Journal of Engineering and Sustainable Development
https://jeasd.uomustansiriyah.edu.iq/index.php/jeasd
https://doi.org/10.31272/jeasd.27.6.9

Vol. 27, No. 06, November 2023
ISSN 2520-0917

Original Research

THE ABILITY OF CALCIUM ION IN THE TREATMENT OF DAIRY WASTEWATER

*Ali A. Hasan[1], Ilham Al-Obaidi[2], Ali F. Hassoon[3]

[1,2] *Civil Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq*
[3] *Electrical Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq*
[1]https://orcid.org/0000-0002-4208-7998
[2]https://orcid.org/0000-0002-0900-9402
[3]https://orcid.org/0000-0002-4981-8407

Received 08/09/2022 ***Revised 23/02/2023*** ***Accepted 28/10/2023***

Abstract: In this article, jar and alum technologies were used as treatment materials. Similar synthetic models have been prepared for wastewater from dairy products. The chemical treatment was performed using the jar inspection method. The laboratory temperature, which was between 20-25 degrees Celsius, is a reference in completing the experiments. Experiments have shown that alum can remove phosphorous by up to 95% according to parameters such as the speed of rotation of the oar and the temperature reached in the research. The value of velocity gradient (G) was 1076.915 sec.-1, which represents the potential energy that could make a better crash between particles to achieve an increase in particle size and then settle. This resulted in an optimum aluminum dose equal to 0.5 mg / L at 20 ± 2 ° C. The role of calcium ions in the removal of pollutants has been observed as a catalyst to complete the treatment process, however, it will reduce the aluminum ion concentration necessary to achieve the treatment, it is not possible to risk adding salts over the salinity of water sources to achieve the treatment.

Keywords: *Dairy wastewater; gradient velocity; alum; phosphorus; calcium*

1. Introduction and Simple Review

The dairy industry is one of the greatest lively manufacturing in the world. This importance comes from the great consumption of water as well as the great consumption of this product. New research has confirmed the quantity of milk products in the world reaches 600 million tons. Due to the large consumption of water, the outcomes of wastewater will be high and may reach 90 % of the total consumption of water. The main items of wastewater discharged from dairy industries are the nutrients in terms of calcium, phosphorus, vitamin A, vitamin D (in products fortified with vitamin D), riboflavin, vitamin B12, protein, potassium, zinc, choline, magnesium, and selenium. The wastewater is bearing as well heavy metals and various salts [1-4]. Alum is the common coagulant that was used in the past and still has been used till now [5-8]. The procedure of treatment has been studied for many years, and the mechanism of hydroxide roots has been explained as well, as shown in equations 1, and 2 below [9, 10].

$$\mathrm{AI^{3+} + 2H_2O \rightarrow AI(OH)_4{}^{2+}} \quad (1)$$

$$\mathrm{AI^{3+} + 2H_2O \rightarrow AI(OH)_{2+} + 2H^-} \quad (2)$$
$$\mathrm{XAI^{3+} + 2.5XH_2O \rightarrow AI_x(OH)2.5x}$$

Clay particles and most of the pollutants that

**Corresponding Author:* *ali137@uomustansiriyah.edu.iq*

build the turbidity body have negative charges. These negative charges will run to aluminum hydroxide which has the opposite charge, and this occurs due to electrical attraction [11-13]. Many scientists referred to different factors; for example, temperature, and velocity gradient which means change in velocity per unit distance which can give an engineering vision of the mechanism of agitation, type of coagulant, time of mixing, intensity of mixing as well as viscosity of the liquid which play a role in the mechanism of treatment. Calcium hydroxide (usually called extinguished lime), and this compound is inorganic with the chemical formula $Ca(OH)2$ [14-16]. It has certain physical properties making it have opportunities to be a great suit for different purposes. Some of these properties are crystal without any color or white dust and are produced when quicklime (calcium oxide) is mixed or slaked with water. This material may have another name such as hydrated lime, lime, and caustic lime [17-22]. Lime may be used in food preparation, finishing works, and decoration, it has multiple faces [23-25]. Recent studies have focused on removing pollutants to recover dairy products as well as dairy by-products, for general usage. Some studies have used coagulants such as $FeCl3$, and they reached that about ninety-nine percent of sample turbidity was confiscated, 80% of protein was recovered and 80% of BOD was diminished at best circumstances (pH 10.0, $FeCl3$ concentration of 0.07% w/v). In alkaline environments, $Fe3+$ ions efficiently neutralized negatively charged colloidal particles directing to coagulation and sweep flocculation [26]. The mainstream of research has been focused on recovery materials or ingredients from dairy products, however; it's very important to occupy conditions of treatment in eliminating the amounts of coagulants amounts and sizes. Engaging the conditions and determinants is important in achieving the best treatment. The main goal of this work is to recruit local materials to remove pollutants included in dairy wastewater. One of the famous local materials located in the surrounding area is lime, which has been used in achieving this work.

