Journal of Engineering Science and Technology
Special Issue on ISSTEC, November (2021) 38 - 46

TREATMENT OF DYES WASTEWATER USING ALUMINIUM SULFATE AND POLY ALUMINIUM CHLORIDE (PAC)

RIYANTO*, LUTHFIA PASHA HANINDYTA

Department of Chemistry, Faculty of Mathematics and Natural Science, Islamic University of Indonesia, Jalan Kaliurang KM 14,5 Sleman, Yogyakarta, Indonesia, 55584
*Corresponding author: riyanto@uii.ac.id

Abstract

The dye waste treatment has been carried out using the coagulation method with Aluminum Sulfate and Poly Aluminum Chloride (PAC) as a coagulant to reduce the concentration of Chemical Oxygen Demand (COD). The purpose of this study is that the dye waste contains a high enough concentration of COD so that it will be very dangerous if it is directly discharged into the environment. This research was conducted using the coagulation method with variations in pH and variations in coagulant mass to determine its effect on decreasing COD concentration, considering that pH and coagulant mass are factors that affect coagulation. Coagulation was carried out with variations in pH 5, 6, 7, 8, and 9 while the mass variations were 0.2; 0.4; 0.6; 0.8; and 1 g. The results of the coagulation process were analysed using a UV-Vis Spectrophotometer with a calibration curve method. The results showed that the best pH and the best mass for Aluminum Sulfate and PAC in reducing the COD of the dyestuff industrial wastewater was pH 9 and a mass of 1 g with a percentage efficiency reduction of COD concentration of 90.04%.

Keywords: Aluminium sulphate, Dyes, Poly Aluminium chloride, Wastewater.

1. Introduction

The dyes industry has developed in the last few decades. Dye waste from the industry has a high value of Chemical Oxygen Demand (COD), turbidity, and various high concentrations of organic chemical contaminants. Organic and inorganic contaminants cause health risks for humans and living things. Dyes and pigments are a large group of dye waste pollutants. This substance is usually used in industrial fields such as textiles, plastics, leather, paints, cosmetics, printing, and paper [1, 2]. Dyestuff wastewater comes from printing and colouring, bleaching, and finishing processes. This wastewater contains high concentrations of dyes, high salinity, and organic matter that is difficult to degrade [3].

Based on their chemical structure, dyes can be divided into various types, namely nitroso, azo, stilbene, diphenylmethane, triphenylmethane, indigoid, amino quinone, indophenol, acridine, amine, and quinoline dyes. Dyes are classified into two, namely synthetic and natural dyes [4]. Approximately 10,000 types of synthetic and natural dyes are produced annually worldwide which weigh approximately between 7.10^5-1.10^6 tons, and a large amount of dye is wasted during the manufacturing and application processes. Many chemicals and dyes that are not used during the dyeing, printing, and textile processes are disposed of as waste into the environment [5, 6].

According to Roussy et al. [7], the most frequently used processes for the treatment of coloured waste are adsorption, for example using activated carbon [8, 9], resins [10], agricultural waste [11-13], microorganisms [14] and biopolymers [15-17]. However, this process usually consists of a simple transfer of pollutants from the dispersed phase to the concentrated phase. The use of expensive materials and the need to control material disposal make this technique not cost-effective. However, processes such as coagulation and flocculation have proven to be simpler and more cost-effective [18-23].

Coagulation/flocculation is one of the most widely used physical-chemical processes to remove dyes in wastewater [24-29]. The advantage of this technique is that the dye can be completely removed from wastewater [25]. Alum coagulants have been reported by Parmar et al (2011) to reduce solid organic compounds and nutrients contained in dairy industry waste [30]. It was also reported by Rui et al (2012) that alum coagulants were more effective in removing COD in leachate than ferric chloride coagulants [31]. The effectiveness of the use of alum coagulants has been reported by Gandhimathi et al. [32] that at an alkaline pH the solution produces a higher COD reduction efficiency than ferric chloride coagulant. This is caused by differences in the coagulant hydrolysis mechanism which is influenced by pH, coagulant dose, and colloid concentration. In the use of alum, the equilibrium that occurs is controlled by $Al(OH)_3$ and $Al(OH)_4^-$ at pH>7.2 and $Al(OH)_3$ and $Al_{13}(OH)_{34}^{5+}$ at pH 5.6-7.2. Adesoye et al., (2014) stated that $Al_2(SO_4)_3.18H_2O$ was able to lower phosphate levels better than $FeSO_4.7H_2O$. $Al_2(SO_4)_3.18H_2O$ has the advantage in wastewater treatment that it covers a wide pH range, namely pH 2-9 unless the effluent has extreme acid or alkaline conditions [33].

