Journal of Hazardous Materials 161 (2009) 431–438

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Performance optimization of coagulation/flocculation in the treatment of wastewater from a polyvinyl chloride plant

F. AlMubaddal, K. AlRumaihi, A. Ajbar*

Department of Chemical Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

ARTICLE INFO

Article history:
Received 13 December 2007
Received in revised form 26 March 2008
Accepted 26 March 2008
Available online 8 April 2008

Keywords:
Flocculation
Coagulation
PVC
Latex
Jar test

ABSTRACT

This paper presents results of an experimental study of coagulation/flocculation process of wastewater generated from a polyvinyl chloride (PVC) plant. The wastewater contains fine chlorine-based solid materials (i.e. latex). Experiments were carried out using a model wastewater which is chemically identical to the actual plant but is more consistent. Inorganic ions ($Al_2(SO_4)_3$, $FeCl_3$ and $CaCl_2$) and a water soluble commercial polyelectrolyte (PE) were added to the wastewater sample. Coagulation efficiency was determined by measuring both the turbidity of the supernatants and the relative settlement of the flocs in the jar test. It was found that aluminum and ferric ions were more efficient than calcium ions as coagulants. The addition of polyelectrolyte was found to improve substantially the coagulation/flocculation process. It was found that the ($Al_2(SO_4)_3$) combined with the polyelectrolyte at certain pH and agitation speed gave the best results compared to calcium chloride or ferric chloride when combined with the same concentration of polyelectrolyte. Only 0.0375 g of a solution of (0.5% $Al_2(SO_4)_3$) was required to coagulate the model wastewater. Ferric chloride (2.5% $FeCl_3$) combined with the polyelectrolyte, on the other hand, required 0.1 g while the optimum turbidity is almost the same. As for calcium chloride (2.5% $CaCl_2$) it was found to be the least effective. The coagulation/flocculation process was found to be dependent on both pH and the agitation speed.

1. Introduction

Polyvinyl chloride (PVC) plants are important production units within the chemical industry of Saudi Arabia. The emulsion polymerization process producing PVC generates large quantities of wastewater. The wastewater contains suspended solids of PVC (i.e. latex particles) with a size ranging from 0.2 μm to few mm [1]. This gives the water a milky appearance. Due to the harmful effects of these chlorine-based particles and the stringent environmental policies, the wastewater has to be treated to remove these particles before it is discharged. Moreover there is an economic incentive to collect these solid particles since they can be sold in the market. The PVC plant in this study has set up a wastewater treatment facility for the removal of these latex particles from water. The main unit in the facility is the clarifier where a number of chemicals are added to help the coagulation/flocculation of the latex particles and consequently the sedimentation. The added chemicals are sodium hydroxide to control the pH, metallic ions (aluminum sulfate, ferric chloride or calcium chloride) and commercial anionic- and/or cationic-based polyelectrolytes (PEs). Currently the dosages of these parameters are selected on a trial and error basis to obtain an adequate settling of the suspended particles. When the coagulation/flocculation process is successful, a solid coagulum forms and settles to the bottom of the clarifier and the clear supernatant water is sent to drain. The concentrated slurry is pumped to a concentrator tank and then to a moving belt for dewatering, drying and disposal. The ad hoc strategy, however, can sometimes fail leading to an overflow of solid particles and causing a severe deterioration of the performance of the wastewater treatment process. The objective of this research is to carry out an experimental study of the parameters affecting the coagulation/flocculation process and to provide some guidelines for the optimum selection of these parameters. The experimental research consists in carrying out jar test experiments [2] on a 'model' wastewater which is chemically identical to the actual plant wastewater but is more consistent. A number of parameters are studied. The first parameter is the type and dosage of the coagulant. Three types of metallic ions were investigated: aluminum sulfate, ferric chloride and calcium chloride. The second parameter is the dosage of a commercial polyelectrolyte. The third parameter is the pH, and the last parameter to be studied is the speed of agitation. The efficiency of coagulation is determined by measuring the turbidity of the supernatants and the relative settlement of the flocs in the jar test.

* Corresponding author. Fax: +966 1 467 8770.
E-mail address: aajbar@ksu.edu.sa (A. Ajbar).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.03.121

It should be noted that coagulation/flocculation is an essential process in water and industrial wastewater treatment [3–6]. The process was found to be cost effective, easy to operate and uses less energy than alternative treatment. Coagulation/flocculation of latex particles was also studied in the literature [7–13]. The solid particles dispersed in water are stabilized by the anionic (negatively charged) surfactant molecules. The colloid stability of the dispersion can be destroyed by adding a positively charged salt that neutralizes the negative charge on the particles causing them to aggregate. The coagulant aggregates the particles into small flocs that slowly settle. The size of the flocs and the rate of settlement are increased by adding an anionic polymeric polyelectrolyte flocculent. Many different types of flocculants are commercially available. However, while the basics of flocculation/coagulation are well-known and the applications of these process are widespread, the optimization of the process depends on the application itself. There are generally no simple theoretical studies that can guide the optimization task and therefore the researcher has to rely heavily on experimental studies to optimize the performance of the process.