2. The Main Characteristics of Dairy Wastewater and Treatment

According to literature achieved previously can be said that the water discharged from the dairy plants is acidic white, with a high fading, as well as the salinity that returns with high conductivity. On the other hand, the existing bicarbonate is the cause of alkalinity. Bicarbonate alkalinity achieved the master role in raising the alkalinity concentration in dairy wastewater. On the other hand; higher level of carbon dioxide and lower level of chloride has been noticed. The decrease in the dissolved oxygen readings has been observed due to the high concentrations of organic materials that can deplete the dissolved oxygen. On the other hand, agricultural wastewater is rich in nutrients if the concentration of phosphorous and nitrate is high [27-31]. Out to different scientists the extent to which the environment was affected by the discharge of dairy wastewater, and the extent of this effect in terms of the release of gases that are the cause of the odor and unacceptable taste in the water and other unsanitary ailments are a few examples [17-19]. Many factors could minimize or maximize the quantities of water usage in dairy activities. Mostly, the discharged wastewater could be outlined briefly below [20-22]:

1. Outcome factory processing.
2. Flushing and cleaning, due to maintenance and daily work.
3. Wastewater discharged from human activities.

The coagulation and flocculation mechanisms are the head of the chemical treatment method used for centuries to remove blemishes. Alum is the most common and deliberate substance in the completion of treatment. An important portion of the main health impact on humans is the relationship of this ion with early dementia. On the other hand, this ion has major effects on the kidneys and causes blood poisoning indirectly by discouraging the work of the kidneys and being drawn to the importance of washing them because of poisoning. For this; it major goal of this article is to look for alternatives [32-35]. Sometimes an ion can be added to the form that contains the same element to remove that element through a mechanism that could be named the common ion effect. This is by dragging the ion to the saturation state achieving the scavenging mechanism and then sedimentation through the trapping mechanism [36-39].

3. Materials and Methods

3.1 Materials

The used compound and elements are:

- Hydrated Aluminum sulfate with chemical formula $Al_2(SO_4)_3.18H_2O$ was poured into 1 liter to make a concentrated solution in 1% of alum liquid, by adding 10 gm. Milleque water has been used with 1 liter. This solution is re-formed every seven days to confirm its inefficiency.
- Sucrose hydrate $C1_2H_{22}O_{11}.H_2O$
- Slaked lime with chemical formula $Ca(OH)_2$
- Ammonium sulfate ($NH_4.2SO_4$).

The jar test procedure has been used to implement this work which is the Jar test model JLT 6 Leaching test VELP Scientific, with all tools and kits that can complete work. The work applied on synthetic samples that have been prepared previously according to global dairy wastewater characteristics.

3.2. Methodology

A. Tools

Although, the jar test is the main item in this work, different apparatuses will assist this item to accomplish the work.

1. A standard 1000 ml graduated cylinder was used to add the artificial model to the beakers.
2. Various apparatuses have been used to add a dose to each beaker with the desired concentration of metal salt; and increase concentration from left to right.
3. Turning on the mixers in two stages, slow then rapid.
4. Finalizing the work by locating the best dosage level by evaluating the supernatant.

B. Synthetic Samples

The synthetic models were prepared according to the characteristics of dairy wastewater, following the latest international standards as mentioned above in paragraph 3.1.

