

Chemical Clarification of Secondary Effluents for Organics and Phosphorus Removal

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(Received 09 April, 1999; accepted for publication 29 April, 2000)

Abstract. Jar test experiments of chemical clarification for organics and phosphorus removal were performed on 24-hour composite trickling filter effluent samples from Riyadh sewage treatment plant (South plant). Tests were conducted using the major coagulants; lime, ferric chloride, alum, and caustic soda. Improvement of clarification was also tested using three polymers; Superfloc A-100 (anionic), Superfloc N-100 (cationic), and Nalcolyte-8100 (polycationic). Analysis of the results has indicated that the average COD and total-P of secondary trickling filter effluents during the study period were 100 mg/l and 6.4 mg/l, respectively. The lowest COD level obtained in jar tests using any of the chemical combinations was 40 mg/l. All coagulants, with the exception of lime, were able to lower total-P to below 1 mg/l without the need for polymers. Lime, however, required an additional 0.4 mg/l of polymer A-100 for proper total-P removal. The selected optimum dosage for lime, alum, and caustic soda was 250 mg/l, whereas, it was 70 mg/l for ferric chloride. Using lime and polymer resulted in the lowest estimated chemical cost of 121 Saudi Riyals (US\$ 32) for 1000 m³ of wastewater.

Introduction

Chemical clarification of wastewater is a process that can be employed for improving effluent quality from conventional biological treatment processes. Lime and salts of iron and aluminium, sometimes with the addition of polymers, are the coagulants typically used for such purpose. The primary aim of using chemicals is improved removal of organic matter (usually measured as BOD, COD, or TOC), suspended solids, and phosphorus. This is usually important when conventional biological treatment is unable to meet certain effluent discharge and/or reuse requirements. Other substances that can be substantially removed or reduced by chemical clarification include suspended inorganic material, calcium, magnesium, silica, fluoride, some heavy metals, bacteria, and viruses [1,2].

Improved organic and phosphorus removal can be achieved in an integrated biological-chemical process or in a separate physical-chemical process. In the former approach, the coagulant may be added either ahead of the primary clarifier or directly to the aeration basin of an activated sludge system. In the later, the coagulants may be added to the secondary effluent with subsequent settling. Phosphorus can also be removed by biological treatment alone by using proper sequencing and producing the appropriate environmental conditions in the treatment process. Ketchum *et al.* [3] compared biological and chemical phosphorus removal in continuous flow and sequencing batch reactors and found identical phosphorus removal. Selection of proper process requires careful evaluation of several points including; effluent quality achievable, flexibility of operation, reliability, and cost [1]. One of the important concerns with integrated biological-chemical process is the increased sludge production and modified sludge characteristics [4].

Phosphorus appears in wastewater as orthophosphate, polyphosphate and organically bound phosphorus. The first two account for up to 70% of influent phosphorus. Orthophosphates are more easily removed by chemical coagulation than the other phosphorus forms. Hence, adding chemicals after secondary treatment (where polyphosphates and organic phosphorus are transformed into orthophosphates) usually results in the best removal [4].

Control of phosphorus in effluent becomes critical when effluents are discharged to surface waters which are generally affected by eutrophication. Reduction of effluent phosphorus to below 1.0 mg/l is considered a general guideline for this purpose [2]. However, the modified objectives for the USA Great Lakes region recommends total phosphorus level of <0.5 mg/l [5].

Applying chemical coagulation for phosphorus removal was reported by many studies dealing with either integrated biological-chemical process or separate physical-chemical processes [6-9]. Chemical clarification of secondary effluents is considered an important process in advanced treatment operations for industrial, potable and non-potable water reuse projects, with lime as the major chemical used in such applications [10-12].

This paper discusses the results of a systematic jar testing study aimed at evaluating the potential of the coagulants; lime, ferric chloride, alum, and caustic soda for removing organic matter and phosphorus from the secondary trickling filter effluents of Riyadh wastewater treatment plant. The effects of polymers of different charge type were also investigated.

