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TREATABILITY OF ALUM IN REMOVAL PHOSPHORUS FROM DAIRY WASTEWATER

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Abstract: In this research, the technique of the jar using alum as coagulant was used as the most common in the world and abundance in the Iraqi environment, the preparation of artificial samples similar to the real dairy wastewater and taking the temperature of the laboratory as a reference in the completion of experiments. Experiments have seen the ability of aluminium sulphate to remove phosphorus from wastewater of the dairy plant by up to 95%. These removals are realized at certain working conditions in terms of the speed of rotation of the paddle which expressed as gradient velocity that achieved at 1076.915 sec^{-1} and the potential energy that can lead to better collision between the particles to achieve an increase in particle size and then sedimentation. This led to optimum dosage of aluminium equal to 0.5 mg/L at 20 °C.

Keywords: *Dairy wastewater, gradient velocity, alum, phosphorus.*

الخلاصة: في هذا البحث تم استخدام اسلوب فحص الجرة كنظام معالجة أولية لمعرفة قابلية إزالة الفسفور بهذه التقنية. تم استخدام الشب والذي يعد المادة الاكثر شيوعا في العراق والعالم لتوفره في البيئة اضافة الى سعره مقارنة ببقية المواد فضلا عن حدود العمل الواسعة كمادة مخثرة في تطبيق المعالجة في درجة حرارة المختبر. أكدت النتائج قابلية الشب في ازالة الفسفور من مياه فضلات معمل الالبان وبنسب وصلت الى 95%. كفاءة الازالة هذه حصلت تحت واقع ظروف عمل تم إيجاده وتحديدها وفقا الى مجموعة من التجارب والبيانات والتي كانت معبرة بسرعة دوران مجاذيف الدوران للجهاز معبرا عنها بانحدار السرعة Velocity Gradient (G)والتي وصلت الى 1076.915 sec^{-1} والتي قادت الى افضل تصادم بين الجسيمات وحصول أفضل ازالة. كانت افضل جرعة للالمنيوم المضلف لتحقيق أفضل إزالة للفسفور هو التركيز 0.5 ملغم لكل لتر في 20 درجة مؤية.

1. Introduction and Scientific Background

The dairy industry is one of the most vital and important industries in the world for two important reasons: its relation to the food and its relationship with water. Recent scientific reports have documented that the world milk product is 600 million tons. These large quantities of products contain a lot of it produces large quantities of heavy water loaded with nutrients, especially phosphorus P, which is a major source of growth of algae and then the algal revolution and subsequent problems.

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Food industry is known to be one of the largest sources of contaminated water produced in many countries and the milk industry is no exception as attention has been paid to the permissible standards for discharging polluted water to water estuaries, the specific regulations for the disposal of polluted water from the milk industry have become more stringent. Although the milk industry is not considered to be highly relevant to acute environmental problems, its environmental impact should be taken into consideration because of its organic pollutants. It should be noted that with the good management of contaminated water using closed circuit, treatment of contaminated water from the milk industry is not that big problem.

Dairy factories discharges of wastewater which have high concentration of phosphorus into water bodies without treatment will causes multi problems like Eutrophication, toxicity, oxygen consumption as well as aesthetic problems [1].These problems make reasons to remove pollution causes before discharging into water bodies Different process used to remove this element from wastewater which is physical, chemical and biological processes. The most important method which is economic to people and can remove pollutants without make upload to the country budget should be using local materials in treatment.

Phosphorus in wastewater takes one of three forms:

-Polyphosphate.

- Naturally bounded.

Orthophosphate is soluble and may be found as phosphoric, or phosphate ion. These forms are regarding to solution pH .Polyphosphates which most complicated form of phosphorus. There are simple ways to convert these compounds to phosphate through hydrolysis or biological activity.