2. Materials and methods

The experiments were carried out using real PVC latex consisting of monomodal 703 latex, 460 nm particle size with solids content of 40% and stabilized by sodium lauryl sulfate (SLS) surfactant. Each sample of latex solution was prepared by diluting in 500 ml of water a volume of 12.5 ml of PVC latex. This constitutes the 'model' wastewater. An other alternative would have been to use real wastewater fed to the PVC treatment plant. However, the composition and the quality of the wastewater fed to the treatment plant is very variable. In addition, the particles are already flocculated because of the presence of recycle water (containing coagulants and flocculants) from the belt filter. The 'model' wastewater, on the other hand, is chemically identical to the actual plant wastewater but does not contain recycle and is therefore not flocculated.

2.1. Sample analysis

In quality monitoring of water, the turbidity value is of great use in many applications. Turbidity was determined by measuring light passing through the sample. Measuring the scattered light at an angle of 90° was proved to be an accurate method particularly at low ranges. The turbidimeter 355 IR/T was used in the measurements. The recorded values are given in Nephelometric Turbidity Units (NTU).

2.2. Experimental

The study consisted of three sets of experiments. The first set was used to study the effect of metal ions ($Al_2(SO_4)_3$, $FeCl_3$ and $CaCl_2$). For each coagulant, dosage was varied from 1 to 30 ml and an optimum value that provided the best coagulation was determined. The second set of experiments was used to determine the effect of the addition of a commercial polyelectrolyte. For this purpose the dosage of the metal ion was fixed at the optimum value found in the earlier step and different amounts of the polyelectrolyte were tested to determine the optimum value. The third set of experiments was used to determine the effect of pH on the coagulation while the last set of experiments involved the study of the effect of agitation speed. The details of the experimental procedure are described in the following:

1. *Coagulants*: three types of coagulants were used: $Al_2(SO_4)_3$, $FeCl_3$ and $CaCl_2$. At the start of the experiments the following dosages were prepared: 0.5% $Al_2(SO_4)_3$, 2.5% $FeCl_3$ and 2.5% $CaCl_2$. Volumes ranging from 1 to 30 ml of coagulants were added to the wastewater sample. For each experiment the turbidity was measured and plotted with time. Each experiment follows the same procedure: a sample of the untreated wastewater was poured into the beaker. While mixing, the pH was adjusted to values in the range of 6–8. The off-center location of mixing blades, i.e. about 6 mm (1/4 in.) from the beaker wall provided better mixing conditions in cylindrical beakers. The desired amount of coagulant solution was added to the beaker. The stirrer was run at 200 rpm for a period of 1 min. Agitation speeds below 200 rpm do not yield quick enough results. The effect of using higher agitation speeds is investigated later in this paper. As for the time of experiments, it was noticed that times larger than 1 min resulted in the formation of foams in the beakers due to the broken fluxes from prolonged mixing. After the agitation the stirrer was turned off and left for 10 min while observing the coagulation of the precipitated particles. After that, a 12 ml of supernatant was removed and its turbidity was measured using the portable turbidity meter. All supernatant samples were removed from the same depth. The turbidity was recorded and plotted with time.
2. *Polyelectrolyte*: for the effect of polyelectrolyte, a commercial polyelectrolyte was used. At start of the experiments, a 0.02% PE solution was prepared and was left for a number of days to ensure it has dissolved. The determination of the effect of the polyelectrolyte involved initial addition of pre-determined optimum dosage of each of the coagulants to the model wastewater. Volumes from 1 to 10 ml of the PE solution were added to the beakers. A similar procedure to previous steps was followed to obtain the turbidity.
3. *pH*: for the effect of pH, the optimal dosages of the coagulant and the polyelectrolyte were first added to the wastewater sample. The pH was varied from 2 to 9 through the addition of sulfuric acid and/or sodium hydroxide, respectively. Each time the turbidity was recorded using the same procedure described in the previous tests.
4. *Agitation*: for the agitation speed, the pH of the wastewater sample was adjusted to the neutral value of 7. The reason is given later in the text. Both the optimum amounts of coagulants and polyelectrolyte were added to the sample. The agitation speed was varied from 200 to 1000 rpm.

3. Results and discussion

3.1. Effect of coagulant type and dosage

The variations of turbidity with time when the model wastewater is coagulated with 0.5% $Al_2(SO_4)_3$ solution is shown in Fig. 1. The range of the aluminum sulfate solution is from 2 to 10 ml. It can be seen that as the volume of aluminum sulfate solution increases the turbidity decreases. We have chosen 5 h as the time to compare the final performance of the metals ions added to the wastewater. From the figure it can be noted that the minimum value of turbidity corresponds to the volume of aluminum sulfate solution in the range of 6–8 ml. We further investigated the effect of adding volumes of 6.5, 7.5 and 8.5 ml. Fig. 2 shows that the best settlement occurs when the volume of aluminum sulfate solution (measured at 300 min) is 7.5 ml. The measured turbidity is at the low value of 20. Fig. 3 shows, on the other hand, the sediment height. The height is 110 ml when the volume of aluminum sulfate solution is 7.5 ml.