Experimental

Twenty-four hour composite trickling filter effluent samples were collected once per week from Riyadh sewage treatment plant (South plant). The effluents were collected after the polishing lagoons and before the chlorination chamber. Jar tests were conducted in the laboratory at room temperature of 21 °C using 2-litre jars on a Phipps & Bird jar test apparatus. For all the experiments, rapid mix time of 2-min, slow mix of 40-min, and 1-h settling was adopted. After settling, 500 ml of supernatant was carefully withdrawn from the top of each jar and analyzed for pH, alkalinity, and turbidity. The remaining sample was neutralized (with either dilute H₂SO₄ or NaOH) and filtered through glass fiber filters and then analyzed for chemical oxygen demand (COD) and total phosphorus (total-P). A portion of the original wastewater sample as received from the plant was also analyzed for COD and total-P. All the analyses were performed according to Standard Methods [13].

Two jar tests were conducted for each of the major coagulants; Lime {Ca(OH)₂}, Ferric chloride (FeCl₃), Alum {Al₂(SO₄)₃.18 H₂O}, and Caustic soda (NaOH). After examining the results of the above jar tests, optimum dosages for the best removal of COD were selected. The selected dosages of coagulants were found adequate to reduce Phosphorus concentration to < 1 mg/l, except for lime. Enhancement of COD and total-P removal was then examined in a series of jar tests using the selected dosage of each major coagulant with variable dosages of three polymers of different charge type. The polymers tested were superfloc A-100 (Anionic), superfloc N-100 (non-ionic) and Nalcolyte 8100 (polycationic). All polymers tested are recommended for water and wastewater applications according to their manufacturer's literature. Concentration of chemical quality parameters for Riyadh wastewater effluent is included in Table 1 [14, 15]. The table includes concentrations of common ions such as Ca⁺⁺, Mg⁺⁺, etc. which may have some influence on the chemistry of coagulants.

Results and Discussion

Results of the jar tests for the removal of COD and phosphorus using lime alone are shown in Fig. 1. Lime dosages above 150 mg/l were necessary in order to get some removal of COD. An optimum dosage of 250 mg/l of lime was needed for COD reduction to approximately 48 mg/l from an original average COD of about 100 mg/l. The optimum dosage is the lowest dosage of coagulant which gives highest removal of COD and/or total-P. For phosphorus, a lime dosage of 200 mg/l was needed to lower total-P level from an average of 6.8 mg/l to 2.5 mg/l. Increasing lime dosage up to 300 mg/l did not improve phosphorus removal.

Table 1. Characteristics of trickling filter effluent (Riyadh Plant) [14, 15]

Parameter	Concentration ^a
pH	7.2
Alkalinity as CaCO ₃	161
Total Suspended Solids (TSS)	24
Total Dissolved Solids (TDS)	836
Chemical Oxygen Demand (COD)	95
Phosphorus (Ortho-P)	6.6
Calcium (Ca ⁺⁺)	101
Magnesium (Mg ⁺⁺)	23
Sodium (Na ⁺)	142
Potassium (K ⁺)	17
Chloride (Cl ⁻)	138
Sulfate (SO ₄ ⁻)	293

^aAll concentrations are in mg/l except for pH (pH units)

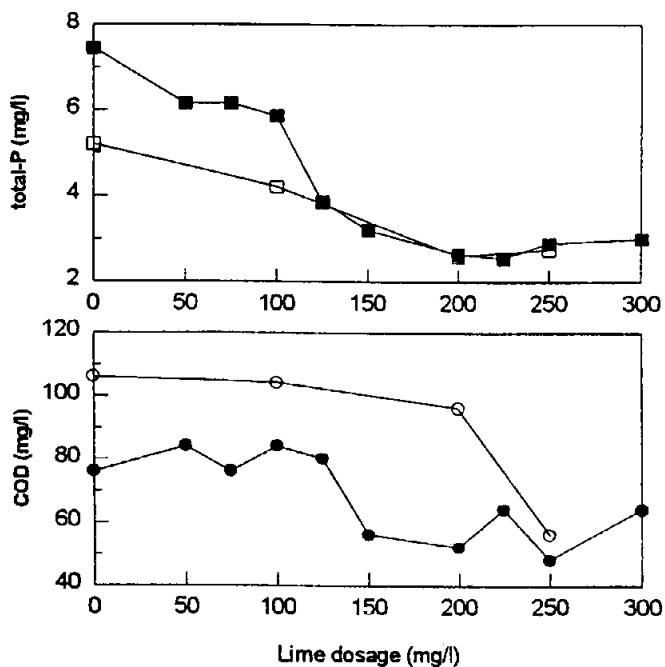


Fig. 1. COD and total-P removal for different dosages of lime.

