Phosphorus Removed from Wastewater as Fertilizer

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Abstract: -

This research is a study concerns in using the complex compound called hydroxyapatite $Ca_5(PO_4)_3OH$ which was obtained by precipitating phosphorus from simulated wastewater using $Ca(OH)_2$ as fertilizer. The concentration of $Ca(OH)_2$ was varied (180-380 ppm) to obtain the best for a fixed phosphorus concentration (5 ppm), stirring speed (400 rpm) and temperature (20 °C). The important thing for a fertilizer is its dissolution in the soil. Therefore; this study investigates the dissolution of the insoluble precipitate (hydroxyapatite) in oxalic acid which is an organic acid not harmful for plants. The dissolution was reversible because oxalic acid is a weak acid. The factors studied were the concentration of oxalic acid (100 -180 ppm), the stirring speed (100 – 500 rpm) and the temperature (20 – 60 °C). The best conditions were taken as that gave the maximum recovery of phosphorus, i.e. the maximum concentration of phosphorus in solution (1.8 ppm). The best conditions were: oxalic acid concentration (160 ppm), stirring speed (200 rpm) and temperature (30°C). Acidity was recorded during the experiments. It was shown that the acidity (as general trend) increased with increasing mixing speed and decreased with increasing temperature. The dissolved phosphorus increased with increasing mixing speed and decreased with increasing temperature. The study reached to enhance the dissolution of the precipitate by using a strong mineral acid like sulfuric acid in addition to oxalic acid with such little amount as two drops (0.5M) in (34ml) solution. The dissolution enhanced and became irreversible. The concentration of dissolved phosphorus was (2 ppm) at the best conditions. The best conditions were applied on a real precipitate obtained by phosphorus recovery from industrial wastewater.

Keywords: phosphorus removal, wastewater treatment, precipitation, hydroxyapatite, oxalic acid, fertilizer.

Introduction:

The main reason for wastewater treatment is to help and maintain lakes, rivers, and streams healthy [6]. If the contaminants are not removed from wastewater, they will go into our waterways. This can threaten health, fishery, and our quality of life. The presence of Phosphorus in wastewater is considered as an important and necessary nutriment for plant and tiny living creature's growth [3]. Discharge large quantities of this nutriment into sources of collecting water will raise the growth of algae and causes eutrophication of lakes, rivers, and streams [1]. This will make disturbance in the balance of these tiny creatures that present in water and may affect oppositely on water quality, mainly by depletion of oxygen as the algae decomposition. Depletion in oxygen level caused harmful effects on fish and other living life, resulting reduction in biodiversity. Discharge phosphorus to a receiving waters comes from many sources [4]. The main sources are agricultural because the use of fertilizers, industrial and domestic wastewater, and deposition of atmospheric [10]. Wastewater treatment classified into three major groups; physical, chemical and biological wastewater treatment. Chemical precipitation, advanced chemical precipitation, ion exchange, biological phosphorus removal, and crystallization techniques are the most common use for phosphorus removal and recovery from wastewater [13]. By chemical precipitation process makes bound as a metal salt within waste sludge, and because of its flexibility, can be used at any level through wastewater treatment [12]. In a previous work [14] the researchers focused on chemical precipitation for phosphorus removal from wastewater by using calcium hydroxide with different concentrations to precipitate phosphorus which produced complex compound insoluble in water (hydroxyapatite). The present research completes the results obtained previously [14] and dissolving the precipitate by adding a weak organic acid (oxalic acid) which is considered as an important substance in soil processes (e.g., mineral weathering and metal detoxification in plants) [15]. From

the industry's viewpoint, it's more promising and useful for recovering phosphorus from wastewater as calcium phosphates than other forms due to its importance in agriculture but it is considered a slightly soluble fertilizer [11]. Calcium phosphate is very useful for plant cell, also important for division of the cells, and for developing the growth of tip of the plant, this is why it's use for seedlings and in growth of young plants [2]. It was attempted to use organic acids such as oxalic acid to increase the dissolution of the complex compound of phosphorus, hydroxyapatite. Therefore; it can be used in agriculture [8]. This research presents a study of using hydroxyapatite as fertilizer by adding organic acid such oxalic acid and enhancing the solubility by adding two drops of sulfuric acid. Also studying the effect of oxalic concentration, stirring speed and temperature on the dissolution process.

