

THE BEHAVIOUR OF ALUMINIUM ION IN TREATMENT OF DAIRY WASTEWATER

*Ali A. Hasan

Civil Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq.

Received 24/9/2021

Accepted in revised form 22/12/2021

Published 1/7/2022

Abstract: In this article, it has been prepared synthetic dairy samples according to the global dairy wastewater characteristics. Has been used the OGAWA SEIKI Ltd apparatus and applied on these samples to predict the behavior of the alum in the treatment process. Physiochemical analyses were achieved to samples before and after treatment to stand on the ability of success. These tests have been achieved according to The experimental tests of characteristics were done as stated by American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). Results showed that behind the high removal, efficiency is many mechanical terms of coagulation, perhaps the most prominent of which is the scavenging mechanism. The effectiveness of the aluminum ion is at a certain limit, in limited pH, an increase in the concentration of this ion means an increase in the concentration of the positive charge and get the inverse effect. due to the wide capacity of aluminum ions to make bonds by combining with negative roots, it has been noticed the percentage removal of phosphorus reached up to 95%. These compounds create aluminum phosphorus flocs. The aluminum phosphorus compounds have gelatinous properties could make enmeshment and attract different particles and then settling in the bottom.

Keywords: Aluminum; Alum; Dairy wastewater; Jar Test; coagulation

1. Introduction

Aluminum salts almost was the most common compound used in the treatment of water and wastewater put in your mind about 16,500tons per year of sulfate in Acid and alkaline factories only in Iraq [1]. This compound may also name an alum. The main objective of alum compounds is to change the case of ions from stable to unstable states. This case will be done by adding opposite charges of compounds to pollutants similar to aluminum sulfates, which has positive charges [2-5]. The majority charge of ions pollution is negative charges, so the role of alum compounds is to moving these pollutants to agglomerate and to enlarge so be bigger [6-8]. This will give more chances to get down. These phenomena could be widely understood when note Fig.1.



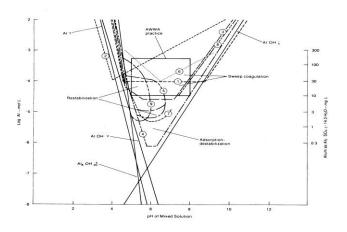


Figure 1. Stability-coagulation diagram for alum [9]

On the other hand, the increase in the use of alum led to an increase in the concentration of residual aluminum in the wastewater after the treatment process. An increase in the concentration of this element has negative effects on the liquefaction network specifically when factories have the permission to discharging water bodies through pipes after treatment and these cases present in developing countries [10-13]. These effects will be including a lowering of the zeta potential of the colloidal bodies when using alum, and an increase in the dose of alum added to the solution will guzzle the alkalinity before the value of the zeta voltage reaches the point achieved for the coagulation process [14-16]. The consumption of alkalinity will lead to the precipitation of aluminum sulfate in the liquefaction and drainage pipes. This precipitation will build scalers on the surfaces of pipes and clogging the path of particles after time [17-19]. This phenomenon may be close to treatment's specialists more water than industrial wastewater treatment specialists.

The effect of this element is not limited to the liquefaction network only [20, 21] but spreads to a decline in the quality of the treated

pollution over due wastewater to the unregulated use of alum. This bad management of work will principal to an increase in the concentration of residual aluminum in aquatic bulk, and thus rising turbidity. All recent studies and what do in the last 20 years confirmed the effect of aluminum ions on health, and its relationship to encephalopathy and early dementia. Furthermore, the aluminum ion will an effect on kidneys and bones due to kidney poisoning and softening bones [22-24].

Studies [25-27] have confirmed that the complex compounds formed by the bonding of the aluminum ion with the hydroxide ion, can also arise from the bonding of aluminum ion with some other alkaline compounds. Roots such as phosphates, sulfates and chlorides, forming bonds alike to that of the hydroxide ion, and formerly producing a grid of polymeric complexes capable of precipitation [28-31].