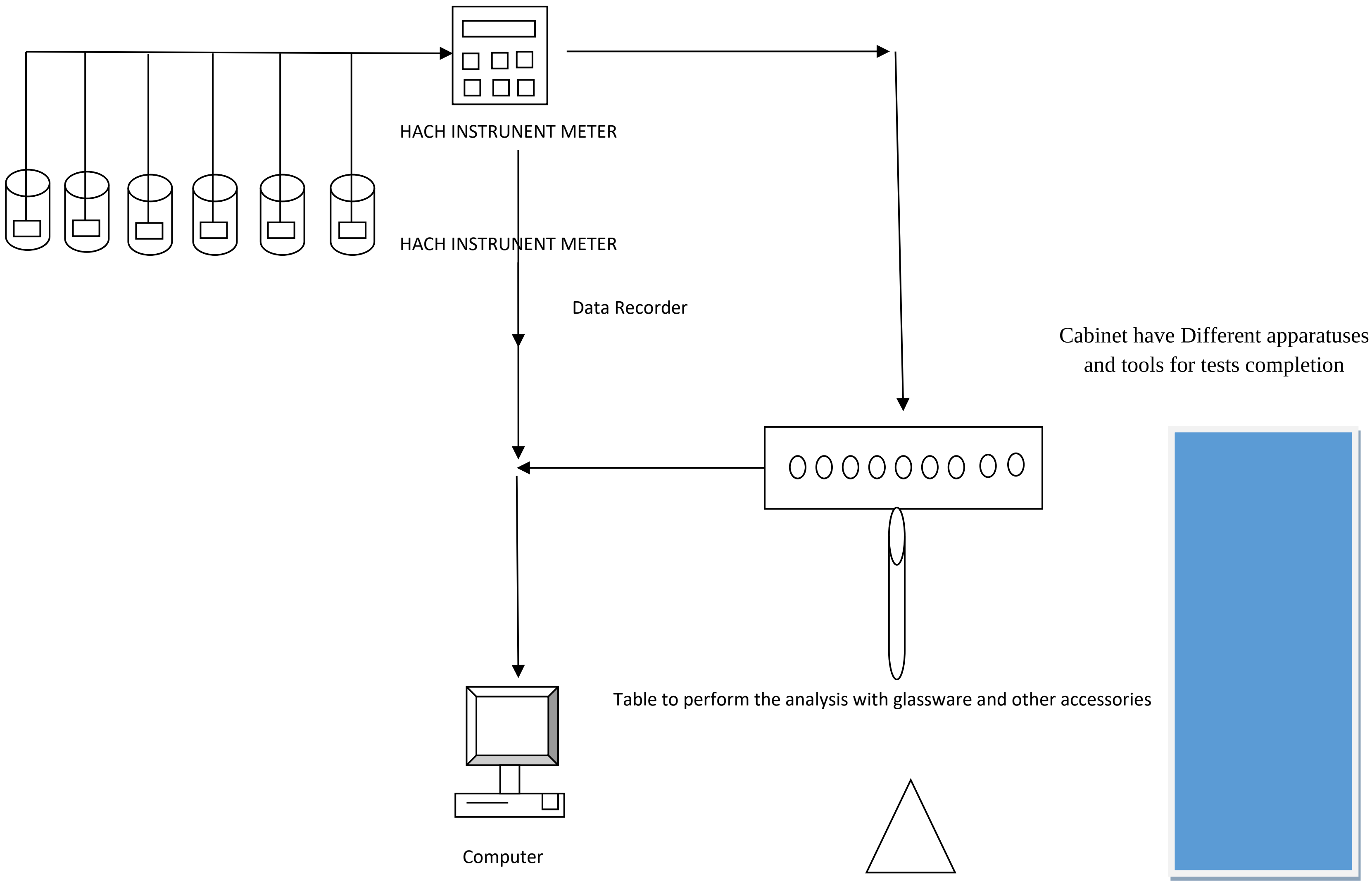

Figure 1. Shows schematic diagram of Jar test procedure used at the lab.

A standard alum solution was prepared weekly and periodically to maintain the properties of the solution unchanged under international standards [40]. To accomplish the work, a laboratory bench scale process was required that represented similar treatment stages in dairy wastewater treatment plants. Therefore, the Jar test process was used to achieve this step, as shown in Fig. 1.

The accomplishing of work will be done after settling and gathering samples for tests. The duration of settling was 20 minutes to finish the procedure. The circumstances under which the Jar test techniques were [41-43];

1- Flash mixing 150 rpm for 3 min.
2- Slow mixing 30 rpm for 20 min.
3- Sedimentation for 20 min.

All tests have been made per [44].