Material and Method: -

Materials: materials used in the research

Name	Formula	Purity %	Source or (company)
Hydroxyapatite	$Ca_5(PO_4)_3OH$		Prepared experimentally
Oxalic acid	$C_2H_2O_4$	99.6 %	CHINA
Deionized water	H_2O	Cond. ≤ 3	IRAQ

Methods: -

Calcium hydroxide was used to precipitate phosphorus from simulated waste water. The best conditions obtained [14] were: $Ca(OH)_2$ concentration (230ppm), stirring speed (400 rpm) and (20 °C) temperature. After precipitation a white powder formed called calcium phosphate (hydroxyapatite).

In this research, the aim of the work is completed by dissolving hydroxyapatite in different concentrations of oxalic acid (100

ppm, 120 ppm, 140 ppm, 160 ppm, and 180 ppm) for (30 min) at fixed stirring speed (300 rpm) and temperature (20 °C). These conditions were chosen after testing. At the best concentration of oxalic acid that dissolves the most of phosphorus, the stirring speed was changed for (100 rpm, 200 rpm, 300 rpm, 400 rpm, and 500 rpm). For the best stirring speed that dissolves more phosphorus the temperature was changed (20 °C, 30 °C, 40 °C, 50 °C and 60 °C), UV- test was made for each sample and phosphorus concentrations were recorded. **Fig.1** shows the apparatus. The best conditions of concentration of oxalic acid, temperature, and stirring speed were also recorded

0.0215 g precipitate hydroxyapatite

Dissolving in 160 ppm oxalic acid

Fig.1 Experimental apparatus.

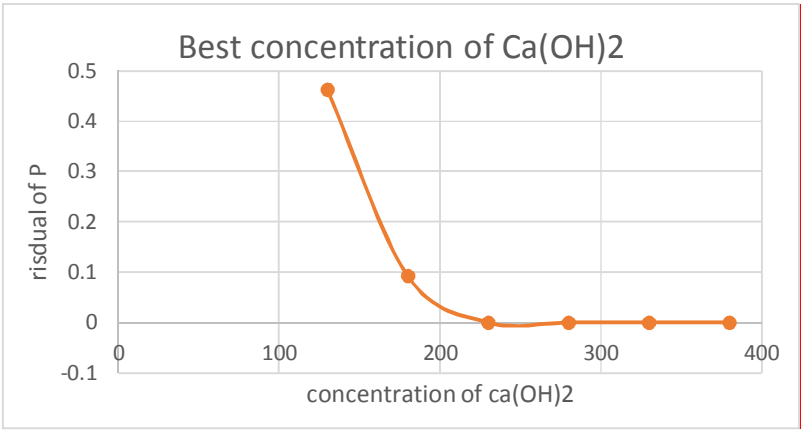

Fig.2 Conditions to precipitate phosphorus from simulated wastewater (230 ppm) calcium hydroxide, (400 rpm) stirring speed, (20 °C) temperature [14].