Alum was used as coagulant which is the common compound worldwide in water and wastewater treatment [2]. Mechanism of coagulation studied for many years to explain ability of hydroxide aluminium in precipitation of colloidal materials [3]. Particles suspended in natural, untreated water normally carry a negative electrical charge. These particles are attracted to the positive charges created by aluminium hydroxides. [4-7], they referred to different factors which play role in mechanism of treatment.

2. Dairy Wastewater Characteristics

From physicochemical studies of dairy waste it was concluded that **w**astewater discharged from milk processing unit is white, acidic with higher Turbidity, Salinity, Electrical conductivity and total dissolved solids. Alkalinity recorded was due to Bicarbonate alkalinity. Higher values of carbon dioxide and lower value of Chloride was noted for the waste water. Dissolved oxygen in waste water was recorded low value due to higher organic matter, BOD and COD. BOD and COD value were quite higher in the waste water indicates its polluted nature. Higher quantity of inorganic nutrients like nitrogen & phosphorus was found in the waste water. Waste water was rich in Protein and Fat content, which can be used as a feed for animals. Most probable number (MPN), value was higher again indicates the polluted nature of waste water [8, 9].

Aenab et al. [10], pointed out that dairy wastewater contributes a lot to the degradation of the environment. Disturbing ecological system, releasing gases that cause odour and taste in water and other insanitary conditions are few examples.

There are different factors contribute in size and type of wastewater produced from dairy factory. These factors may guide to minimize or enlarge volume of wastewater. Generally the main wastewater discharged from this industry can be described briefly as below [11]:

1. Processing waters,

2. Cleaning wastewaters derive mainly from the washing of equipment,

3. Sanitary wastewater.

4. Pre Treatment of Dairy Wastewater

Industrialization and population growth add to the problem of many toxic organic compounds and Eutrophication. So a coagulation-flocculation treatment will be applied to remove source of these problem.

Environmental protection agencies have forced more inflexible regulatory rigid standards and they have started more firm vigil along with some nongovernmental organizations to keep the environment. This trend make treatment very expensive. However this will cause a huge burden for the industries. This necessitates thinking of reuse wastewater for various purposes. The recycling or reuse of water for similar duties mainly depends on availability of suitable process technology for water purification as well as availability of treatment raw materials. With wide fluctuations in industrial effluent quality, this becomes more difficult.

The dairy industry consumes 2 to 6 m^3 of water per tonne of milk entering the plant [12]. Water here is a key processing medium. Water is used throughout all steps of the dairy industry including sanitization, cleaning, cooling, heating and floor washing and obviously the requirement of water is large. As milk contains fats, oils and grease, nutrients such as ammonia or minerals and phosphates, these will add to contamination of receiving water bodies if they are disposed without treatment.

Dairy effluents have many environmental effects i.e. [13]:

- Effects on aquatic life and water bodies,
- Increase Nitrate and Phosphate (Nutrients) leading to Eutrophication, and thus increase pollution,
- Increase BOD and COD values of receiving water bodies.

Generally this wastewater doesn’t contain toxic materials to environment and water bodies as listed in EPA’s standards. Nevertheless; it contains high concentration of dissolved organic components like whey proteins, lactose, fat and minerals [14, 15, and 16].

Coagulation and flocculation are the important treatment practices adopted by water industries around the world for water purification. Conventionally aluminium salts have been used for this purpose for many years. Alum is common product used in water and wastewater purification plants when aluminium (Al^{3+}) salts are used as the primary coagulating–flocculating agents. This salt will be very efficient.

Nevertheless, wastewater treatment plants act as one of the major investments due to high capital cost in addition to operation and maintenance cost. The most important point in developing countries is sufficient finance as well as poor management. These points will lead to produce bad product and have a lot of disadvantages.

Jar Test technique a simplified way to predict types and amount of coagulant which lead to optimum formation of flocs. This procedure includes finding optimum dosage of coagulant as well as optimum parameter of treatment. The idea from adding coagulant is to make destabilization of particle, however increasing chance of collision. This process will lead to enlarge size of particle and settle at the bottom.