4. Results and Discussions

The results obtained from the completion of these examinations are shown in Table 2 and Fig. 2:

Table 2. The reaction process of treatment by using alum.

Balance	Quantity	Element
Alum 2.285 ml------ Al^{3+} =0.8 gm./l ------- Al^{3+} =2.25 mg/l	Al^{3+} =2.25	mg/l
Alum 2.857 ml ----- Al^{3+} =1.00 gm./l ------- Al^{3+} =1.55 mg/l	Al^{3+} =1.55	mg/l
Alum 3.428 ml ----- Al^{3+} = 1.2 gm./l ------- Al^{3+} =1.45 mg/l	Al^{3+} =1.45	mg/l
Alum 4.285 ml ----- Al^{3+} = 1.5 gm./l ------- Al^{3+} =1.7 mg/l	Al^{3+} =1.7	mg/l

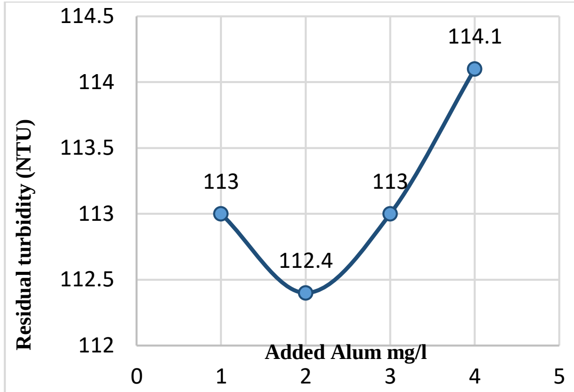

Figure 2. Relationship between added alum (mg/L) and residual turbidity (NTU).

The contexts mentioned above such as velocity gradient (*G*) have been approved according to references and recalculated regarding recent forms [45-47].

- Rapid mixing time is 3 min. Time of flash mixing 3 min.
- Gradient velocity for rapid mixing is (122.79 sec-1, 205.7 sec-1) for 10 °C and 30 °C respectively.
- The best gradient velocity for slow mixing was (31.5, 38.4 sec-1 respectively); the best time for attaining these conditions was found 30 min.

The addition of Lime according to the above bases and the working conditions will be shown in Table 2. Results obtained will guide to preparation (Table 3); which explains using the hydrated lime (HL). Here, the hydrated lime was added on a solution basis and in small quantities to note the effect of this factor on treatment. Although this substance has little solubility in water, the treatment determinants were used to draw this material towards achieving what is required as shown in Fig. 3. From the observation of the two tables, it is concluded that the amount of extinguished lime is twice the amount of alum to achieve treatment, even in proportions that can reach a number close to the removal rate.

As hardness is high in the Iraqi rivers and the environment does not demand increased hardness or increased aluminum to generate many diseases over time, it became necessary to control the determinants of work and treatment.

Table 3. The reaction process of treatment by using the hydrated lime (HL).

Material (Solution)	Equation	Amount g/L
HL 0.694 ml	HL 0.694 ml --- $Ca(OH)_2$ = 0.25 g/L ----- Ca^{2+}	$Ca(OH)_2$ = 0.249
HL 1.389 ml	HL 1.389 ml ---- $Ca(OH)_2$ = 0.5 g/L ----- Ca^{2+}	$Ca(OH)_2$ = 0.8
HL 2.083 ml	HL 2.083 ml ---- $Ca(OH)_2$ = 0.75 g/L ---- Ca^{2+}	$Ca(OH)_2$ = 0.749
HL 2.78 ml	HL 2.78 ml ------ $Ca(OH)_2$ = 1 g/L -------- Ca^{2+}	$Ca(OH)_2$ = 1

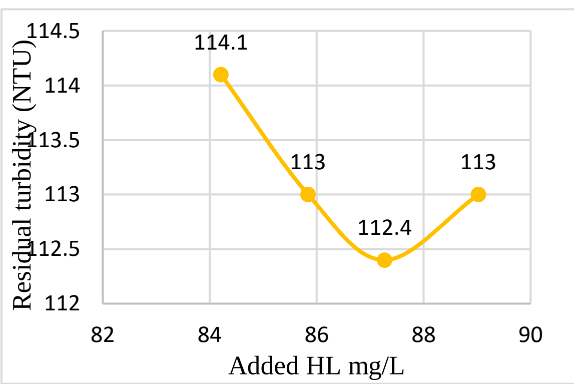

Figure 3. Relationship between added HL (mg/L) and residual turbidity (NTU).