Moreover, it can be seen from Fig. 3 that the sediment height reaches a lower value of 106 ml (measured at 300 min) when the volume of coagulant is 8.5 ml. This may suggest that the volume of 8.5 ml is the optimum dosage for the coagulant. However the difference in the sediment heights for 7.5 and 8.5 ml is only 4 ml which

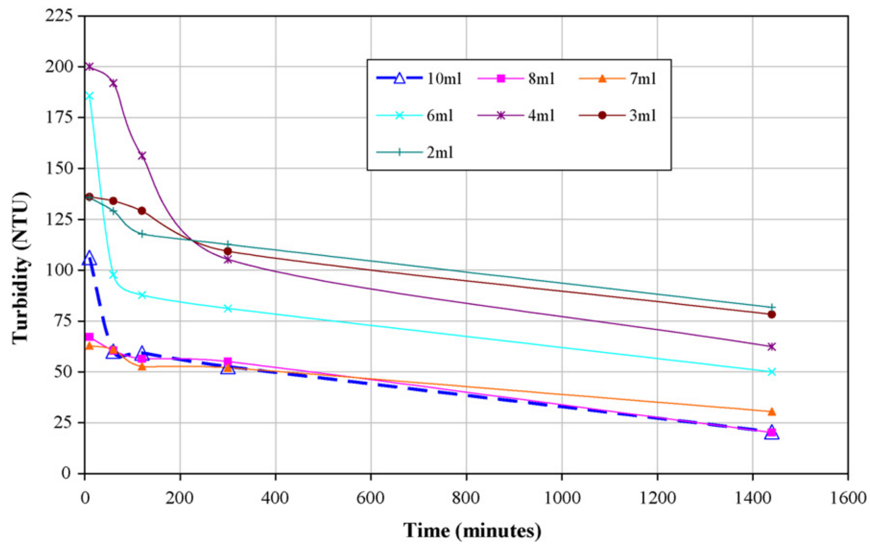

Fig. 1. Variations with time of turbidity of latex coagulated with different amounts of 0.5% of $Al_2(SO_4)_3$ solution.

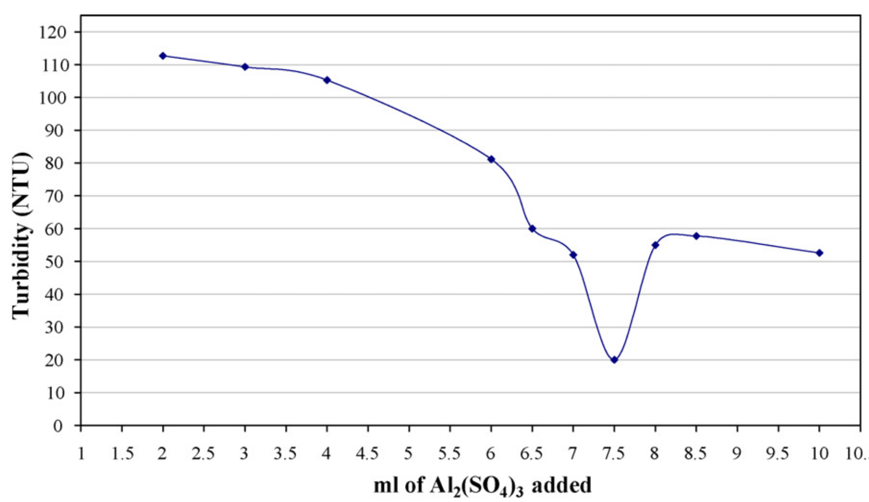

Fig. 2. Turbidity of latex coagulated with different amounts of 0.5% of $Al_2(SO_4)_3$ solution. Settlement time is 300 min.

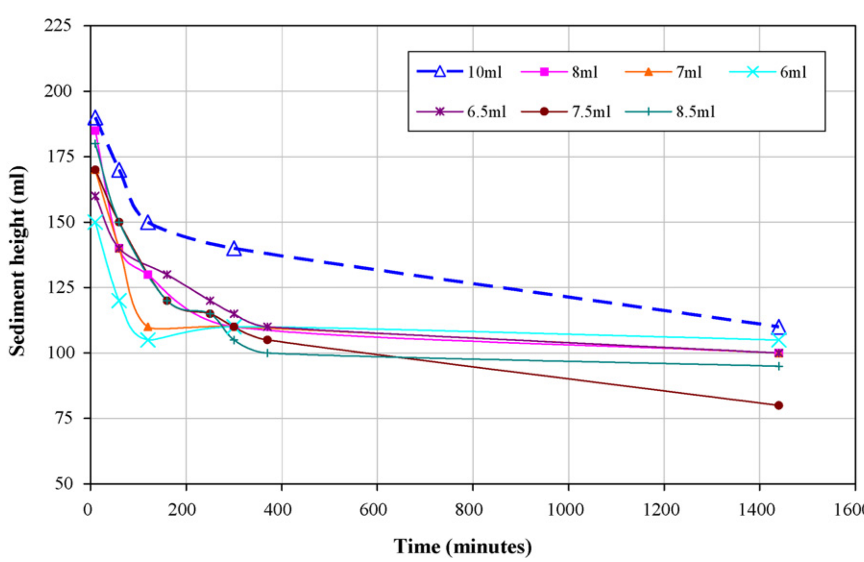

Fig. 3. Variations with time of sediment height of latex coagulated with different amounts of 0.5% of $Al_2(SO_4)_3$ solution.