Results and Discussion: -

The best concentration of oxalic acid in this research was (160 ppm) at (20 °C) for (30 min) which dissolves the most of phosphorus in (0.0215 g) of hydroxyapatite. **Fig.3** shows an oscillation in phosphorus dissolution with an increasing in the global value. This behavior occurs because oxalic acid is a weak acid that makes the dissolution reversible. Although the dissolved phosphorus slightly increases. As it is obvious **Fig.4** shows a similar oscillation behavior when the concentration of dissolved phosphorus is drawn against the stirring speed at constant temperature which may be explained by reversibility of reaction as before. The best value of stirring speed is illustrated from **Fig.4** to be 200 rpm. **Fig.5** shows a clear decrease in phosphorus concentration when it is depicted against the temperature at the best stirring speed 200 rpm which indicates that the reaction is endothermic. The best value is temperature 30 °C. This is an agreement with the literature [7]. It is obvious from **Fig.6** that pH varies continuously with stirring speed which indicates that the dissolution reaction is reversible. It is in the range (7.67-8.24). It is noted that increasing the stirring speed at the beginning increases pH till it reaches 8.24 at 300 rpm because hydroxyapatite dissolves increasingly with stirring but after 300 rpm the complex compound decreases in the dissolution because the high stirring activates the backward reaction as well as the forward reaction. The net effect was with backward reaction i.e. decreasing pH. **Fig.7** shows the effect of temperature on pH at the best value of stirring speed. It is noted that pH decreases consciously with temperature indicating that hydroxyapatite is less dissolved at high temperature. This is because the dissolution reaction is endothermic [9]. The best value is temperature 30 °C. To get best result for dissolving phosphorus a comparison was made among solvents: water, oxalic acid 160 ppm alone and with two drops of sulfuric acid, and sulfuric acid. The results showed that the concentration of phosphorus in water was decreasing at the first 20 min till it reaches a minimum value (0.5ppm) at 20 min. Then it increased to (1.4 ppm) at 50 min. In oxalic acid the dissolution of hydroxyapatite was (1.8 ppm) at 30

min. This value is a bit higher than that for water at 30 min (0.67 ppm). In oxalic acid (160 ppm) with two drops of sulfuric acid the curve shows a continuous increasing. This indicates an irreversible dissolution reaction i.e. the forward reaction was activated by only two drops of a strong acid. Again, at 30 min the dissolved P is approximately 2 ppm which is the highest among the preceding ones. Sulfuric acid shows a curve oscillating between narrow range of phosphorus concentration (1.6 - 2 ppm). This refers to a reversible dissolution despite the strength of sulfuric acid. That is because sulfuric acid used was of low concentration (0.5 M) which is permitted in agriculture. Otherwise the plant will be harmed [5]. A comparison at 30 min with other solvents shows that sulfuric acid dissolved higher concentration of phosphorus (1.9 ppm) than that of oxalic acid with two drops of sulfuric acid. Nevertheless, of the higher dissolution in sulfuric acid the best dissolution of hydroxyapatite was in oxalic acid of 160 ppm with two drops of sulfuric acid under the temperature (30 °C) and 200 rpm stirring speed **Fig.8**.

The best results obtained were applied on a real wastewater sample taken from Al-Rasheed factory. **Fig.9** shows the behavior of phosphorus concentration taken from real wastewater sample starts with (0.87 ppm) then decreases at the first 20 min then starts increasing to (0.88 ppm) at 30 min then deceases after 30 min, in 30 min gives higher dissolution at the best conditions. This is because the dissolution reaction is reversible reaction.

Table.1 summary of results.

solvent	Concentration of P in ppm	Concentration of P in g/l
Oxalic acid 160 ppm	0.6752	0.0006752
Oxalic acid 160 ppm + two drops of H_2SO_4	1.822	0.001822
Sulfuric acid 0.5 M	1.917	0.001917
Deionized water	0.738	0.000738