Figure 2 presents the effects of adding polymers with lime for improving COD and phosphorus removal. Polymers resulted in slight enhancement of COD removal at dosages of 0.4 to 0.6 mg/l, with the lowest COD level achieved of 40 mg/l. It can be seen from Fig. 2 that adding variable dosage of the polymers with a selected dosage of 250 mg/l of lime increased phosphorus removal. Polymer dosages of about 0.2 mg/l with lime reduced total-P level to 1.0 mg/l or less. Almost complete removal of total-P can be achieved using polymers with lime. However, this is not necessary since most phosphorus regulations specify an acceptable phosphorus level of 1.0 mg/l or less [2].

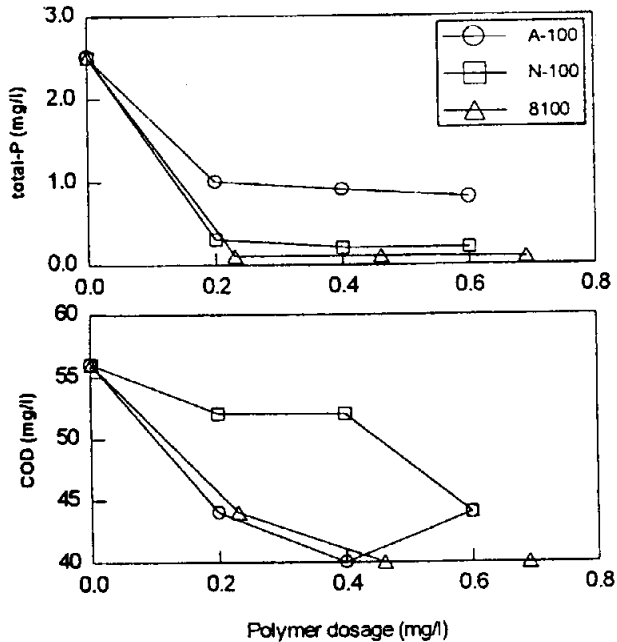


Fig. 2. COD and total-P removal using 250 mg/l lime and variable polymer dosages.

Results of COD and phosphorus removal using ferric chloride alone are presented in Fig. 3. Dosages of ferric chloride above 50 mg/l were necessary in order to reduce COD considerably. An optimum dosage of 70 mg/l ferric chloride was required for maximum COD reduction from an average of 114 mg/l to 56 mg/l. A ferric chloride dosage of 70 mg/l was adequate to lower total-P from an average of 5.5 mg/l to 0.9 mg/l. Increasing ferric chloride dosage to 100 mg/l resulted in almost complete removal of total-P. Fig. 4 shows the effects on COD removal of adding polymers with ferric chloride. High dosages of all polymers resulted in only minor improvement of COD removal, with 40 mg/l residual COD using polymer 8100. Fig. 4 also shows that adding polymers with 70 mg/l ferric chloride dosage results in improved total-P reduction to levels much lower than 1.0 mg/l (if necessary).

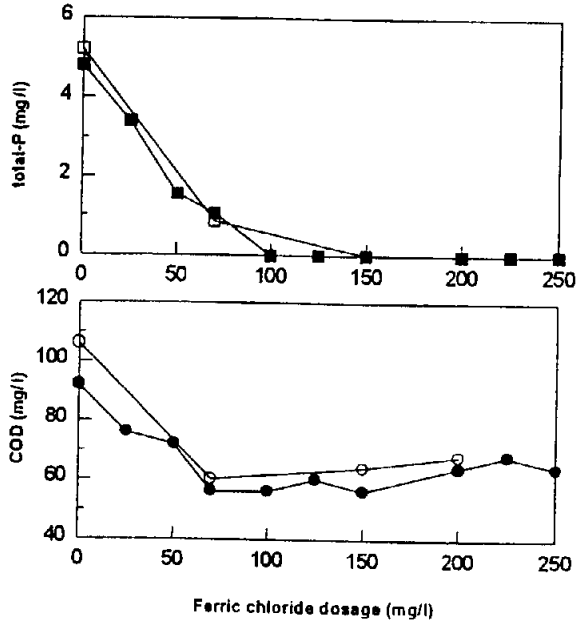


Fig. 3. COD and total-P removal for different dosages of ferric chloride.