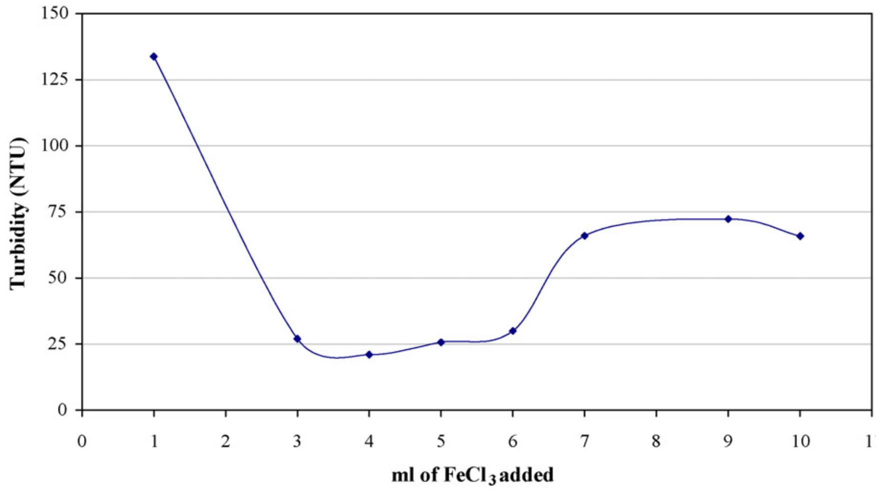

Fig. 4. Turbidity of latex coagulated with different amounts of 2.5% $FeCl_3$ solution. Settlement time is 300 min.

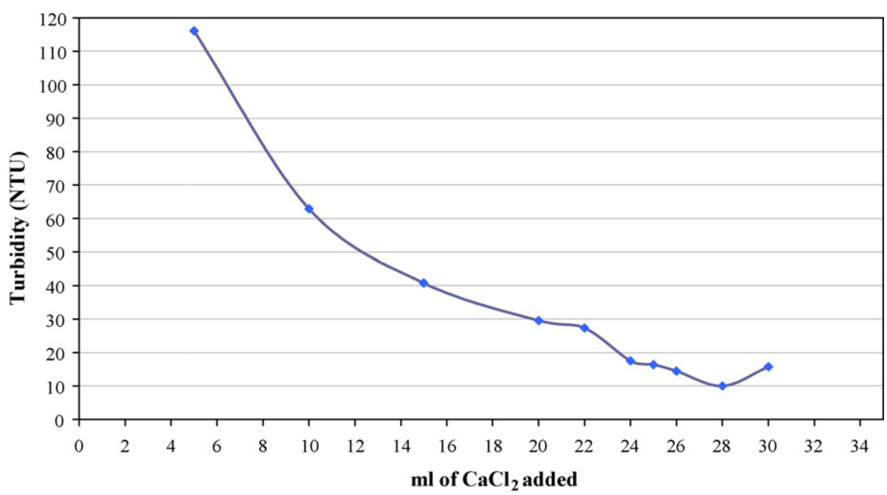

Fig. 5. Turbidity of latex coagulated with different amounts of 2.5% $CaCl_2$ solution. Settlement time is 300 min.

may not be significant. Moreover, Fig. 2 shows that the optimum value of turbidity for 7.5 ml is 20 while it is around 60 (i.e. three times higher) for 8.5 ml. It can also be noticed from Fig. 3 that as time goes by the sediment height decreases even to lower values for 7.5 ml compared to 8.5 ml. For these reasons we can conclude that the optimum dosage for the coagulant is 7.5 ml.

The same experiments were carried out for the effect of ferric chloride on the removal of turbidity. Fig. 4 shows that the clearest

