for (30 min) to allow settling. The best concentration of $Ca(OH)_2$ was determined according to the minimum phosphorus concentration in the solution.

After filtration, the sample was then dried for (24 hr.) to calculate its weight using sensitive balance (Precisa/Switzerland).

For each calcium hydroxide concentration, pH was recorded and Making UV test for phosphorus concentration measurements.

The best $Ca(OH)_2$ concentration was applied to a real wastewater taken from the detergent factory for phosphorus precipitation at constant temperature and stirring speed.

In order to recover phosphorus, the precipitate was dissolved in acidic solution. The dissolution was greatly enhanced in an oxalic acid solution of concentration (160 ppm). The concentration of dissolved phosphorus was recorded against time to study the dissolution kinetics under ambient conditions (20°C and 1 atm) and mixing speed (200 rpm).

3.RESULTS and DISCUSSION

The experimental results show that increasing the concentration of calcium hydroxide reduces the concentration of phosphorus in the simulated wastewater. It was found that phosphorus concentration was minimized at 230 ppm concentration of $Ca(OH)_2$. This means that the reaction reaches completion. Higher concentrations of calcium hydroxide are unnecessarily costing. The results showed that 230 ppm of calcium hydroxide was the best concentration to precipitate phosphorus at a fixed temperature (20°C) and stirring speed (400 rpm) as shown in **Fig.1**. Increasing the concentration of $Ca(OH)_2$ increased the weight of precipitate as illustrated in **Fig. 2**. The formation of hydroxyapatite by precipitation was observed when pH ranged between 9.85 and 11.66 as shown in **Fig. 3**. It is obvious that increasing pH offers good conditions for hydroxyapatite formation. Increasing stirring speed beyond (400 rpm) retards the formation of hydroxyapatite crystals, therefore; the stirring speed was fixed at (400 rpm) throughout the whole experiments. This may be explained due to the formation of nuclei of hydroxyapatite crystals which are growing with increasing stirring speed at intermediate values but increasing stirring speed further destroy them. It is obvious from **Fig. 4** that 100% removal attained at $Ca(OH)_2$ concentration 230 ppm.

The result obtained from the previous experiment is applied to a real wastewater sample taken from Al-Rasheed Factory for Soap. The analysis shows that the real concentration of phosphorus from one of the most sources of pollution was 7.9 ppm which exceeds even the common value. The treatment used was exactly the same as that obtained as the best value of $Ca(OH)_2$ solution but the percentage removal was only 30.69 %. The result of percentage removal for real wastewater seems to be a low value for removing phosphorus. The reason is that 230 ppm of $Ca(OH)_2$ which was the best value to precipitate 5 ppm of phosphorus in the simulated wastewater is inadequate to precipitate 7.9 ppm in the real wastewater. However, it is not believed to precipitate all phosphorus exists in real wastewater because organic phosphorus which definitely exists in real wastewater cannot be removed completely. It has very complex structures that must be dealt with additional agents.

The reason beyond not applying the stoichiometric equation to obtain the required amount of calcium hydroxide to precipitate 7.9 ppm of phosphorus was the limited

Amount of real wastewater:

$$C_B = \frac{230\,ppm}{5\,ppm}\,C_A = 46\,C_A$$

Where C_A: Concentration of P before precipitation, ppm.

C_B: Concentration of calcium hydroxide required to remove all P, ppm

Using stoichiometry to calculate the required $Ca(OH)_2$ concentration is not promising because the precipitation reaction of phosphorus by $Ca(OH)_2$ is very complicated and many approaches were published in this aspect as mentioned in the literature **Maurer, 1999**.
So the kinetics study was essential to explore some ambiguous behavior of the system.
By using the differential method, the rate of reaction including the order of the reaction and the rate constant for the chemical dissolution reaction of phosphorus in oxalic acid was found. **Fig.5** shows the behavior of phosphorus with time during the dissolution reaction. Different slopes were estimated to find the $\frac{dCA}{dt}$ for each CA as listed in **Table 3**.
Fig.6 shows (- ln $\frac{dCA}{dt}$) versus (ln CA) and the best fitting equation was:

$$Y = 0.4296\,X + 2.5987 \qquad \ldots\ldots\ldots\ldots \textbf{(2)}$$

As compared with the linear equation:

$$Y = m\,X + B \qquad \ldots\ldots\ldots\ldots \textbf{(3)}$$

Where Y: -ln $\left(\frac{dCA}{dt}\right)$

X: ln CA

m: slope of the best fit straight line = n order of the reaction.

B: intercept = k reaction- rate constant.

The order of the reaction n = 0.4296
The rate constant of the reaction ln k = -2.5987

And the rate constant k = 0.0743 $(L/mg)^{-0.5704}$. min^{-1}

The rate of the reaction will be

$r_A = K\,C_A^n$

$r_A = 0.0743\,C_A^{0.4296}$ mg/L. min

This result shows that the dissolution reaction is slow because the rate constant is low and the rate of the reaction depends on phosphorus concentration to the power (0.4296). So the dissolution reaction can be classified as rate - controlling reaction.

$$\text{Yield} = \frac{weight\ of\ precipitate}{weight\ of\ limiting\ reactant}$$

the weight of precipitate is 0.0215g in 0.5 L
The weight in 1 L = 0.043 g = 43 mg
The weight of limiting reactant is 5 mg in 1L
Yield = $\frac{43}{5} = 8.6$ which is satisfying yield if it is intended to use the precipitate as fertilizer.

The yield of hydroxyapatite obtained from (230ppm) calcium hydroxide and (5ppm) phosphorus was (8.6 ppm) which is satisfied amount if it is intended to use it as fertilizer.

4. CONCLUSIONS

1. Chemical precipitation of phosphorus by calcium hydroxide reaches 100%. This result was obtained within experimental conditions of this study which are 230 ppm $Ca(OH)_2$, 400 rpm and 20°C.
2. $Ca(OH)_2$ is considered as a chemical regulator of pH in water.
3. Although the result of percentage removal of phosphorus for real wastewater was only 30.69%, recovering 30.69% of phosphorus through recycling is promising.
4. The yield of the hydroxyapatite was 8.6 ppm obtained from 5 ppm phosphorus. This is an important result for recovering and recycling phosphorus as an essential element for living creatures.
5. The dissolving of hydroxyapatite can be enhanced by using an organic acid such as oxalic acid, but the rate of the dissolution reaction is very slow.

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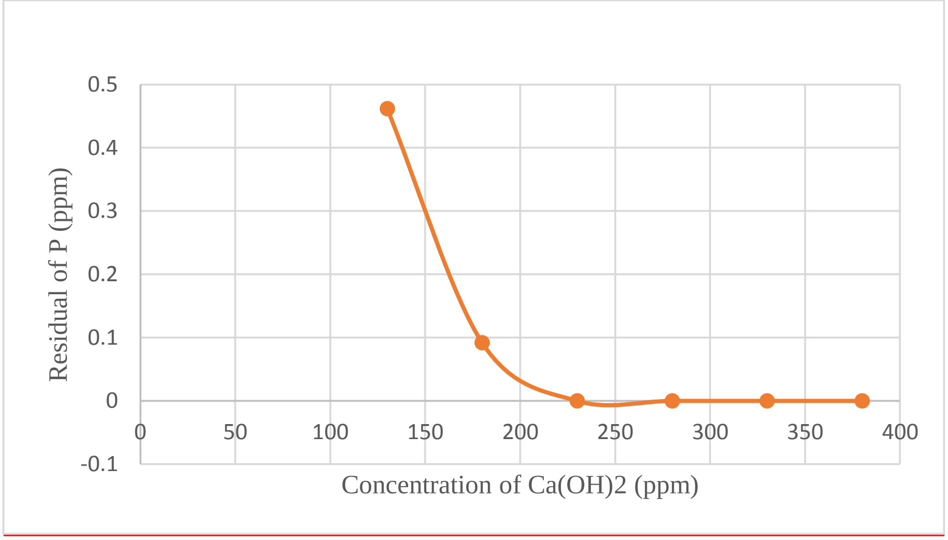

Figure 1. Residual of phosphorus in (ppm) as a function of $Ca(OH)_2$ concentration at 400 rpm stirring speed and 20 °C.