Hence, because the medium has been dealing with is a mixture of compounds and ions in addition to impurities, has become necessary to give an idea of the interaction and behavior of the aluminum ion to achieving treatment. The main objective of this step is to control the behavior of aluminum ions in treatment by organizing the parameters worker with it. The organizing step will lead to reducing the amount of alum in achieving the goal. Organizing might need to raise or reduce the temperature of the bulk. On the other hand, maybe need to add acid or alkaline to a range of the pH with the best treatment.

1.1. Characteristics of Dairy Wastewater

Dairy wastewater is described by the excessive weight of chemical oxygen demand and biochemical oxygen demand [32-35]. These compounds include dissolved and crystallized fats (glycerol, triglycerides), sugars (lactose) and protein (casein) in different aspects maybe colloidal forms, clots, and various shapes.

Wastewater discharged from dairy have fluctuated characteristics in Total Nitrogen, Total Phosphorus, Biological Oxygen Demand and Chemical Oxygen Demand. [36-40]. The explanations of these characteristics are shown in Table 1, below.

Table 1. The	features 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
Total nitrogen (TN) (mg/L)	10
Total phosphorus (TP) (mg/L)	2
TDS (mg/l)	150-450
EC (µ mhos/cm)	300-4000
pH	6.5-7.5
Temperature (°C)	25 - 35

It's could be classified three major categories of dairy wastewater concurring to their source and configuration, as below.

I- Processing water

II-Cleaning wastewater

III-Sanitary wastewater

2. Methodology

2.1.Materials

The research used the following, materials to study the topic:

 Alum in term of Al₂(SO₄)₃.18 H₂O has been added in 1% concentration as diluted solution. The diluted solution has been prepared by dissolving 10 gm of aluminum sulfate in 1 liter of Milluque water.

- Sucrose hydrate C₁₂H₂₂O₁₁.H₂O
- Sodium Phosphate DodecahydrateNa₃PO₄.12H₂O

Ammonium sulfate NH₄.2SO₄. The main tool that has been used in achieving the work of this article is Jar test model OGAWA SEIKI LTD. The synthetic samples that has been prepared at the lab, were giving to the global properties of the dairy wastewater in the world as shown in table [1] above.

2.2. Procedure of Work

•

To describe the identity of these samples, different types of salts has been used. The application of Jar Test Technique is to find out the optimal dosage of the coagulant as well as all parameters related in completing the work., different apparatuses were used as below:

2.2.1. Graduated cylinder with capacity 1000 ml has been used.

2.2.2. To pouring the dosages of coagulants, it has been used graduated pipettes.

2.2.3. Turned on the Jar test machine.

2.2.4. Withdrawal samples to test the characteristics.

2.3. Jar Test Technique (Procedure)

At the end of treatment procedure, it has been made test for these samples to stand on the all characteristics of samples. On the other hand, some conditions have been applied according to global references which are:

1- The intensity of mixing for violent 150 rpm for 3 min.

- 2- The intensity of gental mixing 30 rpm for 20 min.
- 3- Deposition for 20 min.

2.4. Synthetic Samples

Synthetic simulation samples have been prepared to actual models performed from dairy plants; these samples were prepared from salts below:

- The aluminum sulfate with chemical form Al₂(SO₄)₃.18H₂O has been used as a solution in concentration 1% by adds 10 gm. To keep the availability of Alum solution, the solution remade every week.
- The source of sugar such as Sucrose hydrate $C_{12}H_{22}O_{11}.H_2O$, has been used.
- Sodium Phosphate Dodecahydrate Na₃PO₄.12H₂O
- Ammonium sulfate NH₄.2SO₄

All steps above according to reference [41].

3. Results and Discussion

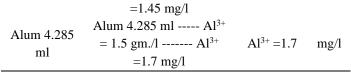
3.1. Role of Alum and Velocity Gradient in Treatment

It is not easy to apply water treatment to dairy wastewater treatment, but many aspects can be benefited from it.

The results obtained from the completion of these analyses are as shown in Table [2] below which has been leading to Fig.2 below:

 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⁺	Al ³⁺ =1.45	mg/l



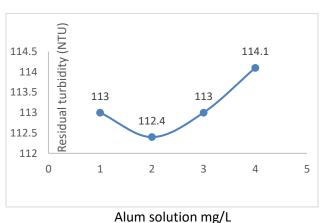


Figure 2. Relationship between added alum (mg/L) and residual turbidity (NTU).