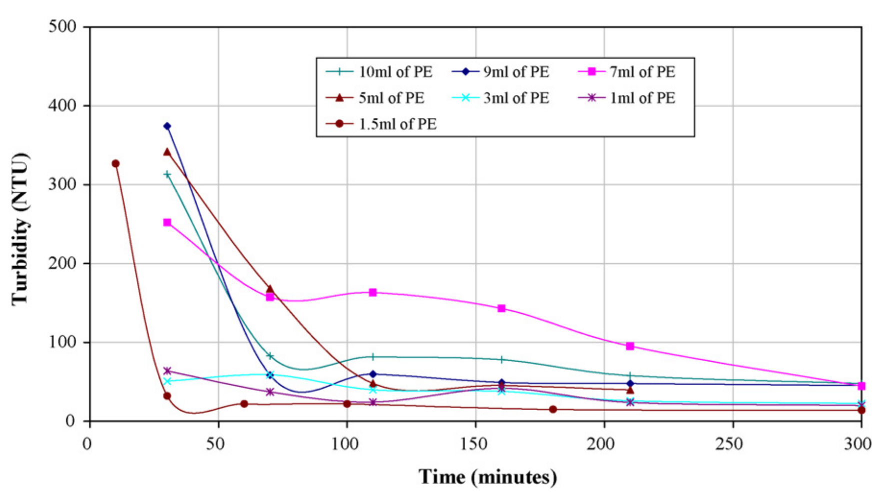

Fig. 6. Variations with time of turbidity of latex coagulated with 7.5 ml of (0.5% of $Al_2(SO_4)_3$) solution and different amounts of 0.02% PE.

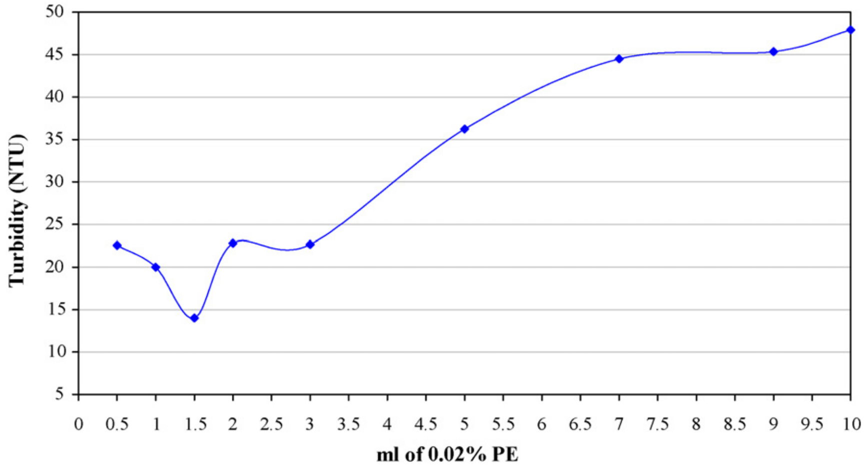

Fig. 7. Turbidity of latex coagulated with different amounts of 0.02% PE and 7.5 ml of (0.5% of $Al_2(SO_4)_3$) solution. Settlement time is 300 min.

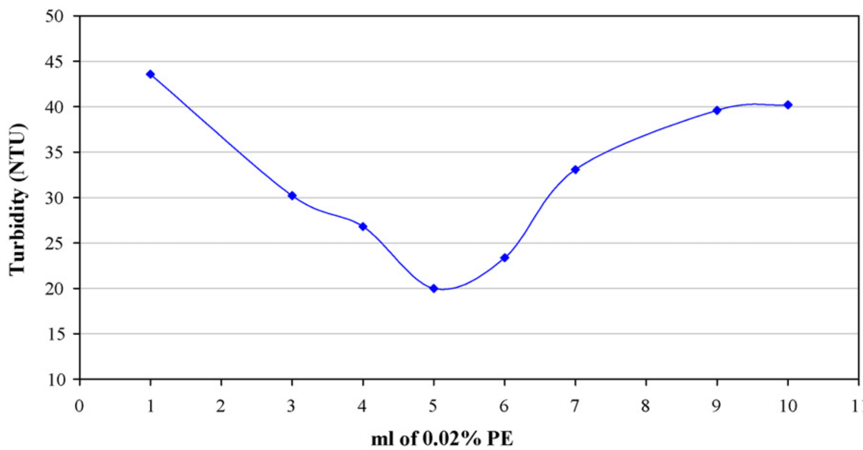

Fig. 8. Turbidity of latex coagulated with different amounts of 0.02% PE and 4 ml of (2.5% of $FeCl_3$) solution. Settlement time is 300 min.

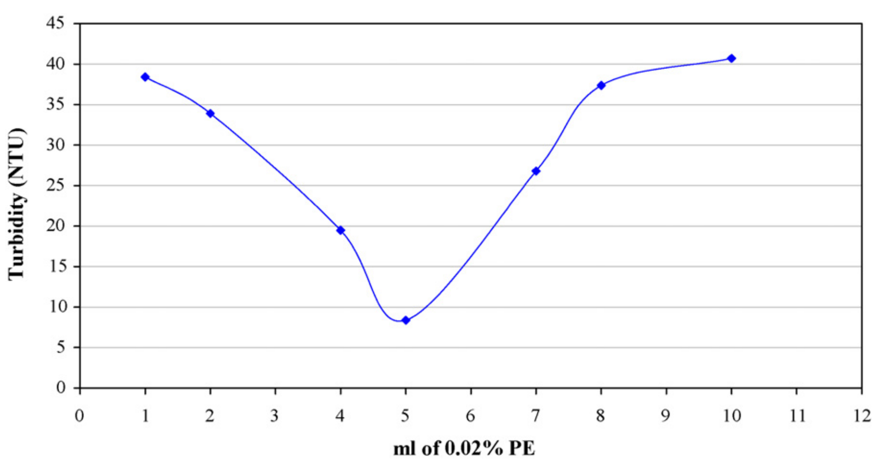

Fig. 9. Turbidity of latex coagulated with different amounts of 0.02% PE and 28 ml of (2.5% of $CaCl_2$) solution. Settlement time is 300 min.