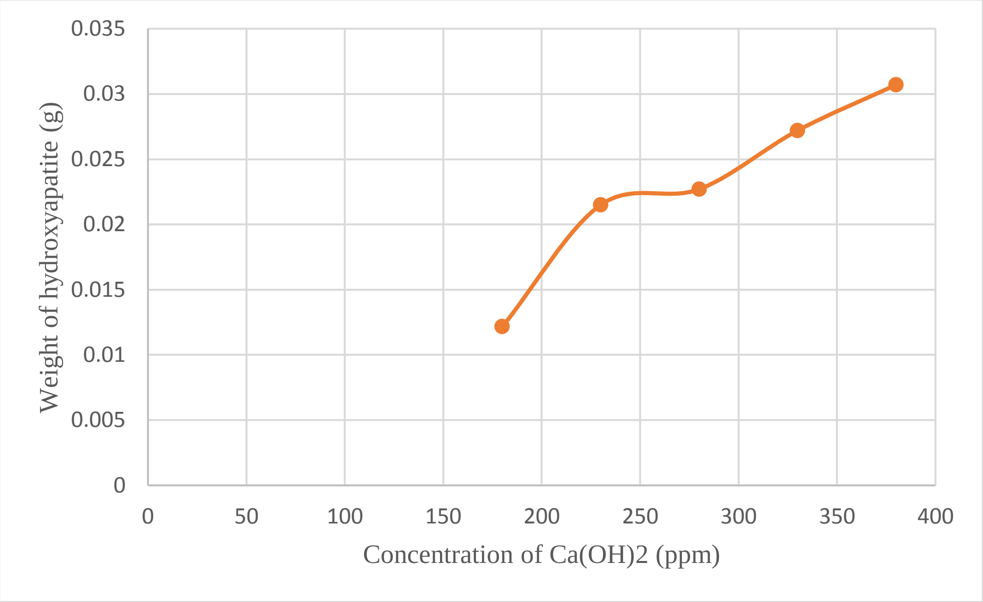

Figure 2. The weight of precipitate as a function of $Ca(OH)_2$ concentration.