This paper presents the results of research on processing dye waste using two chemicals, namely aluminum sulfate, and PAC. This research also treats dye waste with a combination of aluminum sulfate and PAC. This paper also presents data on the effect of pH and coagulant weight on COD reduction. The COD value is a measure of the success of the dye waste treatment process because it generally contains organic compounds.

2. Material and Method

2.1. Instrumentation and material

The tools used in this research are UV-Vis double beam spectrophotometer (Hitachi UH5300), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). The chemicals used in this study were industrial dyestuff ink waste, Potassium Hydrogen Phthalate (KHP), Potassium Dichromate ($K_2Cr_2O_7$), Sulfuric Acid (H_2SO_4), Mercury (II) Sulfate ($HgSO_4$), Silver Sulfate (Ag_2SO_4), Aluminum Sulfate (Aluminum Sulfate), Poly Aluminum Chloride (PAC), Sodium Hydroxide (NaOH). The chemicals used have a pro analysis grade from Merck.

2.2. Method

Amount 50 mL of the dye waste sample was put into a beaker then the pH of the waste was measured first. 1N H_2SO_4 was added to adjust the acid pH, namely 5, 6, and 7. 1N NaOH was added to adjust pH 8 and 9, then a pH buffer was added. Then the coagulant Aluminum Sulfate was added as much to as 0.4 g. After that, it was stirred using a magnetic stirrer for 60 minutes and allowed to stand for 1 day. Then filtered using filter paper. The coagulation filtrate was then analysed with a UV-Vis spectrophotometer and sought the best pH for decreasing COD values. This study also varied the weight of the coagulant to decrease the COD concentration. COD analysis was carried out according to the APHA 5520 D method [34].

3. Results and Discussion

3.1. Characterization of Aluminum sulfate and PVC

Before being used as a coagulant Aluminum sulfate was analysed for morphology and elemental content using Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). The morphological structure of Aluminum Sulfate and its elemental content is shown in Fig. 1.

Figure 1(a) is the morphological structure of Aluminum Sulfate with 1000 times magnification. At 1000x magnification, the surface is rough, irregular, and has no pores. Figure 1(b) with a magnification of 2,000x shows that the surface is rough, uneven, irregular, and has no pores. Aluminum Sulfate contains lumps of various sizes. Figure 1(c) shows the composition of elements in aluminum sulfate, namely Al, O, S, and C with masses of 5.92, 76.55, 5.82, and 11.71%, respectively.

Figure 2(a) shows the morphological structure of PAC at 1000x magnification. At a magnification of 1000, the surface is irregular, consisting of elongated thin sheets and heterogeneous in size. Figure 2(b) shows the morphological structure of PAC with a magnification of 2,000x showing an uneven and irregular surface. Figure 2(c) shows that the PAC coagulant contains elements O, Cl, Al, and C with a mass of 54.91, 12.87, 15.74, and 16.49%, respectively.

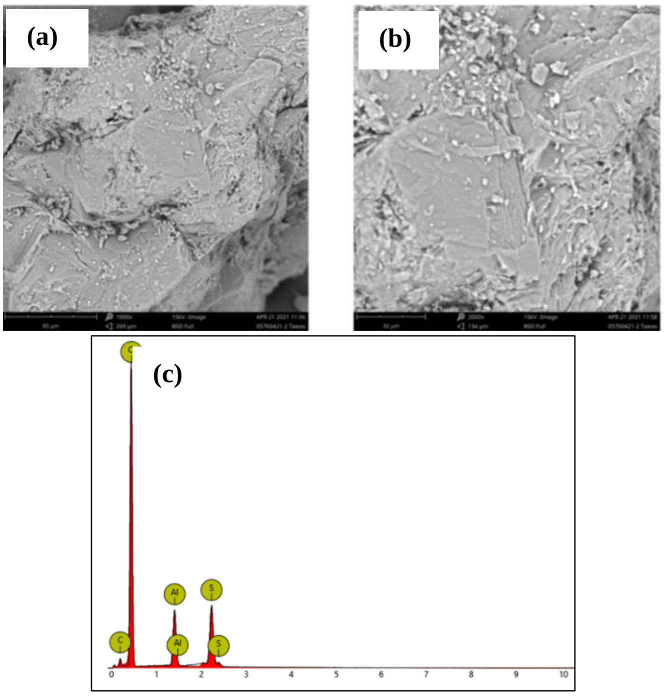


Fig. 1. SEM image with magnification (a) 1.000x,
(b) 2.000x, and (c) and EDX spectra of aluminum sulfate.