Table 1
Results summary of coagulation with and without polyelectrolyte

Metal ions	Metals alone					Metals with polyelectrolyte (PE)		
	Concentration of solution (%)	Optimum ml of solution	Optimum g of metal	Optimum turbidity	Optimum sedimentation height	Optimum g of PE	Optimum turbidity	Optimum sedimentation height
Al^{3+}	0.50	7.5	0.0375	20	110	0.0003	14	110
Fe^{3+}	2.50	4	0.1	21	150	0.001	20	150
Ca^{2+}	2.50	28	0.7	10	135	0.001	23	140

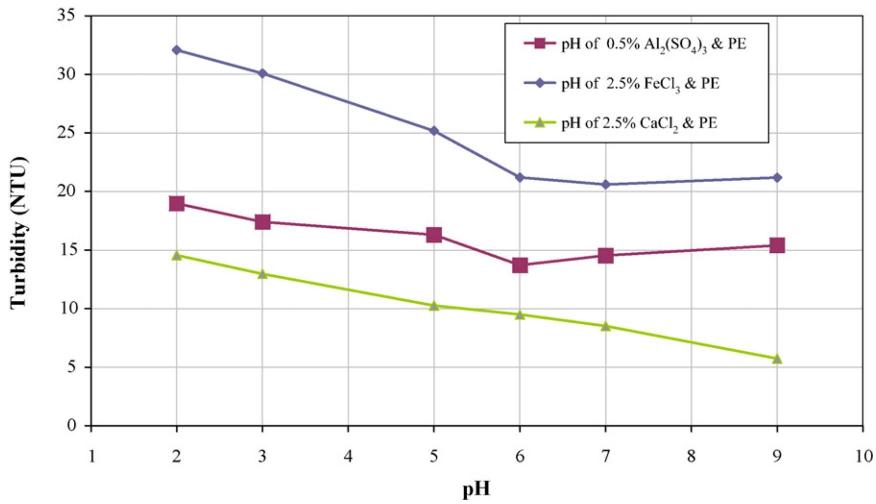

Fig. 10. Turbidity of latex coagulated at different pH. Settlement time is 300 min.

supernatant was achieved by 4 ml of 2.5% $FeCl_3$ solution and the turbidity is at the low value of 21. It can be noted that unlike aluminum ions there is large range (from 3 to 6 ml of ferric chloride) for which the turbidity exhibits minimum values.

The coagulation effects of 2.5% calcium chloride solution are shown in Fig. 5. The optimum volume of calcium chloride solution is 28 ml and the turbidity is at the low value of 10. The optimum sediment height is found to be 135 ml. It can be seen from Fig. 5 that unlike the effect of aluminum or ferric ions the turbidity decreases continuously with the added volumes of calcium chloride.

3.2. Effect of polyelectrolyte

The wastewater model sample used in the previous experiments was prepared by the addition of aluminum sulfate solution at the pre-determined optimum value of 7.5 ml. Fig. 6 shows the effect of the addition of various quantities of polyelectrolyte solution on the coagulation process. It can be noted from the figure that the minimum value of turbidity corresponds to a volume of polyelectrolyte solution in the range of 1–3 ml. The effects of addition of 0.5, 1.5, and 2 ml of the polyelectrolyte were further investigated. Fig. 7 shows that the best settlement occurs for a volume 1.5 ml of polyelectrolyte solution (measured at 300 min) and the turbidity is at the low value of 14. The improvement in the coagulation/flocculation was noticeable since with aluminum sulfate alone (at the optimum value of 7.5 ml) the turbidity is 20 after 5 h. When the polyelectrolyte was added at the optimum value of 1.5 ml the turbidity reached a value of 22 after 1 h. The polyelectrolyte improved coagulation by increasing both the rate of settlement and clarity of the supernatant.

The combined effect of ferric chloride and the polyelectrolyte is shown in Fig. 8 where the coagulant volume was set at predetermined optimum value of 4 ml. Fig. 8 shows that the best settlement occurred for a volume of 5 ml of polyelectrolyte solution and the turbidity is at the low value of 20. The optimum height was found to be 150 ml.

Finally, the combined effect of polyelectrolyte and calcium chloride is shown in Fig. 9. Again, the volume of coagulant was set at the optimum value of 28 ml found before. Fig. 9 shows that the best settlement occurred for a volume of 5 ml of polyelectrolyte solution and the turbidity is at the low value of 23. The optimum height, on the other hand, was 140 ml. It is clear that the combination of calcium chloride and the studied commercial PE did not improve the coagulation/flocculation process. It is for this reason that different types of commercial polyelectrolytes are tested in the industry for each coagulant.