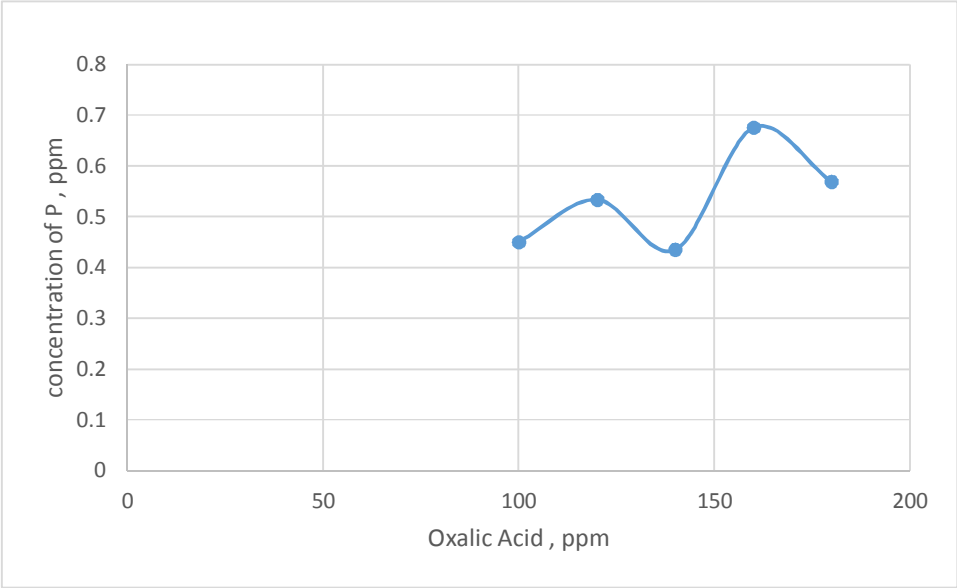

Fig.3 concentration of phosphorus in oxalic acid at fixed stirring speed 300 rpm and temperature 20 °C.

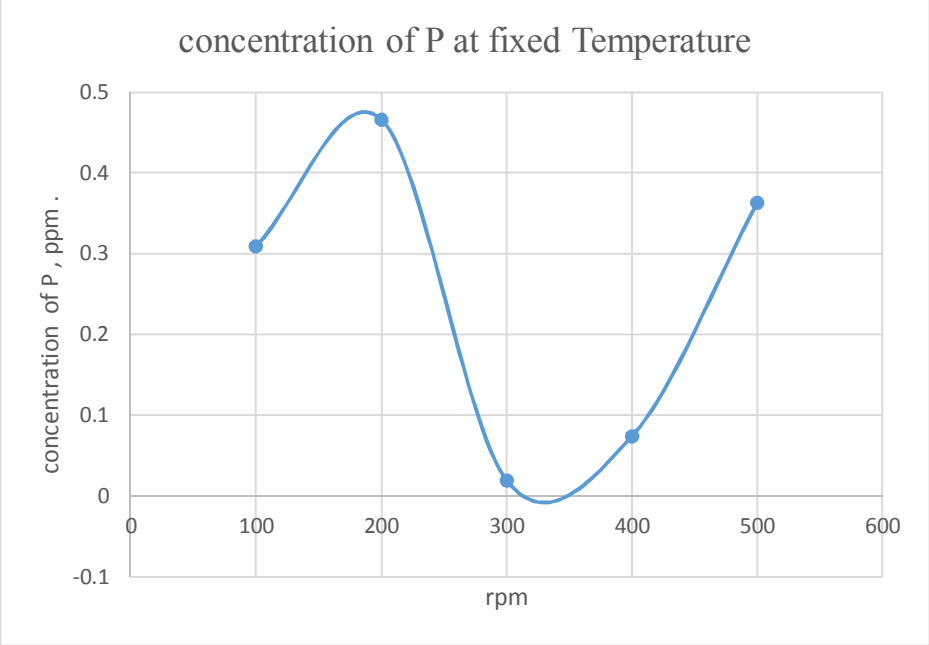

Fig.4 concentration of phosphorus as a function of stirring speed at the best concentration of oxalic acid 160 ppm and fixed temperature 20°C.