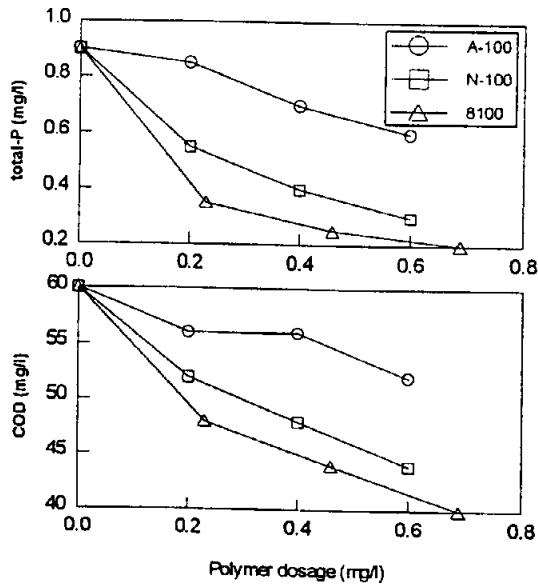


Fig. 4. COD and total-P removal using 70 mg/l ferric chloride and variable polymer dosages.

Results of COD and phosphorus removal using alum alone are shown in Fig. 5. Alum dosages higher than 125 mg/l were required for significant COD reduction. An optimum alum dosage of 200 mg/l was required to reduce COD from an average of 103 mg/l to approx. 60 mg/l. An alum dosage of 175 mg/l was needed to lower total-P level from an average of 6.5 to 0.35 mg/l. Higher alum dosages resulted in increased phosphorus removal. The combined effect of 250 mg/l alum and variable polymer dosage can be seen in Fig. 6. Adding polymers with 250 mg/l alum resulted in slight improvement of COD removal, with a high dosage of 0.7 mg/l of polymer 8100 produced the lowest obtained COD level of 40 mg/l. Adding variable dosages of polymers with 250 mg/l alum does not seem to be necessary for phosphorus removal, since alum alone is capable of sufficient phosphorus removal.

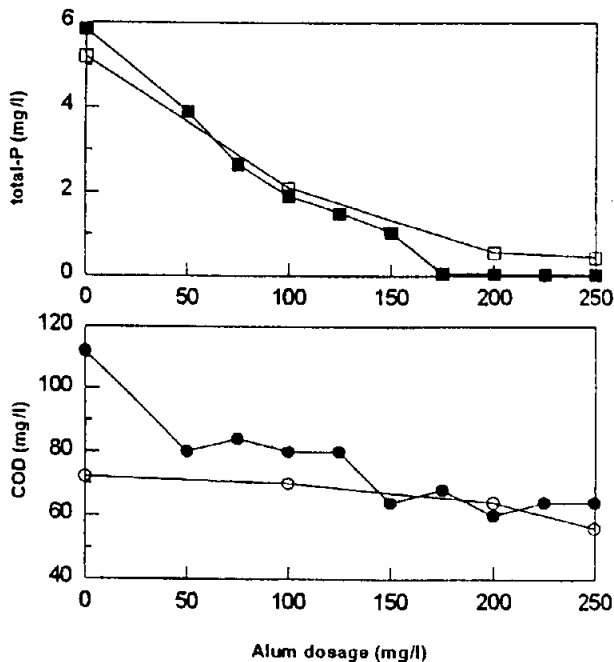


Fig. 5. COD and total-P removal for different dosages of alum.

Caustic soda (sodium hydroxide) was investigated in this research as an alternative to lime. If this chemical is proved to be technically and economically feasible, its use is always recommended. Systems for handling and dosing liquid caustic soda are much simpler and have less operation and maintenance problems contrary to what is normally encountered with lime dosing systems [1]. COD and phosphorus removal using caustic soda alone can be seen in Fig. 7. Dosages of caustic soda above 175 mg/l are required for improved COD removal. An optimum caustic soda dosage of 250 mg/l was required for reducing COD from an average of 106 mg/l to 56 mg/l. Caustic soda dosage of