Generally the effectiveness of coagulants used in this treatment depends on nature of the waste. Water, being affected by such factors as temperature, pH, and especially the specific proportions of organic, inorganic, and biological particles that constitute the suspended solids. In addition, it is usually found that combinations of coagulants attain much higher performance of treatment; nevertheless this treatment again depends on the composite nature of the wastewater source.

2. Materials and Methods

2.1 Materials

The materials used in this topic are:

- Alum $Al_2(SO_4)_3.18$ added to 1 litre and used as solution in concentration 1% by adds 10 gm. to 1 litter of distilled water. This solution is remade every week to ensure its effectiveness.
- Sucrose hydrate $C_{12}H_{22}O_{11}.H_2O$
- Sodium Phosphate Dodecahydrate$Na_3PO_4.12H_2O$

Ammonium sulfate$NH_4.2SO_4$. Apparatus used in this study is Jar test model JLT 6 Leaching test VELP Scientifica, with all apparatuses and tools can complete work.

Coagulation–decantation tests were carried out on an average sample of 1 L. Samples prepared at Lab according to global characteristics of discharged dairy wastewater as shown in table [1].

Table 1: the characteristics of dairy wastewater factories

Chemical compositions	Synthetic Samples
COD (mg/l)	1000-3000
Nitrate (NO_3^-) (mg/l)	0.2-16
TP (mg/l)	18-27
Chloride (mg/l)	20-100
Sodium (Na^+) (mg/l)	50-750.
Turbidity (NTU)	40-50
TSS (mg/l)	200-1200
TS (mg/l)	150-2500
TDS (mg/l)	150-450
EC (μ mhos/cm)	300-4000
pH	6.5-7.5
Temperature (°C)	25 – 35

2.2 Procedure of Work

This topic achieved through usage of artificial samples were prepared using kaolin clay as a source of turbidity and suspended solids. These samples contain different types of salts which give us the same identity of raw samples. The most important point is to reach optimum dosage of coagulant by using Jar Test Technique. The last process achieved to reach aim through different steps. Briefly to achieve this treatment, different apparatuses were used as below:

2.2.1 Using the 1000 ml graduated cylinder, add 1000 ml wastewater (artificial sample), to each beaker.

2-1.2 using the graduated pipettes, dose each beaker with the desired concentration of metal salt, increasing concentration from left to right.

2.1.3 Then been operate stirrer to simulate plant process.

2.1.4 Determine best dosage level by analysis of supernatant

II Jar Test Technique

The results achieved with Jar test have been taken after physical settling. Time of physical settling arranged 90 min - 150 min. The conditions under which the Jar test technique were;

1- Flash mixing 150 rpm for 3 min.

2- Slow mixing 30 rpm for 20 min.

3- Sedimentation for 20 min.

2.3 Sampling

Artificial simulation samples were prepared to real samples discharged from dairy factories; these samples were prepared from salts below:

- Alum $Al_2(SO_4)_3.18$ added to 1 litre and used as solution in concentration 1% by adds 10 gm. to 1 litter of distilled water. This solution is remade every week to ensure its effectiveness.
- Sucrose hydrate $C_{12}H_{22}O_{11}.H_2O$
- Sodium Phosphate Dodecahydrate$Na_3PO_4.12H_2O$
- Ammonium sulfate$NH_4.2SO_4$

From other hand alum were prepared each week to keep chemical characteristics of solution.

The above work was done according to standards [17].

3. Results and Discussion

The results obtained from the completion of these examinations are as shown in Table [2] below which leads us to Figure (1) below:

These experiments have been operated on 2 litters of samples. Based on these experiments the values above should be divided by 2.