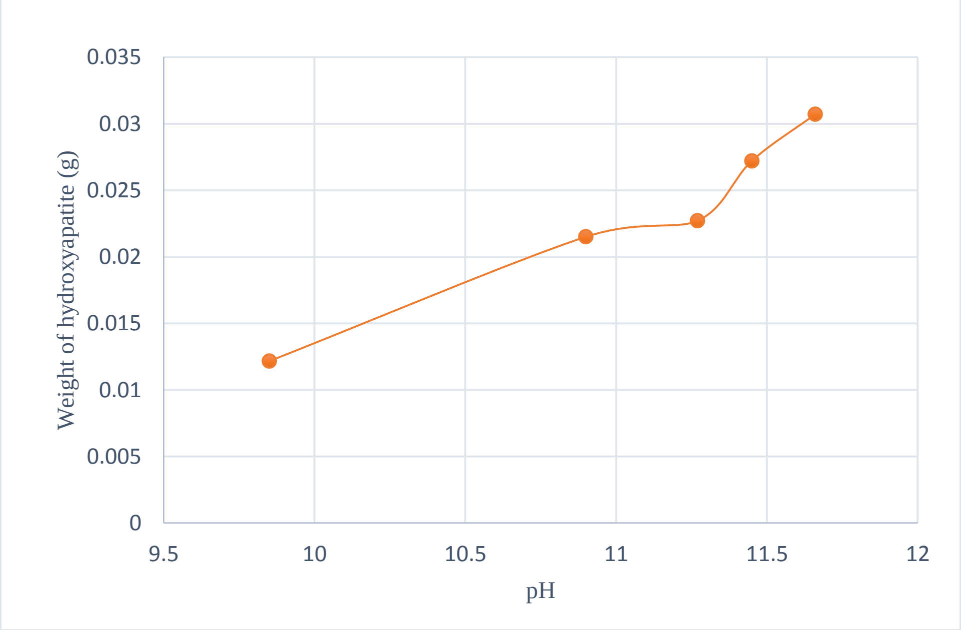

Figure 3. Hydroxyapatite weight (gm) as a function of the solution pH.

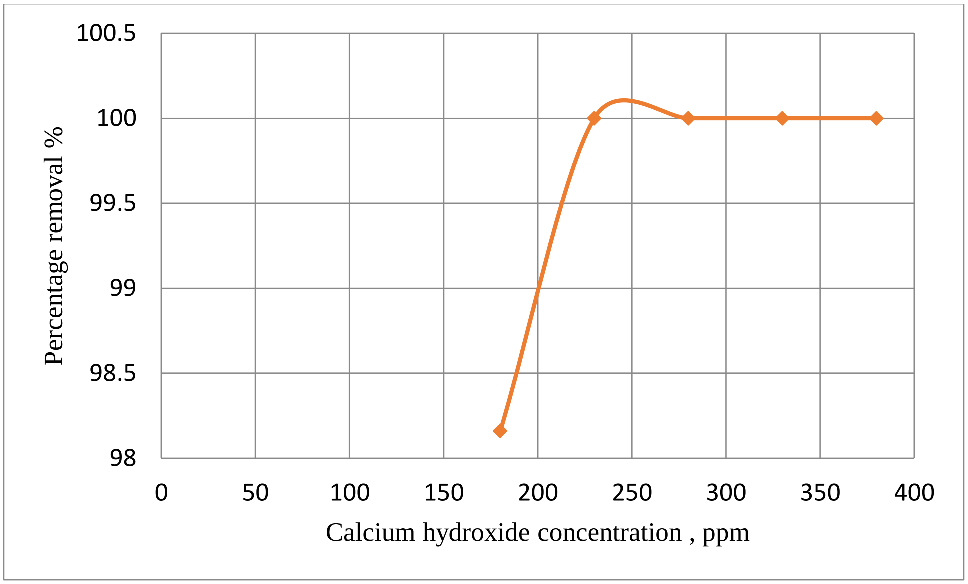

Figure 4. Percentage removal of phosphorus as a function of $Ca(OH)_2$ concentration.