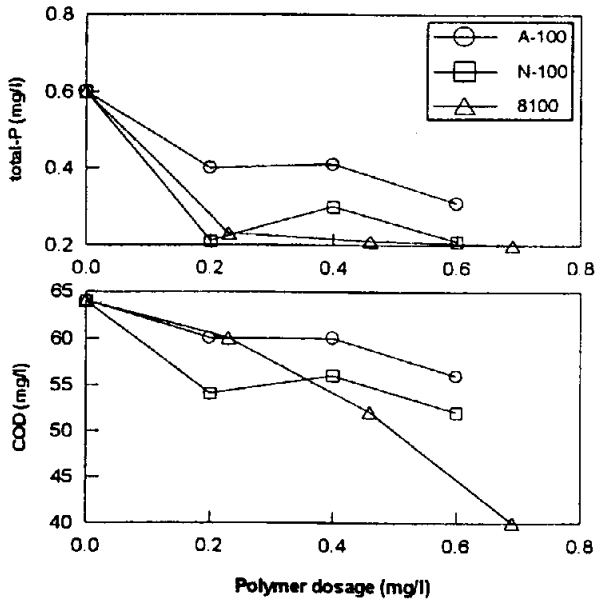


Fig. 6. COD and total-P removal using 250 mg/l alum and variable polymer dosages.

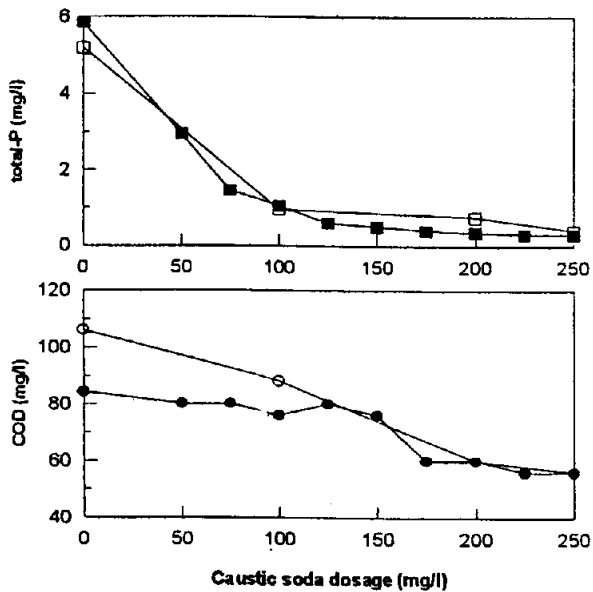


Fig. 7. COD and total-P removal for different dosages of caustic soda.

approximately 175 mg/l was required in order to lower total-P level from an average of 6.0 mg/l to 0.6 mg/l.

The effects on COD by adding variable dosages of polymers with 200 mg/l caustic soda are shown in Fig. 8. Little improvement in COD removal was obtained. In fact, negative effects were realized at some polymer dosages, indicating the necessity to carefully conduct several repeated experiments with narrow ranges of polymer dosage in order to actually select an optimum dosage. Adding polymers to caustic soda may not be necessary for phosphorus removal, since caustic soda alone is quite effective for phosphorus removal (see Fig. 8).

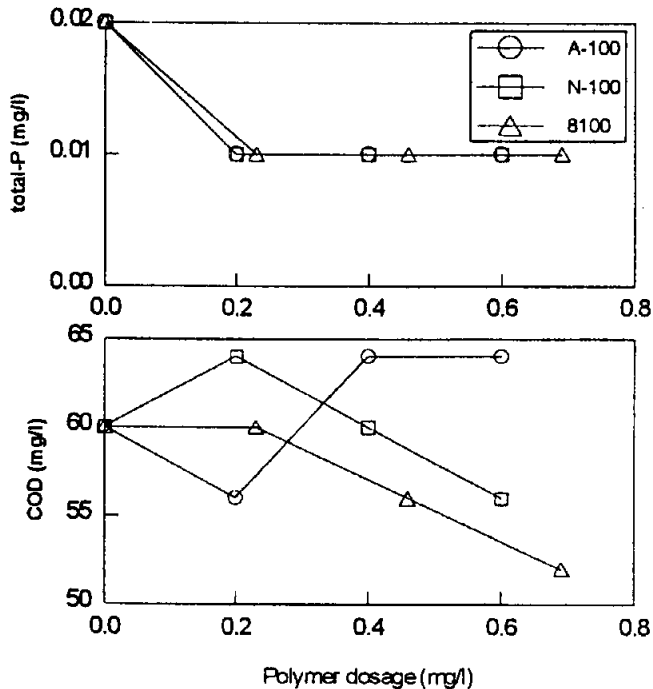


Fig. 8. COD and total-P removal using 200 mg/l caustic soda and variable polymer dosages.