Table 2: The reaction process of treatment

Material (Solution)	Equation	Amount	Unit
Alum 2.285 ml	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	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	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	Alum 4.285 ml ----- Al^{3+} = 1.5 gm./l ------- Al^{3+} =1.7 mg/l	Al^{3+} =1.7	mg/l

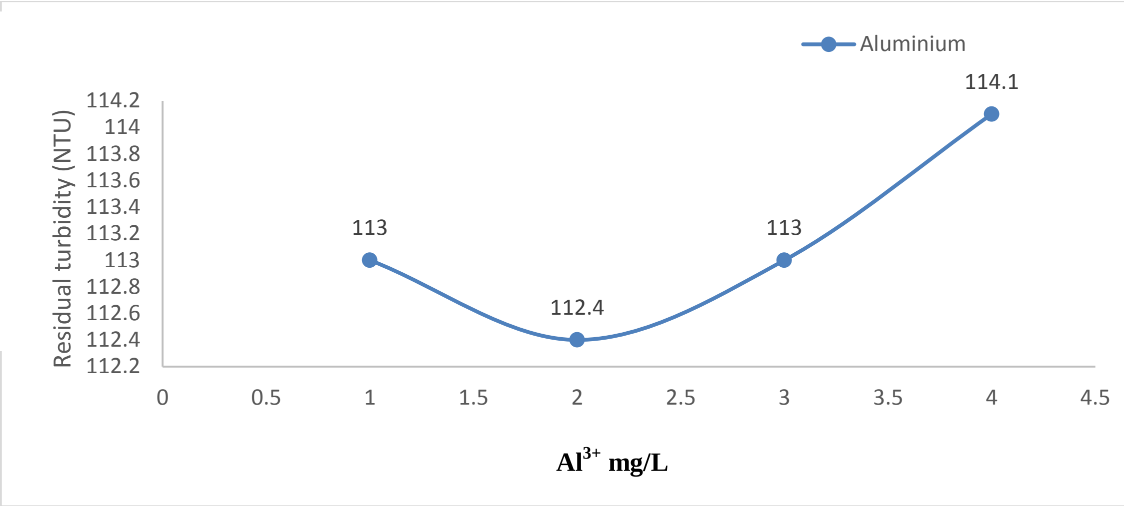

Figure 1: Relationship between added alum (mg/L) and residual turbidity (NTU).

Some factors have been approved according to references [18, 19].

- Time of flash mixing 3 min.
- Velocity gradient of flash mix is (122.79 sec^{-1}, 205.7 sec^{-1}) for 10 °C and 30 °C respectively, which mean temperatures of lab and samples.
- Optimal values were derived from the regression value at a slow blending and blending speed (31.5, 38.4 sec^{-1} respectively), While the optimal sintering period was found 30 min.

Mixing of these samples with coagulant can be achieved through mechanical agitation or hydraulic agitation. In this work mechanical agitation used through Jar test technique. The intensity of agitation required for optimum rapid mixing and flocculation is measured by the *G* value [18]. The *G* value concept, developed by Camp and Stein (1943), is widely used in designing rapid mixing and flocculation processes [20], and is defined by the equation (1).Last equations were applied at this topic and results shown in Figure (2).

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

Which W= Dissipation function,

μ = absolute viscosity Kg/m.sec.

This equation (2), can be represent in other term which is,

$$G = \frac{\sqrt{CdA\rho v^3}}{2\mu v} \quad (2)$$

Where is v = Linear velocity of paddle brushes relative to fluid velocity and this can be calculated from this equation (3),

$$v = 2\pi rn/60 \quad (3)$$

Where,
r = Rotational radius (m),
n = Number of rotation in minute,
A = Area of blade (m^2),
ρ = Density of fluid,
V = Volume of liquid (m^3).