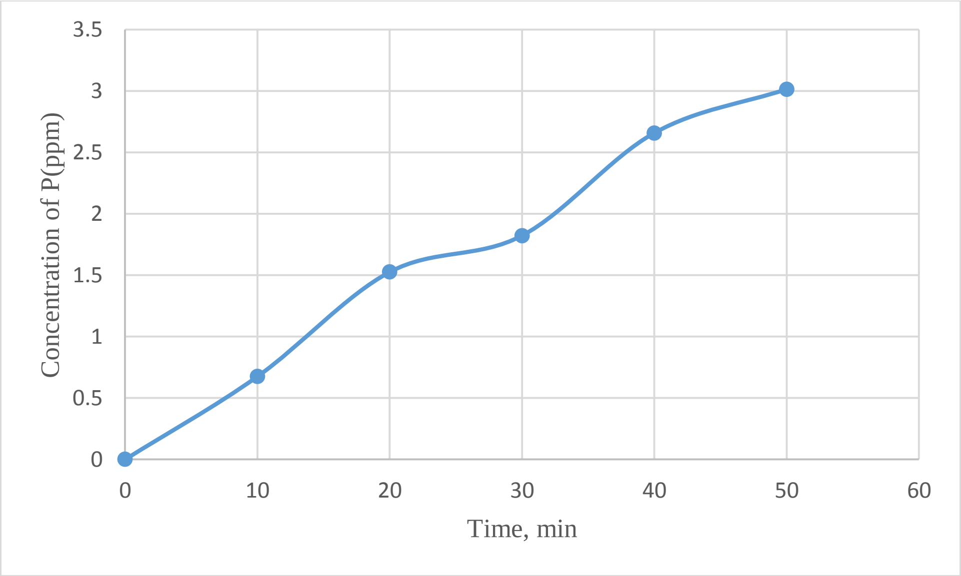

Figure 5. The concentration of P obtained from a simulated sample of 230 ppm $Ca(OH)_2$ with time dissolved in oxalic acid**.**

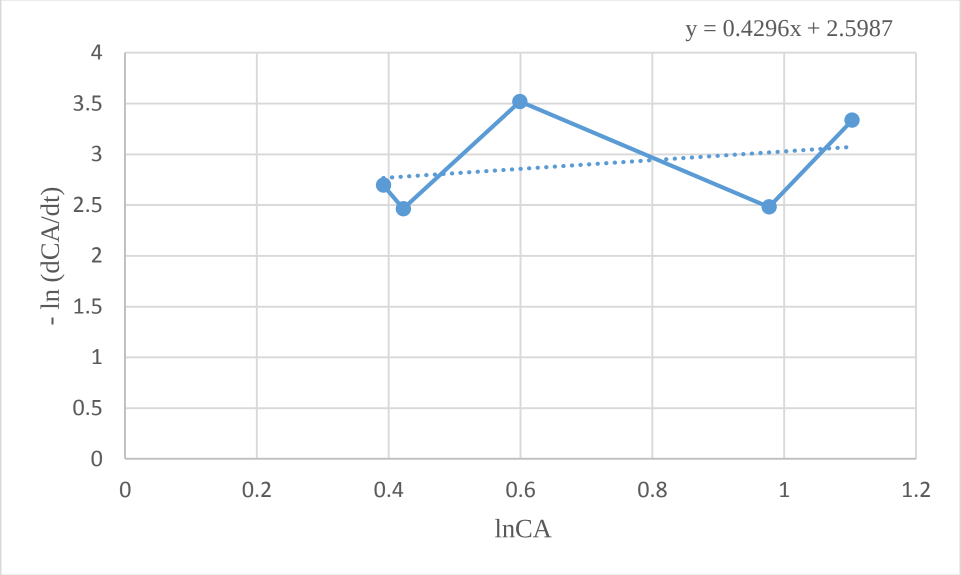

Figure 6. (-ln ($\frac{dCA}{dt}$))vs ln CA for a precipitate obtained in the simulated sample with 230 ppm $Ca(OH)_2$ the solvent is oxalic acid.

Table 2. Comparison of the present work with previous works.

Name of the researcher	PH	Percentage Removal	Precipitating agent	Type of Wastewater
Sawsan and Haider(2009)	5.7-6	83%	Alum	Simulated wastewater
Per Olof Persson and Bengt Hultman(2010)	---------	95%	Magnetite	Simulated wastewater
Ehssan (2012)	4	85%	Aluminum Sulphate	Simulated wastewater
Ehssan (2012)	8.5-10	80%	Iron Sulphate	Simulated wastewater
Present Research (2017)	10.9	100%	Calcium Hydroxide	Simulated wastewater

Table 3. The kinetic data of dissolution of phosphorus in oxalic acid.

Time (min)	C_A (ppm)	Ln C_A	-Ln (d C_A/dt)
10	0.6752	0.392	-2.695
20	1.526	0.422	-2.464
30	1.822	0.599	-3.519
40	2.658	0.977	-2.481
50	3.014	1.103	-3.335