Table 2 presents a summary of selected dosages of the major coagulants and polymers required for the highest COD removal. It is clear that with or without the polymers, the lowest COD level that could be obtained is 40 mg/l. The effects of polymers in this regard were minor to moderate. A summary of selected dosages for reducing total-P to 1.0 mg/l or less is presented in Table 3. All major coagulants except lime do not need polymer addition in order to lower total-P to less than 1.0 mg/l. Lime, however, with dosages up to 300 mg/l was unable to lower total-P to 1.0 mg/l.

Table 2. Selected dosages of coagulant and polymer for highest COD removal

Coagulant		Polymer		Residual COD (mg/l)	After settling		
Type	Dosage (mg/l)	Type	Dosage (mg/l)		pH	Alkalinity (mg/l)	Turbidity (NTU)
Lime {CaO}	250	No Polymer	--	48	9.7	142	4.6
	250	A-100	0.4	40	9.7	142	1.7
	250	N-100	0.6	44	9.7	171	1.1
	250	8100	0.46	40	9.8	173	1.6
Ferric Chloride {FeCl ₃ }	70	No Polymer	--	56	7.2	116	4.1
	70	A-100	0.6	52	6.9	116	2.7
	70	N-100	0.6	44	7.1	115	2.6
	70	8100	0.69	40	6.9	116	2.6
Alum {Al ₂ (SO ₄) ₃ .14 H ₂ O}	250	No Polymer	--	55	6.8	100	2.6
	250	A-100	0.6	56	6.7	101	2.3
	250	N-100	0.6	52	6.9	100	2.1
	250	8100	0.69	40	6.7	100	2.1
Caustic Soda {NaOH}	250	No Polymer	--	56	9.9	282	3.8
	200	A-100	0.2	56	9.9	304	0.9
	200	N-100	0.6	56	9.9	303	2.1
	200	8100	0.69	52	9.8	302	1.9

Table 3. Selected dosages of coagulant and polymer for residual phosphorus of 1.0 mg/l or less

Coagulant		Polymer		Residual total-P (mg/l)
Residual total-P (mg/l)	Dosage (mg/l)	Type	Dosage (mg/l)	
Lime {CaO}	250	No Polymer	-	2.55
	250	A-100	0.2	1.00
	250	N-100	0.2	0.25
	250	8100	0.23	0.15
Ferric Chloride FeCl ₃ }	70	No Polymer	-	0.9
	70	A-100	No need	-
	70	N-100	No need	-
	70	8100	No need	-
Alum {Al ₂ (SO ₄) ₃ .14 H ₂ O}	175	No Polymer	-	0.5
	250	A-100	No need	-
	250	N-100	No need	-
	250	8100	No need	-
Caustic Soda {NaOH}	175	No Polymer	-	0.6
	200	A-100	No need	-
	200	N-100	No need	-

Residual turbidity after coagulation-flocculation processes is always of concern. High turbidity after settling result in poor performance of the following filtration process. Table 2 shows that the highest turbidity levels after settling were in the range 2.6 to 4.6 NTU using the coagulants alone. Although improved turbidity removal below these levels doesn't appreciably improve COD removal, it is quite important for filter performance. Addition of polymers have improved turbidity removal with all coagulants used, especially with lime and caustic soda.

An attempt is made here to compare the cost of chemicals required for COD and phosphorus removal. Table 4 shows the calculated costs for selected dosages of the coagulants needed for the reduction of COD to an average of 50 mg/l and total-P to below 1.0 mg/l. Since lime alone was unable to lower total-P to the required level, polymer A-100 at a dosage of 0.4 mg/l was chosen to be added with lime. The lowest cost of chemicals obtained was 121 Saudi Riyals (US\$ 32)/1000 m³ of wastewater using lime and A-100 polymer. The highest was 425 Saudi Riyals (US\$ 113)/1000 m³ using alum. Selection of the proper chemical depend, in addition to chemical costs, on the dosing system involved, expected operation and maintenance requirements, and sludge characteristics.

Table 4. Estimated cost of chemicals for COD and Phosphorus removal

Chemical	Form	Cost ^a SR ^b /ton	Dosage mg/l	Cost for COD & total-P removal SR ^b /1000 m ³
Lime {Ca (OH) ₂ }	Powder	459	250	115
+ Polymer A-100	Powder	14418	0.4	6.0
				----- 121
Ferric Chloride {FeCl ₃ }	Liquid (40%)	1300	70	228
Alum {Al ₂ (SO ₄) ₃ 18H ₂ O}	Powder	1700	250	425
Caustic Soda {NaOH}	Liquid (49%)	560	250	286

^a Current cost of raw chemicals as sold in Riyadh.