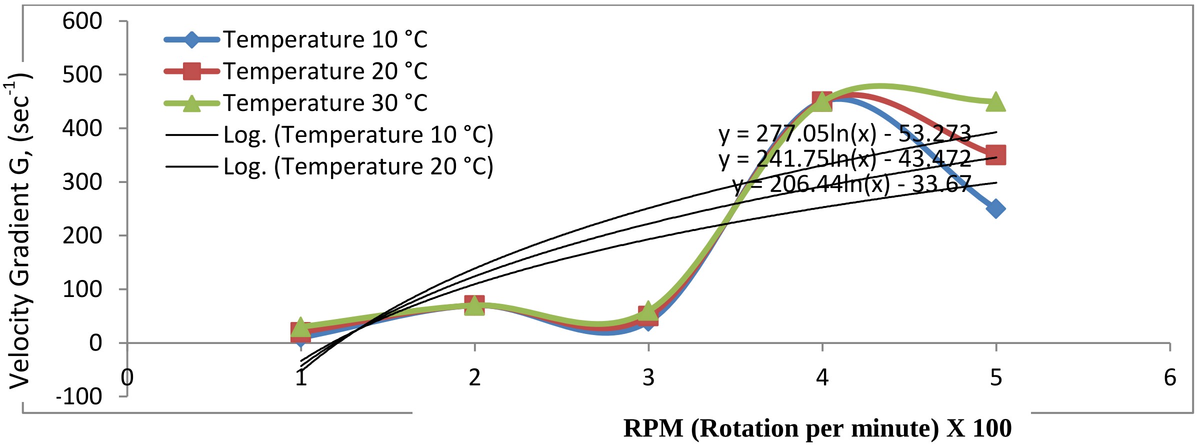

Figure 2: Relationship between the rotation of the paddle per minute and velocity gradient at different temperatures.

Capacity of alum is not restricted in the removal of turbidity only, but it can remove P which comes at some time as general information. This mechanism of removal which known as settling removal will remove P as well when net of aluminium hydroxide built. From other hand P can make Hydrogen phosphate which has similar characteristics of aluminium hydroxide from ability to sedimentation and this process described at Figure (3).

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

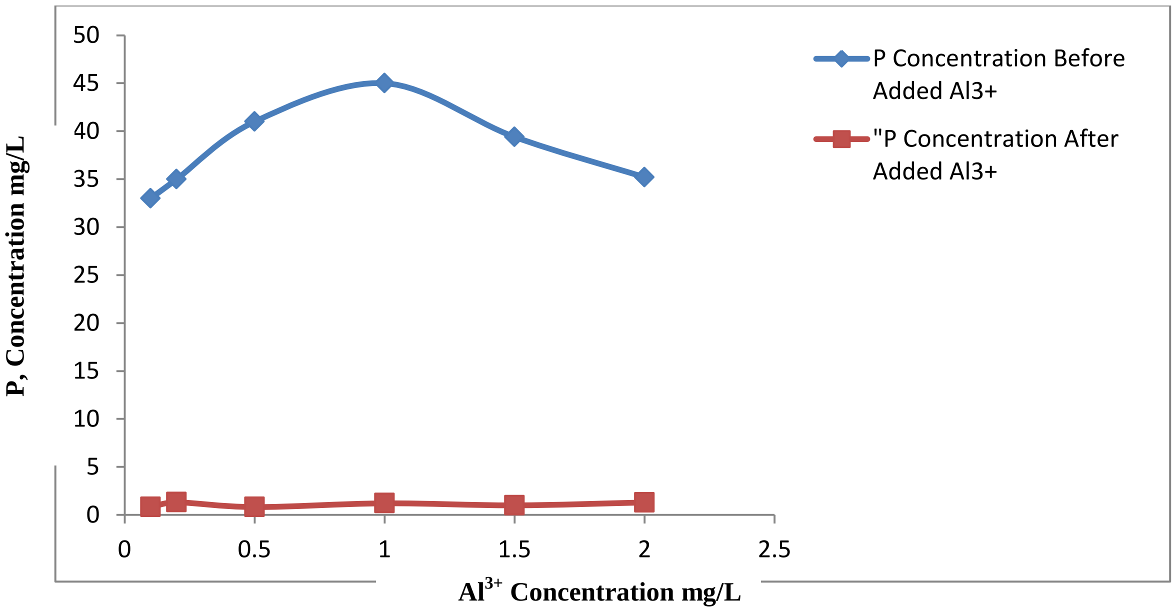

Figure 3: The Relationship between concentrated aluminum and concentrated phosphorus.