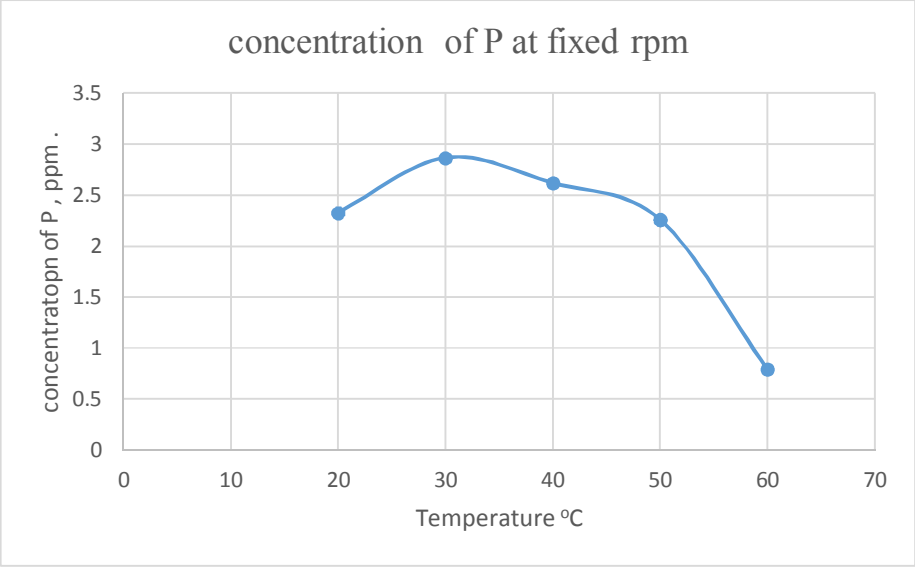

Fig.5 concentration of phosphorus as a function of temperature at the best concentration of oxalic acid 160 ppm and fixed stirring speed 200 rpm.

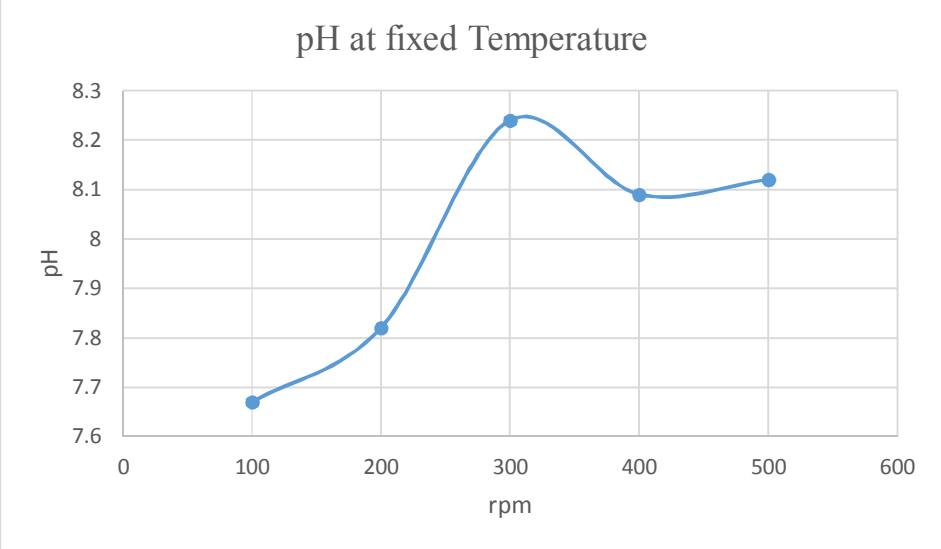

Fig.6 pH behavior with increasing stirring speed at the best concentration of oxalic acid 160 ppm and fixed temperature 20°C.