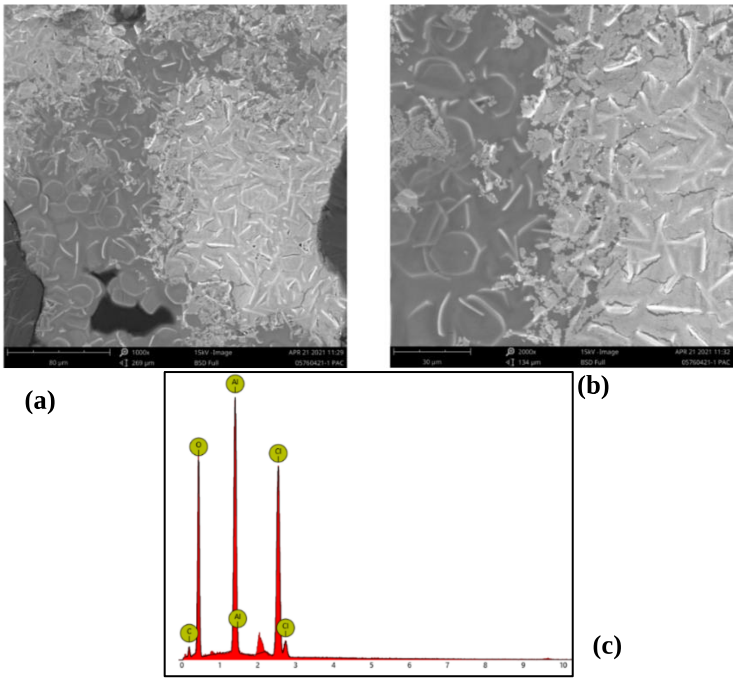


Fig. 2. SEM image with magnification
(a) 1.000x, (b) 2.000x, and (c) EDX spectra of PAC.

3.2. The effect of pH and weight on decreasing COD concentration with aluminum sulfate as a coagulant

The dye waste is purple and viscous, after the processing is carried out by the coagulation method. Waste after being processed changes colour to clear white and decreases in viscosity. The colour change of the waste is shown in Fig. 3. Figure 3 shows that there has been a significant colour change. Aluminum Sulfate coagulant with variations in pH can bind organic substances in dye waste into sludge/floc.

Figure 4(a) shows the effect of pH on the COD concentration reduction process by coagulation method using Aluminum Sulfate. Based on Fig. 4(a) aluminum sulfate can work well as a coagulant for liquid waste dyes at pH 9. This happens because, in an alkaline atmosphere, Al^{3+} in water is hydrolysed to form positively charged complexions that can bind suspended particles that are negatively charged. The addition of an Aluminum Sulfate coagulant tends to lower the pH of the solution because Aluminum Sulfate produces H^+ ions after reacting with water