From Figure (3), it has been deduced that the optimum value of Al^{3+} is 0.5 Mg/l. The percent of removal of phosphorus will reach to 95.7%~96% by 1.45 mg/L of aluminium ion as shown at Figure (4).

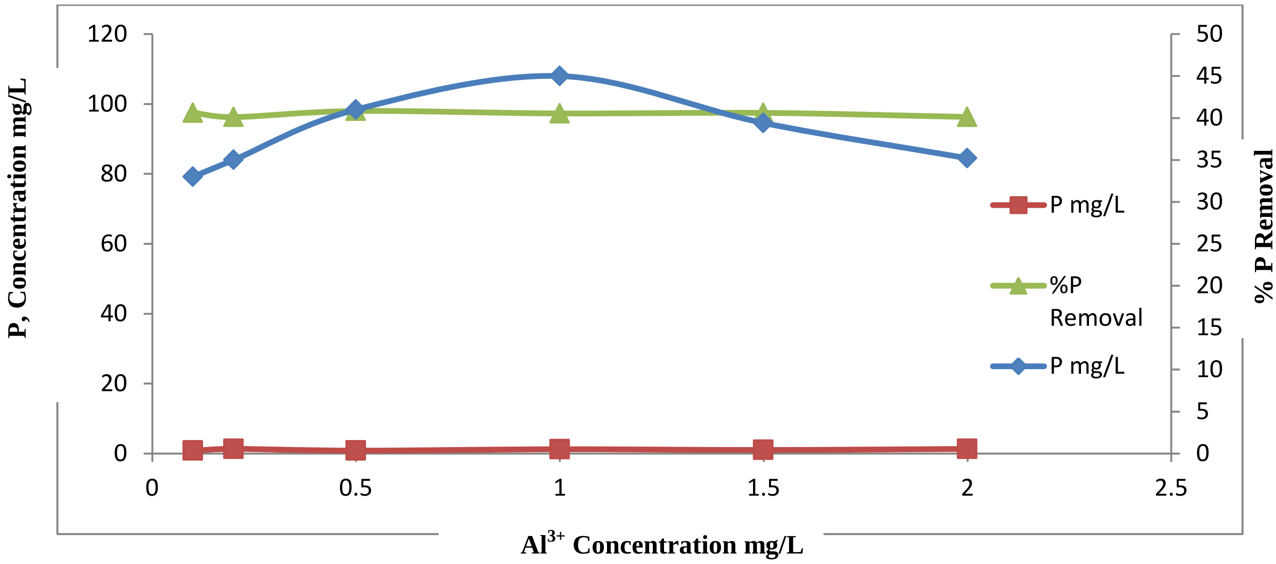

Figure 4: The Relationship between concentrated aluminum and concentrated phosphorus.

As shown from Figure (5); the relationship between added aluminium and residual phosphorus from one side as well as gradient velocity from other side at 20 degree centigrade. The optimum concentration of aluminium to make this process is 0.5 mg/L and this will lead to make residual phosphorus 0.68 mg/L at gradient velocity equal to 1076.915 sec^{-1}.

From this figure also it can be seen that velocity gradient can guide to rotation of paddles to make optimum treatment.

All these parameters can be obtained from equation (4) below.

$$y = 701.95x + 725.94 \qquad (4)$$

It can be seen the removal efficiency of phosphorus will increase with increasing of phosphorus concentration. This process achieved due to sweep mechanism of phosphorus hydroxide will be start after create phosphorus hydroxide one add aluminium sulphate.

By the way a number of attempts have been made at each point in the form and several experiments have been carried out to Figure (5).