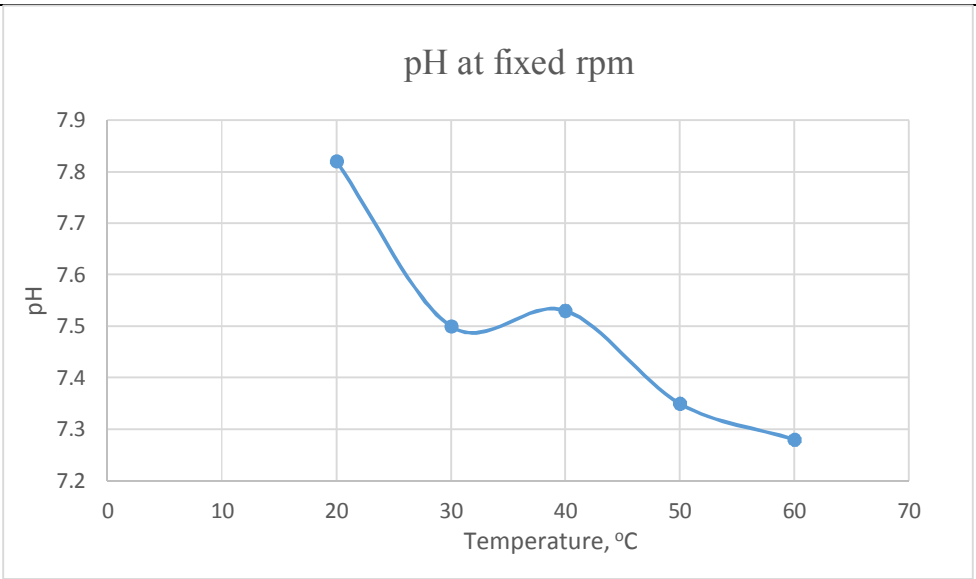

Fig.7 pH behavior with increasing temperature at the best concentration of oxalic acid 160 ppm and fixed stirring speed 200 rpm.

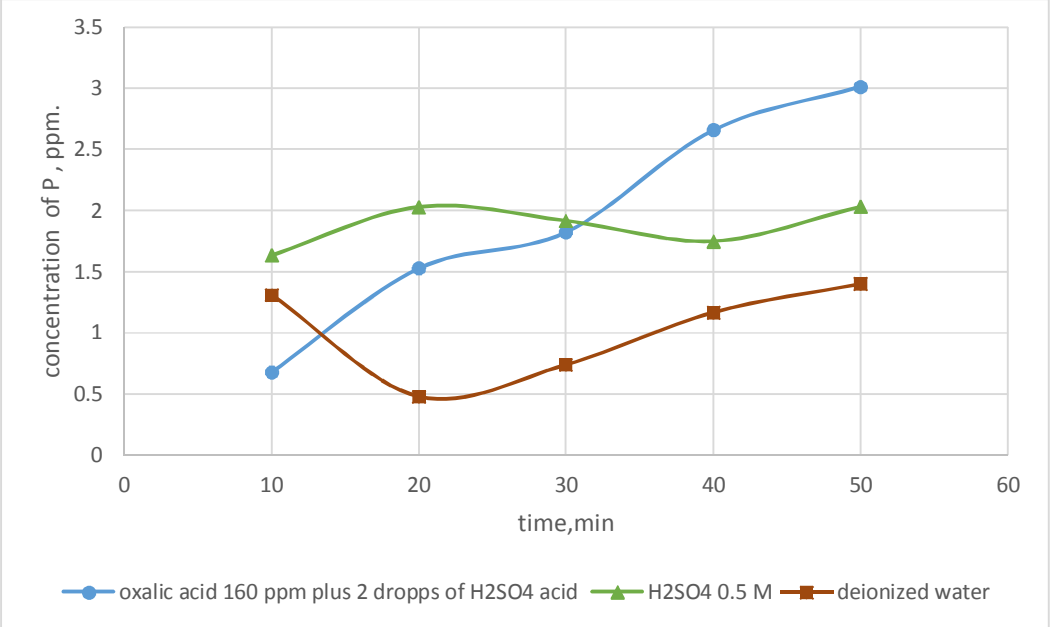

Fig.8 Concentration of P dissolved with time in different solvents: oxalic acid 160 ppm with two drops of sulfuric acid ,0.5 M sulfuric acid and deionized water at constant stirring speed 200 rpm and temperature 30 °C.