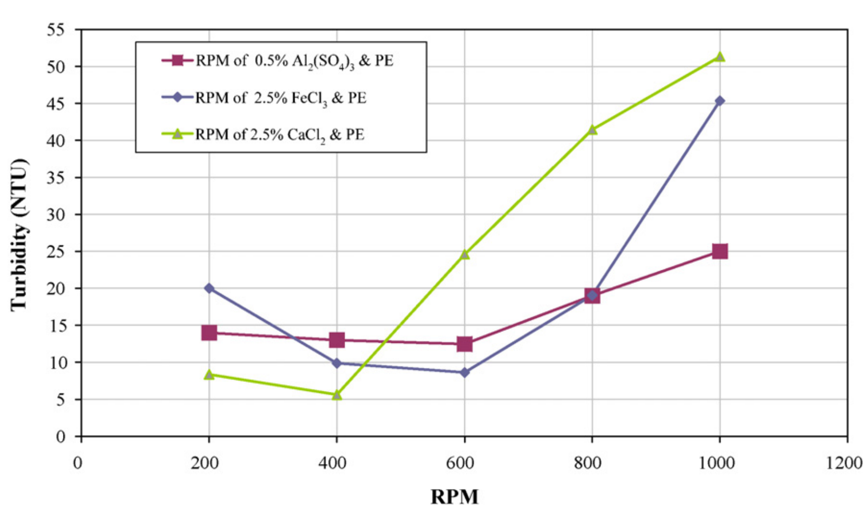

Fig. 11. Turbidity of latex coagulated at different agitation speeds. Settlement time is 300 min.

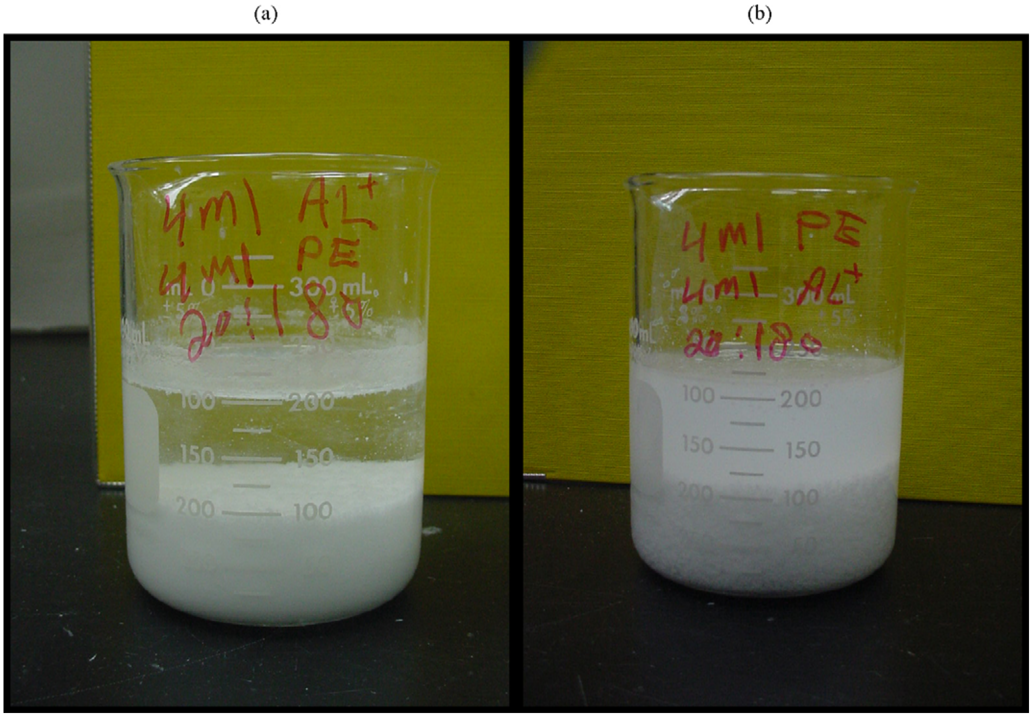

Fig. 12. (a) Adding metal ions first then polyelectrolyte. (b) Adding polyelectrolyte first.

3.3. *Effect of pH*

Fig. 10 shows the effect of pH on the coagulation/flocculation process for the combination of polyelectrolyte and each of the coagulants set at the pre-determined optimum value. The pH was varied from 2 to 9. It can be seen from the figure that for aluminum sulfate and polyelectrolyte the change in turbidity with the pH is not significant. As for ferric chloride and polyelectrolyte the turbidity decreases noticeably as the pH is increased until the pH value of 6. The turbidity is almost unchanged for larger pH values. As for the effect of pH on the pair of calcium chloride and polyelectrolyte, it can be seen that the turbidity decreases continuously over the studied range of pH values. It can be concluded therefore that, overall, acidic values of pH deteriorate the settling of the particles and may encourage corrosion in real applications. For these reasons the optimum values of pH should be in the range of 6–8.