The calcium ion in removing turbidity and the concentration of the hydrated lime ion is approximately between 0.49-0.63 grams per liter to achieve removal compared to approximately 0.8 to 1 gram per liter employing alum. This concentration is about half the weight. Water, in general, does not need an increase in the concentration of calcium salts and an increase in hardness, nor an increase in the concentration of aluminum.

The intensity of stirrer required for gathering the best possible rapid mixing value and then achieving flocculation is measured by the *G* value [19]. This *G* value was studied by Camp and Stein first at (1942), [47]. Generally, this parameter could be used in designing rapid mixing and flocculation processes [47-51]. This parameter may be defined by equation "1". The last equations were applied to this study and the results are shown in Fig. 4.

$$G = \sqrt{W}/\mu \qquad (1)$$

Where W= Degeneracy role,

μ = absolute viscosity Kg/m.sec.

$$G = \sqrt{P/\mu} \qquad (2)$$

Where P = Power per unit volume, kg·m−1s−3

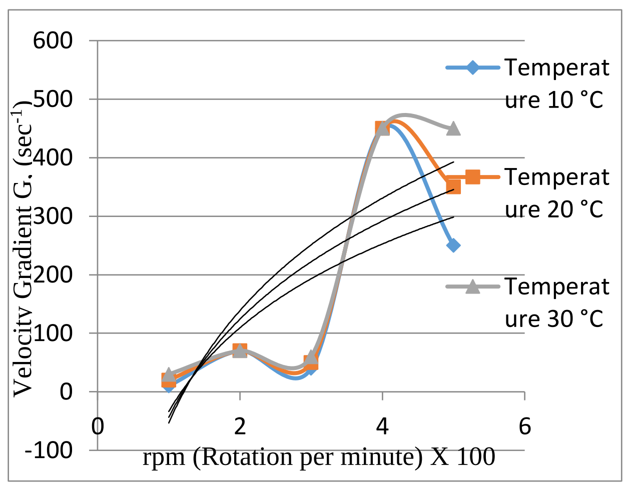

Figure 4. Relationship between the rotation of the paddle per minute and velocity gradient at different temperatures.

From observing Fig. 5, phosphorus can make aluminum hydroxide-like hydroxyl roots and has nearly the same properties as compounds. This advantage allowed it to make compounds that have the chance to settle and attract all pollutants in the same way by different mechanisms. These phenomena could be noticed in Fig. 3 and Fig. 4. It has been deduced that the optimum value of alum, approximately is about 2 mg/L which is about 0.5 mg/L aluminum ion. The percentage of removal of phosphorus will reach 95.7%~96% by 1.45 mg/L of the aluminum ion.

$$Al^{3+} + H_nPO_4^{3-n} = AlPO_4(S) + n\,H^+ \quad (4)$$

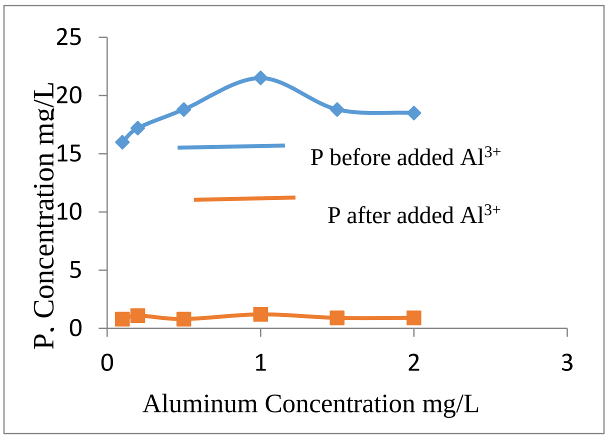

Figure 5. The Relationship between concentrated aluminum and concentrated phosphorus.

The role of alum in the treatment process was indicated as shown in Fig. 2 and the best elimination of the turbidity occurred by adding alum of approximately 2 mg per liter and the remaining browning was approximately 112.4. The same removal is achieved when the added calcium concentration is approximately equal to 87.5 mg per liter, as shown in Fig. 3. Here in this research, the hydrated lime (HL) was tried as a coagulant and added in the form of a liquid to avoid losing much of the material is added, so it goes to the bottom due to the lack of melting of this substance. It is observed from Fig. 2 that the calcium ions are directed towards attraction with phosphorus compounds of negative charge. On the other hand, these new compounds may be suspended by a network of crystalline aluminum hydroxides, which results in a decrease in the concentration of aluminum, phosphorus, and calcium.