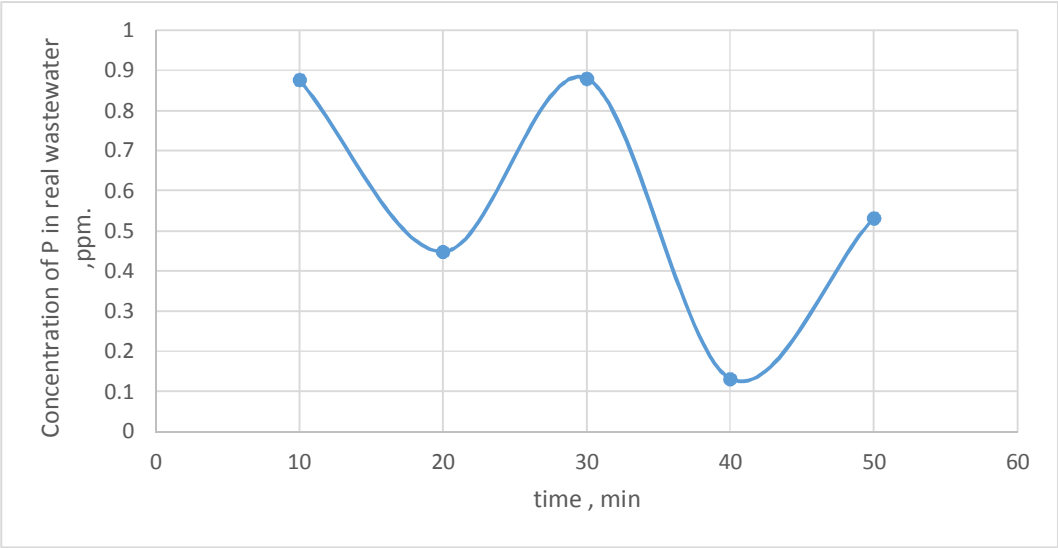

Fig. 9 Concentration of P in a real wastewater dissolved with time in oxalic acid 160 ppm with two drops of sulfuric acid at constant temperature 30 °C and 200 rpm stirring speed.

Conclusion: -

1. Hydroxyapatite dissolution can be improved by using an organic acid such as oxalic acid.
2. Organic acids such as oxalic acid increases phosphorus uptake from soil, growth and yield improvement of aerobic plants.
3. Using mineral acids for the dissolution of hydroxyapatite by adding a very small amount to the organic acid improves the dissolution without harming plants.

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ازالة الفسفور من المياه المطروحة كسماد

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الخلاصة:-

هذا البحث يتضمن دراسة استعمال مركب معقد يسمى هيدروكسي ابتايت الناتج من ترسيب الفسفور من مياه مطروحة محاكاة باستعمال هيدروكسيد الكالسيوم (المأخوذ من بحث سابق) كسماد. تركيز هيدروكسيد الكالسيوم يتغير من (180-380) ملغرام/لتر للحصول على افضل تركيز للفسفور (5 ملغرام/لتر)، سرعة الخلط (400 د/ثا), و درجة الحرارة (20 درجة مئوية). الشيء المهم في السماد هو ذوبانيته في التربة. لذألك هذه الدراسة تتحقق من ذوبانية الراسب (هيدروكسي ابتايت) في حامض ألأوكزاليك الذي يعتبر حامض عضوي ضعيف غير مضر للنباتات. الذوبانيه تكون انعكاسيه بسبب حامض الاوكزاليك حامض ضعيف. العوامل المدروسة في هذا البحث هي تركيز حامض الاوكزاليك (100-180) ملغرام/لتر، سرعة الخلط (100-500) د/ثا. ودرجة الحرارة (20-60) درجة مئوية. أفضل الظروف المأخوذة هي التي تعطي اعلى استرداد للفسفور، مثل اعلى تركيز للفسفور في المحلول (1.8 ملغرام/لتر). افضل الظروف هي: (160ملغرام/ لتر) تركيز الاوكزاليك , (200 د/ثا) سرعة الخلط , و درجة الحرارة (30 درجة مئوية) . الدالة الحامضية ايضا سجلت خلال التجارب. تبين ان الدالة الحامضية (كسلوك عام) تزداد بزيادة سرعة الخلط وتقل بزيادة درجة الحرارة. هذه الدراسة توصلت الى تحسين اذابة الراسب (هيدروكسي ابتايت) بإضافة حامض قوي هو حامض الكبريتيك الى حامض الاوكزاليك بكميه قليلة جدا تصل الى قطرتين (0.5 مولاري) بحجم (34 مل). الإذابة سوف تتحسن ويصبح التفاعل غير انعكاسي. تركيز الفسفور المذاب (2 ملغرام/لتر). أفضل النتائج تطبق على راسب حقيقي مأخوذ من استرداد الفسفور من مياه مطروحة صناعيا.

الكلمات المفتاحية: ازالة الفسفور، معالجة المياه المطروحة، ترسيب، حامض الاوكزاليك, هيدروكسي ابتايت, سماد .