Some factors have been approved according to reference [43,42]

These situations have been collected as below:

- Time of violent mixing 3 min.
- The velocity gradient of the violent mix is (122.79 sec-1, 205.7 sec-1) for 10 °C and 30 °C respectively, which mean the temperatures of the 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.

The power of stir required for optimal rapid mixing and flocculation is measured by the G value [42]. The G value concept, grown by Camp and Stein (1943), is widely used in designing rapid mixing and flocculation processes [44] and is defined by the equation (1). The last equations were applied to this topic and the results are shown in Fig.3.

$$G = \sqrt{W/\mu} \tag{1}$$

Which W= Dissipation function, μ = absolute viscosity Kg/m.sec.

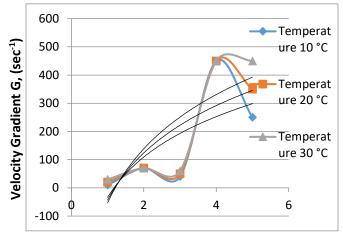
This equation (2), can be represented in another term which is,

$$G = (\sqrt{Cd} A\rho v^3)/2\mu v \tag{2}$$

Where is v = Linear velocity of paddle brushes relative to fluid velocity and this can be calculated from this equation,(3) $v = 2\pi rn/60$ (3)

Where,

r = Rotational radius (m), n = Number of rotation in minute, A = Area of blade (m²), ρ = Density of fluid, V = Volume of liquid (m³).



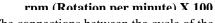


Figure 3. The connections between the cycle of the paddle per minute a velocity gradient at various temperatures.

3.2. Forms and Chemical Structures of Aluminum Compounds

The existence of the adsorption mechanism means dimeric aluminium hydroxide and then monomeric. Note equations 4, 5. After completion of these phenomena, polymeric aluminium hydroxide (Polynuclear complexes) will be created according to the chemical formula $\begin{bmatrix} AI_x(OH)_{2.5x}^{0.05x} \end{bmatrix}$, see equation (6).

$$AI^{3+} + 2H_20 \rightarrow AI(0H)_4^{2+}$$
 (4)

$$AI^{3+} + 2H_2O \rightarrow AI(OH)_{2+} + 2H^-$$
 (5)
 $XAI^{3+} + 2.5XH_2O \rightarrow AI_x(OH)2.5x$

$$0.5x + 2.5XH^{-}$$
 (6)

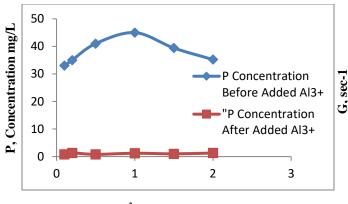
On the other hand, the enmeshment (scavenging) mechanism will start on Aluminum hydroxide amorphous in large amounts as shown in equation 7.

$$AI^{3+} + 3H_20 \rightarrow AI(0H)_3 + 3H^+$$
 (7)

These fundamentals may be applied to other roots to some extent. The removal of phosphorus could be attained due to building aluminium phosphors in same time as shown in equation (8), below.

$$Al^{3+} + H_n PO_4^{3-n} = AlPO_4(S) + n H^+$$
 (8)

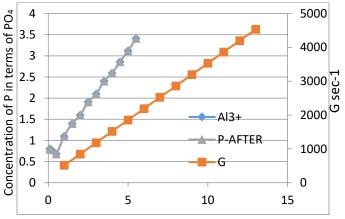
These mechanisms and procedures are implemented in one path to achieve one goal which is the removal of pollutants like phosphor (The main term of pollution in dairy wastewater), as shown in Fig. 3. In the same way, achieving goals includes reducing the concentration of residual aluminium in treated samples. Keep in mind the pH, Temperature, and some other parameters and determinants have been arranged regarding the Jar test procedure.



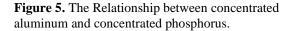
Al³⁺ Concentration mg/L

Figure 4. The connections between heavy aluminum and heavy phosphorus.