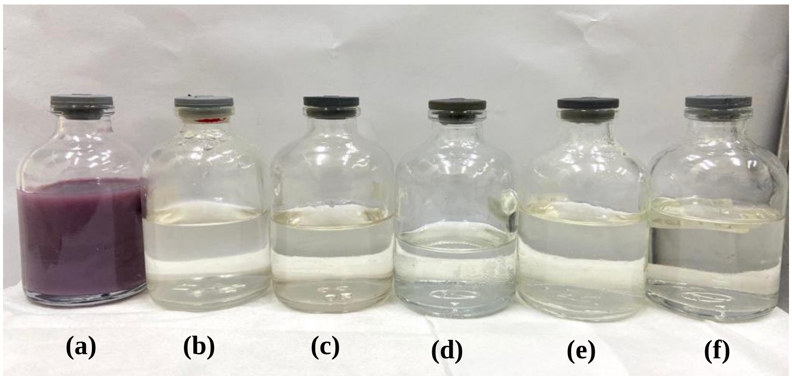
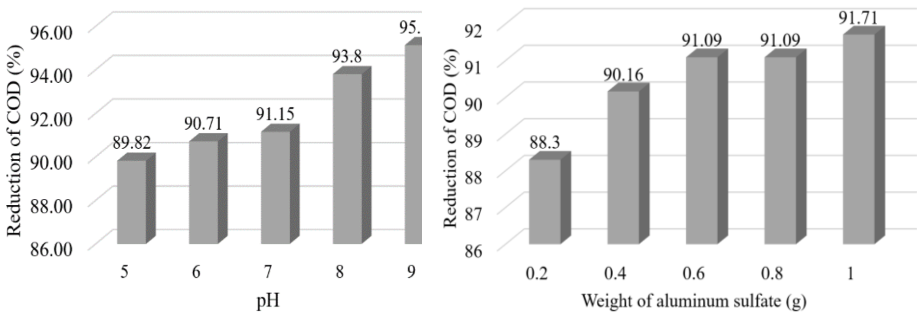


Fig. 3. Changes in the colour of the dye wastewater after being treated with aluminum sulfate using different pH, where (a) before treatment (b) pH 5, (c) pH 6, (d) pH 7, (e) pH 8, (f) pH 9.



(a) **(b)**

Fig. 4. The effect of pH (a) and weight (b) to the reduction of COD in dye wastewater using aluminum sulfate

The reaction for hydrolysis of Al in water is as follows:

$$Al_2(SO_4)_3 + 6H_2O \leftrightarrow 2Al(OH)_3 + 6H^+ + SO_4^{2-}$$

This reaction causes H+ ions to be released and causes the pH of the solution to become more acidic. The higher the concentration of aluminum sulfate, the more H+ ions are released so that the pH of the water decreases. Figure 4(b) shows that the addition of aluminum sulfate weight effects decreasing the COD concentration. The addition of coagulant weight causes the coagulant concentration to increase so that the frequency of collisions also increases.

3.3. The effect of pH and coagulant weight on COD reduction in dye wastewater treatment using PAC

Figure 5(a) shows the effect of pH on reducing COD in the treatment of dye waste with PAC. pH 9 showed the greatest decrease in COD concentration among other pHs. The coagulation process using PAC reaches the highest efficiency at pH 7-10. At a pH below 7, PAC will experience charge neutralization, because PAC has a high enough positive charge so that it maintains its charge neutralization capacity.

Figure 5(b) shows the effect of PAC weight on COD reduction. Coagulant weight is an important factor that can affect the decrease in COD concentration. The appropriate weight of the coagulant affects the floc formation process so that it runs well and optimally. The more coagulant added will increase the collision frequency of the positive charge of the coagulant with the negative charge of the colloid. However, if there is an excessive addition will result in saturation and will interfere with the COD reduction process.

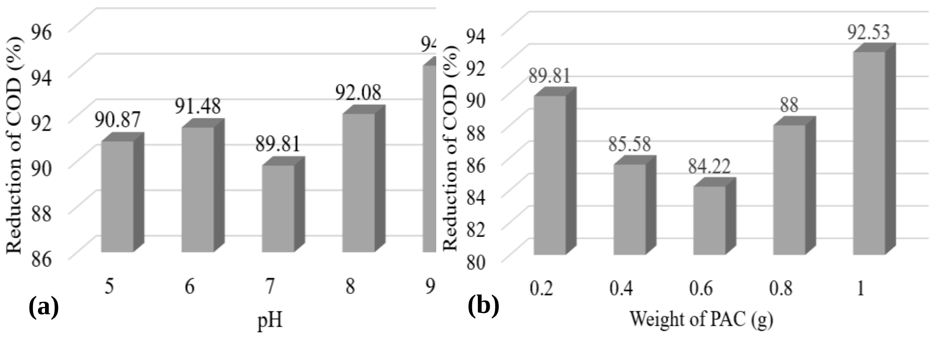


Fig. 5. The effect of pH (a) and weight (b) to the reduction of COD in dye wastewater using PAC.