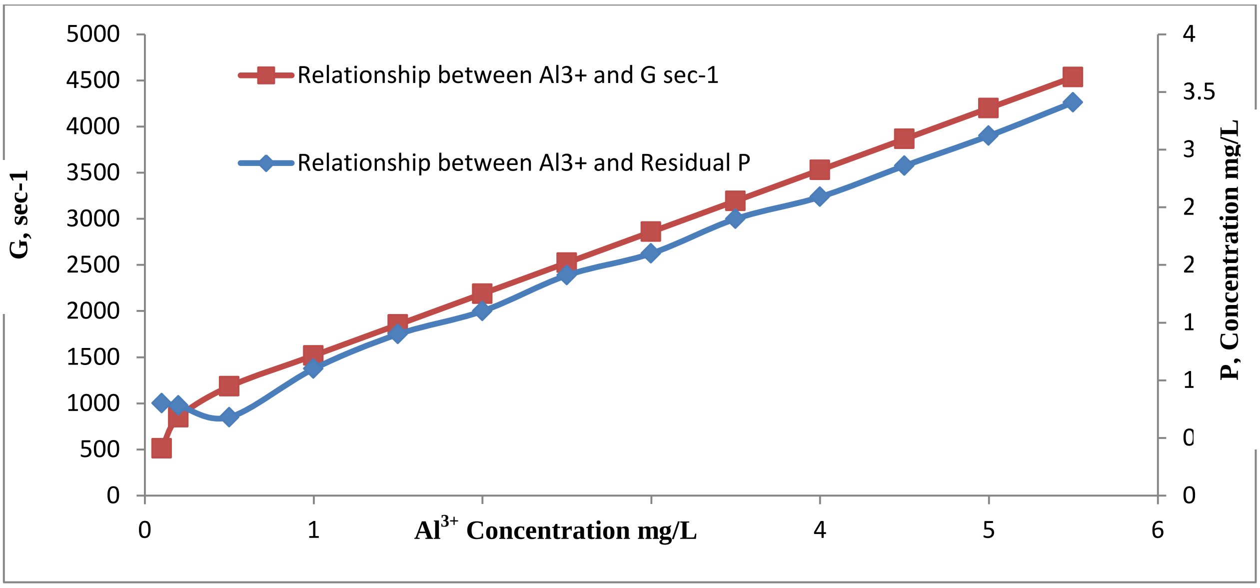

Figure 5: The Relationship between concentrated aluminum and % phosphorus removal, G.

This procedure will use different speeds [20] and different concentrations of coagulant to reach optimum dosage and will change parameters for removal undesirable materials.

Speeds of paddle will measured after each step as gradient velocity which can give more clearly image about mechanism of work [21]. In this procedure will be tried different patterns of coagulants solids and liquid. Liquid solution of coagulants will be at different concentration to reach optimum work [22, 23]. At this work will be used different chemicals like (NaOH, HCl) specified molarities to control pH [24]. However, the main idea of this stage is to observe behaviours of removal the materials which contribute in membrane fouling like organic, inorganic and suspended materials.

4. Conclusions

1- Ability of aluminium ion in removes phosphorus up to 95%, and creates aluminium phosphorus Flocs and these gelatinous characteristics which have ability go down.

2- The optimum concentration of aluminium to remove phosphorus is 0.5 mg/L. At this concentration velocity gradient will equal to 1076.915 sec^{-1} which the aluminium ion can achieve the best removal of phosphorus at 20 ° C.

3 - Aluminium phosphate to remove the turbidity through the mechanism of scavenging, which leads to reduce the scarcity with phosphorus at the same time.

4- The best temperature to achieve the best treatment and removal of phosphorus is 20 °C, therefore the best gradient velocity will be achieved which can agglomerate phosphorus with phosphorus gelatine and go down.

5. Recommendations

1- Treatment of dairy wastewater by alum at Iraq need to make further studied and applications.
2- Applied parameters of treatment like (Temperature of liquid, Coagulant type, *G*, pH, Rotation speeds of paddles, Try different type of coagulant, etc.

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