From Fig. 2, it has been deduced that the optimum value of Al^{3+} is 0.5 Mg/l. This confirmed the explanation above. Fig. 5 below shows the activity of aluminium ion in treatment. confirmed the creates of aluminium phosphate. This process has been continued with the rise of gradient velocity to some extent. At a point the flocs built will be broken if the mixing is still violent. The translation of this explanation with its figure is shown in Fig. 6 below.



Concentration of added Aluminum ion mg/l-calculated in alum.



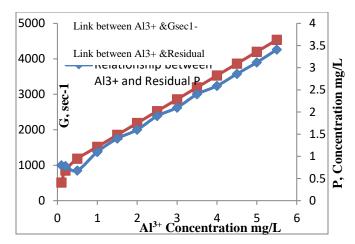


Figure 6. The Relationship between concentrated aluminum and % phosphorus removal, G.

The best way to achieving the value of parameters it's to confirm one of the variants and changes the other variants [42].

The paddle rotation prepared as velocity will be measured each try. As mentioned above and according to (Camp and Stein)'s relation, the velocity gradient will be known. [43]. In this turn, it has been used different dosage of coagulant solution [46, 47]. for controlling the point of reaction, it should be control on the value of pH, and this has been achieved by (NaOH, HCl) specified molarities to control pH [48].

4. Conclusion

- The random use of alum in the treatment of dairy wastewater leads to an increase in the concentration of aluminum residues. This increases the turbidity of the treated wastewater leaving the plant, furthermore to treatment problems and other health problems.
- Behind the high removal, efficiency is many mechanical terms of coagulation, perhaps the most prominent of which is the scavenging mechanism. The

encouraging the value of the pH of this liquid and its closeness to neutralization and the adsorption mechanism of other positive ions on the surfaces of gelatinous compounds then achieving the neutralization of pollutants like suspended solids.

- The effectiveness of the aluminum ion is at a certain limit, in limited pH, an increase in the concentration of this ion means an increase in the concentration of the positive charge and get the inverse effect. The direction of the negative sulfate radical to equalize this charge was originally present in its alum composition, leading to an increase in the percentage of lost sulfate. The reducing the remaining turbidity and pollutants originally as a result of misuse of alum insinuating to the processor that high removal efficiency happened. This process has been led to an increase in the composition of the remaining aluminium. Since dealing with natural models, the ions have a role in influencing the coagulation mechanics and the behavior of the aluminum ion.
- Contribution of sodium, potassium and • other positive ions in the models of The reduction treatment. of ions concentration after treatment hints at the probability of these ions in the treatment mechanism. The sweep coagulation (scavenging coagulation) gave more possibilities to attaining the removal process. The sharing activity depended on the physical and chemical properties of ions like ionic and atomic diameters. These case has been noticed in the treatment of dairy wastewater by using alum. The article indicates the capacity

of aluminum ions, which carry a greater valency than sodium and potassium and have certain physical characteristics such as the smallest ionic radius of them in the equation of colloids. But without bonds of aluminum hydroxide compounds the activity of ions will be non-existent. 5. The natural models overcame the increase in bicarbonate concentration due to the decrease in the pH value due to the addition of acidoriented alum.

- The tendency of hydroxides, phosphates, nitrates and other negative roots to a large extent, and carbonates and chlorides to a lesser degree, to the formation of coordination compounds capable of sedimentation of colloids. Combining these ions with aluminum hydroxide compounds will reduce turbidity and sources of pollution. The tendency of sulfates to form positively charged compounds that also contribute to raising the efficiency of removal. The last phenomenon of sulfate will occur once the common ion effect start.
- The most confirmation cited above about the inclination of aluminum ion toward negative roots is the removal percentage of phosphate which reached 95%. This elimination has been attained due to the building of aluminum phosphate which has the ability to precipitation.
- The necessity of controlling the parameter of treatment as well as the determinants. This section may need to heat by heater or cooling by adding ice. All of all is to organize the temperature of the liquid. On the other hand, controlling pH is under request by

adding alkaline or acid to organize the parameter of treatment.