The velocity gradient affects the circumstance of the treatment by making the materials enlarge or fracture these compounds when the intensity is huge. The explanation of Fig. 6, will be the translation of this phrase. It has been found that the best concentration of aluminum ion to accomplish the treatment is 0.5 mg/L. The residual phosphorus in this figure will be 0.68 mg/L at a gradient velocity equal to 1076.915 sec-1.

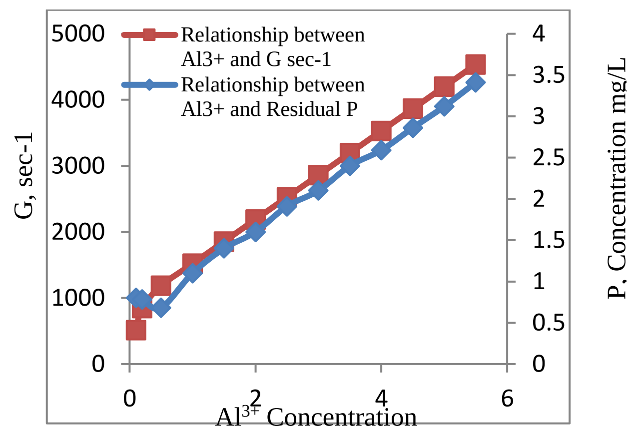

Figure 6. The Relationship between concentrated aluminum and % phosphorus removal, G.

The constraints could be attained from equation "5" below.

$$y = 701.95x + 725.94 \quad (5)$$

Mainly, an increase in items in the samples will raise the occasions of removal, due to the scavenging mechanism. On the other hand, as mentioned above the capability of phosphorus to make aluminum phosphorus arises, which has the ability to precipitate.

The Jar test procedure will use different dosages and different speeds as well as determination was changed until reaching the best parameters of treatment. The intensity of agitation was measured after each performance such as gradient velocity [22, 51-54]. To finalize the work and make computability of treatment with all conditions it has been used many patterns of coagulants; such as liquid or solids. In this article, the liquid shape has been used, then achieve the work [22, 55, 56]. To achieve this work, it’s important to arrange the circumstances by using different chemicals such as (NaOH, and HCl) in identified molarities to manage pH [57-61].

It can be seen, that the aluminum phosphate removes turbidity through the scavenging procedure, which hints at a decrease in the phosphorous concentration at the same time. The calcium ions have a role by cross-attraction with the phosphorous root and are attached to the aluminum hydroxide network and then reduce the phosphorous concentration.

5. Conclusions

The results showed the ability of extinguished lime to remove phosphorous and an ability to reach approximately the same value, but with concentrations that reach twice the alum concentration.

The aluminum sulfate can make the best removal of phosphorus at 20 °C, and the presence of calcium ions led to a reduction of aluminum by a quarter, but this does not mean risking adding calcium salt and increasing the hardness of the water.

Calcium ions have the ability to form a floc but in a weak way and have the tendency to stick with the aluminum hydroxide floc through a group of different mechanisms,

The best concentration of added aluminum capable of removing phosphorus is 0.5 mg/L. This removal was achieved within a speed gradient of 1076.915 s-1,

The optimum aluminum concentration achieved in the above process was 0.5 mg/L and this led to the remaining phosphorus being 0.68 mg/L with a gradient speed equal to 1076.915 s-1.

The aluminum ion can build with bonds of phosphorus hydroxides at 20 °C Multi chemical structures could have the ability to precipitate,

The presence of calcium ions led to excellent removal at the fordable circumstances mentioned above.

Acknowledgment

The authors would like to thank Civil Engineering in the College of Engineering at Mustansiriyah University for their help and support in writing this article, as well as for all working at the lab.

The authors would like to thank RMIT University in Australia for their help and support in achieving this article, as well as all working at the lab.

Author’s contributions

The responsibilities have been distributed to authors according to their fields:

Ali A. Hasan got the chemical field,

Ilham Al-Obaidi has arranged the mathematical equations, Ali F. Hasoon has made the Excel programming part.

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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