Table 1 shows that a mixture of Aluminum Sulfate and PAC can reduce the COD concentration by 90.04%. This decrease in COD concentration occurs due to the addition of Aluminum Sulfate and PAC coagulant into the waste, resulting in the addition of cations to neutralize the negative charge of the waste colloid particles and Van der Waals forces occur so that the particles will collide and form larger particles and settle to the bottom of the solution. (floc). The mixture of Aluminum Sulfate and PAC in reducing COD in dye waste is not beneficial because there is no synergistic effect

Table 1. Decreasing COD Concentration in the treatment of dye waste with mixed coagulant

Sample	COD (mg/L)	Reduction of COD (%)
Dyes wastewater before treatment	36.566,67	90.04
Dyes wastewater after treatment using aluminum sulfate + PAC	3.641,67	

4. Conclusions

The effect of pH variations on Aluminum Sulfate and PAC coagulants showed that the best pH for reducing the COD concentration of dyestuff industrial waste was pH 9, which were 95.13% and 94.2%, respectively. The effect of weight variation on Aluminum Sulfate and PAC coagulant showed that the best mass to reduce the COD concentration of dyestuff industrial waste was 1.0 g with a decrease in COD concentration of 91.71% and 92.53%, respectively. Coagulant mixture of Aluminum Sulfate and PAC with an optimum weight of 1.0 g and pH 9 can reduce the COD concentration of dyestuff industrial waste by 90.04%.

References

1. Shah, M.P. (2018). Bioremediation-Waste Water Treatment. *Journal of Bioremediation & Biodegradation*, 9 (1), 1-10.
2. Wazir, M.B.; Daud, M.; Ali, F.; and Al-Harthi, M.A. (2020). Dendrimer assisted dye-removal: A critical review of adsorption and catalytic degradation for wastewater treatment. *Journal of Molecular Liquids,* 315, 113775.
3. Sun, W.; and Yang, K. (2020). Discussion on Printing and Dyeing Wastewater Treatment Methods. *IOP Conference Series: Earth and Environmental Science*, 514.
4. Al-Kdasi, A.; Idris, A.; Saed, K.; and Guan, C.T. (2004). Treatment of textile wastewater by advanced oxidation processes, *Global Nest: The International Journal.* 6, 222-230.
5. Chowdhury, M.F.; Khandaker, S.; Sarker, F.; Islam, A.; Rahman, M.T.; and Awual, R. (2020). Current treatment technologies and mechanisms for removal of indigo carmine dyes from wastewater: A review. *Journal of Molecular Liquids,* 318.
6. Katheresan, V.; Kansedo, J.; and Lau, S.Y. (2018). Efficiency of various recent wastewater dye removal methods: a review. *Journal of Environmental Chemical Engineering,* 6(4), 4676-4697.
7. Roussy, J.; Chastellan, P.; Vooren M.V.; and Guibal, E. (2005). Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers. *Water SA*, 31, 3.
8. Wu, F.C.; Tseng, R.L.; and Juang, R.S. (2001). Adsorption of dyes and phenols from water on the activated carbons prepared from corncob wastes. *Environmental Technology,* 22(2), 205-213.
9. Yang X.Y.; and Al-Duri, B. (2001). Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon. *Chemical Engineering Journal*, 83(1), 15-23.
10. Karcher, S.; Kornmuller, A.; and Jekel, M. (2002). Anion exchange resins for removal of reactive dyes from textile wastewaters. *Water Research,* 36(19), 4717-4724.
11. Annadurai, G.; Juang, R.S.; and Lee, D.J. (2002). Use of cellulosebased wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials,* B92 (3), 263-274.