Acknowledgements

The author would like to thank the college of engineering, civil DEPT. and the laboratories of civil and environmental engineering in Iraq, for the support to achieve this article.

Conflict of interest

The author declares that there are no conflicts of interest regarding the publication of this manuscript.

5. References

- 1. Reconstruction and Development Framework. IRAQ RECONSTRUCTION and INVESTMENT, FEBRUARY 2018. p. 301.
- 2. Hem, S.L. and H. HogenEsch, Aluminumcontaining adjuvants: properties, formulation, and use. Vaccine adjuvants and delivery systems, 2007: p. 81-114.
- 3. Verma, A.K., R.R. Dash, and P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. Journal of environmental management, 2012. 93(1): p. 154-168.
- 4. Vesilind, P.A., J.J. Peirce, and R.F. Weiner, Environmental pollution and control. 2013: Elsevier.
- 5. Hocking, M.B., Handbook of chemical technology and pollution control. 2016: Elsevier.
- Muisa, N., et al., Utilization of alum sludge as adsorbent for phosphorus removal in municipal wastewater: A review. Journal of Water Process Engineering, 2020. 35: p. 101187.
- 7. Vepsäläinen, M. and M. Sillanpää, Electrocoagulation in the treatment of

industrial waters and wastewaters, in Advanced Water Treatment. 2020, Elsevier. p. 1-78.

- Bahrodin, M.B., et al., Recent advances on coagulation-based treatment of wastewater: Transition from chemical to natural coagulant. Current Pollution Reports, 2021: p. 1-13.
- Amirtharajah, A. and K.M. Mills, Rapid-mix design for mechanisms of alum coagulation. Journal-American Water Works Association, 1982. 74(4): p. 210-216.
- Rao, S.R., Surface chemistry of froth flotation: Volume 1: Fundamentals. 2013: Springer Science & Business Media.
- 11. Dassanayake, K., et al., A review on alum sludge reuse with special reference to agricultural applications and future challenges. Waste Management, 2015. 38: p. 321-335.
- Teh, C.Y., et al., Recent advancement of coagulation–flocculation and its application in wastewater treatment. Industrial & Engineering Chemistry Research, 2016. 55(16): p. 4363-4389.
- Gomes, S.D.C., et al., Progress in manufacture and properties of construction materials incorporating water treatment sludge: A review. Resources, Conservation and Recycling, 2019. 145: p. 148-159.
- Ostolska, I. and M. Wiśniewska, 14. Application of the zeta potential measurements to explanation of colloidal Cr 2 O 3 stability mechanism in the presence of the ionic polyamino acids. Colloid and polymer science, 2014. 292(10): p. 2453-2464.
- Carlson, J. and S. Kawatra, Factors affecting zeta potential of iron oxides. Mineral Processing and Extractive Metallurgy Review, 2013. 34(5): p. 269-303.

- Hunter, R.J., Zeta potential in colloid science: principles and applications. Vol. 2. 2013: Academic press.
- 17. 18. Crowley, D., Health and environmental effects of landfilling and incineration of waste: a literature review. -1014, 2003.
- 18. Amjad, Z., The science and technology of industrial water treatment. 2010: CRC press.
- 19. Liu, J., L. Zhang, and Z. Liu, Environmental Pollution Control. 2017: De Gruyter.
- Tommaso, 20. Chemical G., et al.. characterization and anaerobic biodegradability of hydrothermal liquefaction aqueous products from mixed-culture wastewater algae. Bioresource technology, 2015. 178: p. 139-146.
- 21. Huang, H.-j. and X.-z. Yuan, Recent progress in the direct liquefaction of typical biomass. Progress in Energy and Combustion Science, 2015. 49: p. 59-80.
- Crisponi, G., et al., Chelating agents for human diseases related to aluminium overload. Coordination Chemistry Reviews, 2012. 256(1-2): p. 89-104.
- 23. Crisponi, G., et al., The meaning of aluminium exposure on human health and aluminium-related diseases. Biomolecular concepts, 2013. 4(1): p. 77-87.
- 24. Tomljenovic, L., Aluminum and Alzheimer's disease: after a century of controversy, is there a plausible link? Journal of Alzheimer's Disease, 2011. 23(4): p. 567-598.
- 25. Cicek, V. and B. Al-Numan, Corrosion chemistry. 2011: John Wiley & Sons.
- 26. Wade, K. and A.J. Banister, The Chemistry of Aluminium, Gallium, Indium and Thallium: Comprehensive Inorganic Chemistry. 2016: Elsevier.