3.4. *Effect of agitation speed*

Fig. 11 shows the effect of agitation on coagulation/flocculation process for the combination of polyelectrolyte and each of the coagulants set at the pre-determined optimum values. For the reasons given in the previous section, the pH in all the experiments was set at the neutral value of 7. The agitation speed was varied from 200 to 1000 rpm. It can be seen that, overall, the agitation speed has an effect on the turbidity. For the combination of aluminum sulfate and polyelectrolyte, and ferric chloride and polyelectrolyte, the turbidity decreases with agitation speed until it reaches a minimum value around 600 rpm and then increases. The optimum value of agitation speed for this pair is therefore 600 rpm. For the combination of calcium chloride and polyelectrolyte it can be seen that the turbidity decreases with agitation speed until it reaches a minimum value around 400 rpm and then increases.

3.5. *Order of adding the chemicals*

The last issue to be investigated is the order of adding the different chemicals. Fig. 12(a) shows, for instance, a picture of the sample of model wastewater when the metal ions (Al^{3+}) were added first followed by polyelectrolyte while Fig. 12(b) shows the effect of adding the polyelectrolyte first. It is clear from the figure that the metal should be added first since Fig. 12(b) shows a cloudy coagulation. The reason is that the PVC is already negatively charged (because of the effect of sodium lauryl sulfate as discussed previously). Adding the negatively charge polyelectrolyte first leads to a repulsion between the particles.

4. Conclusions

The results of this optimization study are summarized in Table 1. It can be seen from this table that aluminum sulfate (0.5% $Al_2(SO_4)_3$) combined with the polyelectrolyte gives the best results because only 0.0375 g is required to coagulate the model wastewater and because the amount of polyelectrolyte required is only 0.0003 g. Ferric chloride (2.5% $FeCl_3$) combined with polyelectrolyte at the shown optimum values is slightly less effective since it requires 0.1 g while the optimum turbidity is almost the same. The required amount of polyelectrolyte is on the other hand larger. Calcium chloride (2.5% $CaCl_2$) combined with the polyelectrolyte was found to be the least effective. The pH values should be selected in the range of 6–8 while the optimum agitation speed in the lab scale apparatus was found to be 600 rpm for both aluminum sulfate and polyelectrolyte and ferric chloride and polyelectrolyte. As for calcium chloride and polyelectrolyte the optimum agitation speed was found to be 400 rpm.

References

[1] P.A. Lovell, M.S. El-Asser, Emulsion Polymerization and Emulsion Polymers, John Wiley & Sons Ltd., 1997.

[2] Z. Satterfield, Jar Testing: Technical Brief of National Environmental Service Center, vol. 5, 2005, pp. 2–4.
[3] K. Ching-Jey, A. Gary, B. Curtis, Factors affecting coagulation with aluminum sulfate-I, Water Res. 22 (1988) 853–862.
[4] M. Franceschi, A. Girou, A.M. Carro-Diaz, M.T. Maurette, E. Puech-Costes, Optimisation of the coagulation–flocculation process of raw water by optimal design method, Water Res. 36 (2002) 3561–3572.
[5] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samara, Coagulation–flocculation pretreatment of sanitary landfill leachates, Chemosphere 53 (2003) 737–744.
[6] N.Z. Al-Mutairi, M.F. Hamoda, I. Al-Ghusain, Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant, Bioresour. Technol. 95 (2004) 115–119.
[7] D.Z. Gunes, J.P. Munch, M. Dorget, A. Knaebel, F. Lequeux, Flocculation, deflocculation, and ions migration in latex suspensions, J. Colloid Interface Sci. 286 (2005) 564–572.
[8] O.S. Amuda, I.A. Amoo, O.O. Ajayi, Performance optimization of coagulant/flocculant in the treatment of wastewater from a beverage industry, J. Hazard. Mater. 129 (2006) 69–72.
[9] L. Erikson, A. Barbo, P. Stenius, Formation and structure of polystyrene latex aggregates obtained by flocculation with cationic polyelectrolytes. 1. Adsorption and optimum flocculation concentrations, Colloids Surf. A: Physiochem. Eng. Aspects 70 (1993) 47–60.
[10] O. Larue, E. Vorobiev, C. Vu, B. Durand, Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions, Sep. Sci. Technol. 31 (2003) 177–192.
[11] M.I. Aguilar, J. Sáez, M. Lloréns, A. Soler, J.F. Ortuño, V. Meseguer, A. Fuentes, Improvement of coagulation–flocculation process using anionic polyacrylamide as coagulant aid, Chemosphere 58 (2005) 47–56.
[12] L. Beal, Y. Chevalier, Mechanisms involved in the stabilization of latex particles by adsorbed block copolymers in emulsion polymerization process, Colloids Surf. A: Physicochem. Eng. Aspects 270 (2005) 26–32.
[13] D.Z. Gunes, J.P. Munch, M. Dorget, A. Knaebel, F. Lequeux, Flocculation, deflocculation and ions migration in latex suspensions, J. Colloid Interface Sci. 286 (2005) 564–572.