12. Morais, L.C.; Goncalves, E.P.; Vasconcelos, L.T.; and C.G. Gonzalez Beca, C.G. (2000) Reactive dyes removal from wastewaters by adsorption on Eucalyptus bark-adsorption equilibria. *Environmental Technology*, 21(5), 577-583.
13. Robinson, T.; Chandran, B.; and Nigam, P. (2002). Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. *Environment International*, 28(1), 29-33.
14. Fu Y.; and Viraraghavan, T. (2003). Column studies for biosorption of dyes from aqueous solutions on immobilised Aspergillus niger fungal biomass. *Water SA*, 29(4), 465-472.
15. Choi, J.H.; Shin, W.S.; Lee, S.H.; Joo, D.J.; Lee, J.D.; Choi, S.J.; and Park, L.S. (2001). Application of synthetic polyamine flocculants for dye wastewater treatment. *Separation Science and Technology*, 36(13), 2945-2958.
16. McCarrick, P.; Tobin, J.; and Guibal, E. (2003). Comparative sorption of dyes on chitosan and activated carbon. *Separation Science and Technology*, 38(12-13), 3049-3073.
17. Wu, F.C.; Tseng, R.L.; and Juang, R.S. (2001). Enhanced abilities of highly swollen chitosan beads for colour removal and tyrosinase immobilization. *Journal of Hazardous Materials*, 81(1-2), 167-177.
18. Chiou, M.S.; and Li, H.Y. (2002). Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials*, 93(2), 233-248.
19. Chu, W. (2001). Dye removal from textile dye wastewater using recycled alum sludge. *Water Research*, 35(13), 3147-3152.
20. Kacha, S.; Derriche, Z.; and Elmaleh. S. (2003). Equilibrium and kinetics of colour removal from dye solutions with bentonite and polyaluminium hydroxide. *Water Environment Research*, 75(1), 15-20.
21. Kim, T.H.; Park, C.; Shin, E.B.; and Kim, S. (2004). Decolorization of disperse and reactive dye solutions using ferric chloride. *Desalination*, 161(1), 49-58.
22. Metes, A.; Koprivanac, N; and Glasnovic, A. (2000). Flocculation as a treatment method for printing ink wastewater. *Water Environment Research*, 72(6), 680-688.
23. Zemaitaitiene, R.J.; Zlobaite, E.; Klimaviciute, R.; and Zemaitaitis, A. (2003). The role of anionic substances in removal of textile dyes from solutions using cationic flocculant. *Colloid Surface A*, 214(1-3), 37-47.
24. Asadollahfardi, G.; Zangooei, H.; Motamedi, V.; and Davoodi, M. (2018). Selection of coagulant using jar test and analytic hierarchy process: a case study of Mazandaran textile wastewater. *Advances in Environmental Research*, 7, 1-11.
25. Mane, V.S.; and Babu, P.V.V. (2011). Evaluation of performance of Coagulation/Flocculation method for the removal of dyes from aqueous solutions. In: Institute Technology, N.U. (Ed.), *International Conference on Current Trends in Technology*. Ahmedabad, Gujarat, 1-6.
26. Pokhrel D.; and Viraraghavan, (2004). Treatment of pulp and paper mill wastewater: a review. *Science of the Total Environment*, 333, 37-58.
27. Sadri, M.S.; Moghaddam, M.M.R.; and Arami, M. (2010). Coagulation/ flocculation process for dye removal using sludge from water treatment plant:

optimization through response surface methodology. *Journal of Hazardous Materials*, 175, 651-657.

28. Satyawali, Y.; and Balakrishnan, M. (2008). Wastewater treatment in molasses-based alcohol distilleries for COD and colour removal: a review. *Journal of Environmental Management*, 86, 481-497.
29. Zonoozi, M.H.; Alavi, M.M.R.; and Arami, M. (2008). Removal of acid red 398 dye from aqueous solutions by coagulation/flocculation process. *Environmental Engineering and Management Journal*, 7, 695-699.
30. Parmar, K.A.; Prajapati, S.; Patel, R.; and Dabhi, Y. (2011). Effective use of ferrous sulfate and alum as a coagulant in treatment of dairy industry wastewater. *Journal of Engineering and Applied Science*, 6(9), 42-45.
31. Rui, L.M.; Daud, Z.; and Latif, A.A.A. (2012). Coagulation-flocculation in leachate treatment by using ferric chloride and alum as coagulant. *International Journal of Applied Engineering Research*, 2, 1929-1934.
32. Gandhimathi, R.; Durai, N.J.; Nidheesh, P.V.; Ramesh, S.T.; and Kanmani, S. (2013). Use of combined coagulation-adsorption process as pretreatment of landfill leachate. *Iranian Journal of Environmental Health Science and Engineering*,10, 24.
33. Adesoye, A.M.; Olayinka, K.; Olukomaiya, O.O.; and Iwuchukwu, P.O. (2014). The removal of phosphates from laundry wastewater using alum and ferrous sulphate as coagulants. *International Journal of Innovation and Scientific Research*, 8, 256-260.
34. APHA. (2017). *Standard method for the examination of water and wastewater 23rd edition.* Washington DC: American Public Health Association.