- 27. Cavezza, F., et al., A review on adhesively bonded aluminium joints in the automotive industry. Metals, 2020. 10(6): p. 730.
- 28. Dorozhkin, S. V. (2012). "Amorphous calcium orthophosphates: nature, chemistry and biomedical applications." Int. J. Mater. Chem 2(1): 19-46.
- 29. Manamperuma, L. D. (2016). "Optimisation of the coagulation process to improve plant availability of phosphorus in wastewater sludge."
- 30. Abo-Zaid, S. M. B. (2019). Comparing Poly Aluminum Chloride and Moringa Seeds as Alternative for Water Coagulations, Sudan University of Science and Technology.
- 31. Azam, H. M., et al. (2019). "Phosphorous in environment: characteristics the with distribution and effects. removal mechanisms, treatment technologies, and factors affecting recovery as minerals in engineered and systems." natural Environmental Science Pollution and Research 26(20): 20183-20207.
- Lee, H., et al. (2003). "Optimizing bioconversion of deproteinated cheese whey to mycelia of Ganoderma lucidum." Process Biochemistry 38(12): 1685-1693.
- 33. Tikariha, A. and O. Sahu (2014). "Study of characteristics and treatments of dairy industry waste water." Journal of applied & environmental microbiology 2(1): 16-22.
- Choi, H.-J. (2016). "Dairy wastewater treatment using microalgae for potential biodiesel application." Environmental Engineering Research 21(4): 393-400.
- 35. Bortoluzzi, A. C., et al. (2017). "Dairy wastewater treatment using integrated membrane systems." Journal of environmental chemical engineering 5(5): 4819-4827.

- 36. Martín-Rilo, S., et al. (2015). "Treatment of dairy industry wastewater by oxygen injection: performance and outlay parameters from the full scale implementation." Journal of Cleaner Production 86: 15-23.
- 37. Kolev Slavov, A. (2017). "General characteristics and treatment possibilities of dairy wastewater–a review." Food technology and biotechnology 55(1): 14-28.
- 38. Vijayaraghavalu, S., et al. (2019). Treatment and Recycling of wastewater from dairy industry. Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future, Springer: 91-115.
- 39. Patra, F. and R. K. Duary (2020). Waste from Dairy Processing Industries and its Sustainable Utilization. Sustainable Food Waste Management, Springer: 127-154.
- 40. Shi, W., et al. (2021). "Dairy processing sludge and co-products: A review of present and future re-use pathways in agriculture." Journal of Cleaner Production: 128035.
- 41. APHA, AWWA, WPCF, "Standard Methods for the Examination of Water and Wastewater", 23th, 2017.
- 42. Letterman, R. D., et. al., "Influence of Rapid Mix Parameters on Flocculation", Journal of AWWA, Vol. 65, 1973.
- 43. Eckenfelder, W., and Wesley, Jr., "Industrial Water Pollution Control", McGraw-Hill, Inc., New York, 2000.
- 44. Shammas, N.K. (2005). "Coagulation and Flocculation," In: Physicochemical Treatment Processes (vol. 3). "Handbook of environmental engineering (Eds. L.K. Wang, Y.-T. Hung, N.K. Shammas). Humana Press, Totowa, NJ, USA.
- 45. Alley, E.R. (2007). "Water Quality Control Handbook," 2nd ed., McGraw-Hill, NY, USA.

- 46. Luo, C. (1998). "Distribution of velocities and velocity gradients in mixing and flocculation vessels: Comparison between LDV data and CFD predictions."
- 47. Black, A., et al. (1957). "Review of the jar test." Journal (American Water Works Association) 49(11): 1414-1424.
- 48. Sajjad, M. (1995). "Effect of various mixing devices and patterns on flocculation kinetics in water treatment."