^b 1 US \$ ≅ 3.75 SR

Conclusions and Recommendations

Jar test experiments of chemical clarification were conducted on 24-hr composite trickling filter effluent samples from Riyadh wastewater treatment plant using coagulants; lime, ferric chloride, alum, and caustic soda and polymers; Superfloc A-100 (anionic), Superfloc N-100 (cationic), and Nalcolyte-8100 (polycationic). The following conclusions and recommendations were obtained:

- The average COD and total-P of trickling filter effluents during the study period were 100 mg/l and 6.4 mg/l, respectively. The lowest COD level reached through chemical clarification using any of the chemical combinations was 40 mg/l. This indicates that for reuse applications which require lower COD levels, additional or other tertiary treatment alternatives may be needed.
- With the exception of lime, all chemical coagulants tested were effective in lowering total-P level to below 1.0 mg/l without the need for polymers. Lime, however, was only able to lower total-P to 2.55 mg/l, which indicates the need for polymer addition for further phosphorus removal.
- The selected optimum dosages of chemicals for COD and total-P removal were; lime (250 mg/l) plus polymer A-100 (0.4 mg/l), ferric chloride (70 mg/l), alum (250 mg/l), and caustic soda (250 mg/l).
- The cost of chemicals for COD and total-P reduction for 1000 m³ of trickling filter effluent were estimated as; lime (SR 121), ferric chloride (SR 228), alum (SR 425), and caustic soda (SR 286).
- It is recommended that other system characteristics be evaluated before a certain scheme may be selected. Such evaluations should include availability of the chemicals, dosing system required, operation and maintenance requirements, and characteristics of generated sludges.

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إزالة المواد العضوية والفوسفور من مياه الصرف المعالجة ثانويا باستخدام الترسيب الكيميائي

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قسم الهندسة المدنية ، كلية الهندسة ، جامعة الملك سعود ، ص. ب. ٨٠٠ ،

الرياض ١١٤٢١ ، المملكة العربية السعودية

ملخص البحث . تم خلال هذا البحث إجراء عدد من اختبارات الترسيب الكيميائي على عينات من مياه الصرف الصحي المعالجة بعملية المرشحات الحيوية بمحطة الصرف الصحي بمدينة الرياض ، وذلك بهدف تخفيض تركيز المواد العضوية والفوسفور . حيث تم تحديد كفاءة عدد من كيمياويات الترسيب الرئيسة وتكلفتها والتي شملت : الجير ، كلوريد الحديدك ، الشب والصودا الكاوية ، كما قام البحث بدراسة مدى تحسين كفاءة المواد السابقة في عملية الترسيب باستخدام بعض المروبات المساعدة والتي شملت بوليمرات سالبة الشحنة أو موجبة الشحنة أو متعادلة . وقد بلغ متوسط تركيز المواد العضوية (COD) في المياه المعالجة بالمحطة قبل الترسيب الكيميائي ١٠٠ ملجم / لتر كما بلغ متوسط تركيز الفوسفور الكلي ٤ ، ٦ ملجم / لتر . وقد أمكن تخفيض تركيز COD باستخدام الترسيب الكيميائي إلى حد أدنى مقداره ٤٠ ملجم / لتر . ولوحظ أن جميع كيمياويات الترسيب الرئيسة التي تم دراستها ، ماعدا الجير ، استطاعت تخفيض تركيز الفسفور إلى أقل من ١ ، ٠ ملجم / لتر دون الحاجة إلى كيمياويات مساعدة ، بينما في حالة الجير كانت هناك حاجة إلى إضافة ٤ ، ٠ ملجم / لتر من البوليمر سالب الشحنة . وكانت الجرعة المثالية باستخدام كل من الجير ، الشب والصودا الكاوية حوالي ٢٥٠ ملجم / لتر ، وفي حالة كلوريد الحديدك حوالي ٧٠ ملجم / لتر . وبدراسة تكلفة المواد الكيماوية ، اتضح أن استخدام الجير مع البوليمر يؤدي إلى أقل تكلفة ، حيث بلغت ١٢١ ريال (٣٢ دولار أمريكي) لكل ١٠٠٠ متر مكعب من المياه .