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Phosphorus Removal from Trickling Filter Effluents by Fly Ash

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Abstract. The removal of phosphorus from secondary trickling filter effluents by precipitation with fly ash was studied in comparison with the conventional coagulant, lime. The optimum dosage of fly ash, as determined by jar test experiments, was 2500-4000 mg/l as compared to only 100 mg/l for lime to reduce soluble phosphorus of up to 5.9 mg/l to less than 1.0 mg/l as P. For fly ash, prolonged rapid mix time improved the quality of the treated effluent to an appreciable extent. The pH and dissolved oxygen of secondary effluent appeared to have a significant effect on solution phosphate reduction with higher removals for high values of pH and dissolved oxygen concentration.

Introduction

Phosphorus is one of the main nutrients which causes the growth of algae and plants in water bodies due to eutrophication. Phosphorus concentrations less than 1.0 mg/l in wastewater effluents discharged to lakes, estuaries, and rivers is generally considered as acceptable from a eutrophication point of view. Although, phosphorus is essential for the growth of micro-organisms in biological waste treatment processes, it has been well established by many investigators that wastewaters contain surplus phosphorus that is more than what is needed for bio-treatment. In the United States, for example, raw wastewaters normally contain around 10 mg/l of total phosphorus, of which 70% is soluble [1;2].

It has also been found that a maximum of 20-30% of phosphorus is removed during biological processing of wastewaters by conventional treatment methods [2-4]. This leaves far more than 1.0 mg/l of phosphorus in the effluents. The soluble phosphorus concentration in the trickling filter effluent of Riyadh's wastewater treatment plant averaged 6.2 mg/l in the year 1413 H [5]. Hence, additional processing or modification to the existing treatment schemes is warranted for proper control of phosphorus levels.

Chemical precipitation by salts of iron and aluminium or lime along with polyelectrolytes is the most popular tertiary wastewater treatment method for phosphorus removal. Waste pickle liquor, a waste from steel industries, is one of the coagulants used for the precipitation of phosphorus for economic reasons [6]. Efforts have been made by many investigators to find efficient and more economical materials and methods for reducing phosphorus in wastewater effluents.

Recently, fly ash, an industrial solid waste of thermal power plants, has been demonstrated to be a feasible material for the removal of organics [7;8], phenols [9], fluoride [10], and heavy metals [11-14] from water and wastewater. Fly ash is defined by ASTM [15] as finely divided residue that results from the combustion of ground and powdered coal. It is composed chiefly of silica, alumina, iron, and calcium oxides (lime). ASTM divides fly ash into two distinct classes based on the coal source: class F, from bituminous coal, and class C, from sub-bituminous and lignite coal origins. Sub-bituminous and lignite ashes have comparatively higher lime content and lower amounts of silica, alumina, and ferric oxide than class F and hence are termed "high lime" fly ashes.

In the present investigation lignite fly ash was utilized as a coagulant for the precipitation of phosphorus from trickling filter effluents. The results of the study conducted at varying experimental conditions are discussed in this paper.

Materials and Methods

The fly ash used in this investigation was of lignite coal origin and had the composition shown in Table 1, as provided by the source supplier. High purity commercial lime was obtained from one of the local treatment plants. The wastewater effluents were collected from the secondary trickling filter wastewater treatment plant of King Saud University, Riyadh, Saudi Arabia. The samples were collected just before the chlorination chamber, once a day, for a period of one week. Jar test experiments were run using a Phipps and Bird apparatus.

Total Organic Carbon (TOC) determinations were performed on a Dohrmann DC-190 TOC analyzer. All other parameters were measured in accordance with Standard Methods [16].

Table 1. Characteristics of fly ash (lignite coal origin)

Constituent	% by weight
SiO_2	51.19
Al_2O_3	24.66
Fe_2O_3	4.96
CaO	13.14
MgO	2.39
SO_3	1.03
Na_2O	0.38
K_2O	1.10
Others	1.15
Total	**100.00**

Results and Discussion

Characteristics of secondary effluent

The concentration of some important parameters of the secondary trickling filter effluent collected before chlorination is presented in Table 2. The mean and the range values given in the table reflect the characteristics of the effluent for a one week period. The pH of the effluent is around neutral and there is no great variation in the alkalinity and hardness as indicated by low standard deviation values (see Table 2). However, the ortho-P varied from 4.4 to 5.9 mg/l as P. The conductivity remained uniform indicating low variation in the dissolved solids concentration.

Characteristics of fly ash leachate

Humenich *et al.* [17] conducted laboratory batch and column leaching experiments and found that lignite fly ashes release various inorganic materials into water. The major ash leachate species found were calcium and sulfate. In addition to these, trace elements; aluminium, arsenic, boron, phosphorus, selenium, silicon, and zinc were found in concentrations having some significance.

Since fly ashes of the same classification can differ in composition, a jar test experiment was performed to characterize the leachate from the fly ash and also the commercial lime used in this study. The experimental procedure was similar to that

Table 2. Characteristics of secondary effluent (KSU plant)

Parameter	Mean concentration[a]	Range	No. of samples η	Standard deviation s
pH	–	7.1 - 7.5	5	0.16
Alkalinity[b]	48	42 - 51	5	4.50
Calcium hardness	210	188 - 232	5	18.04
Total hardness	261	248 - 284	4	19.72
Ortho-P	5.1	4.4 - 5.9	5	0.62
COD	32	26 - 38	5	7.16
Turbidity (NTU)	5.4	3.2 - 7.8	5	2.24
Conductivity (μS/cm)	1075	1050 - 1100	4	28.86

[a] Concentrations are in mg/l, except for pH, and where stated otherwise.

[b] Alkalinity and Hardness in mg/l as $CaCO_3$.

used for actual wastewater effluents. However, only one dose (1000 mg/l) was applied to both distilled water (DW) and tap water (TW) systems. Tap water was chosen because it was found out that it contains inorganic constituents similar to wastewater effluents.

The results of the leaching experiment are shown in Table 3. The pH, alkalinity, hardness, ortho-P and sulfate concentrations of both DW and TW were increased due to the addition of fly ash. pH and alkalinity changes may be due to the release of bicarbonate, carbonate and hydroxyl ions from the minerals present in the fly ash. Calcium and sulfate releases may be from calcium oxide, calcium sulfate, etc. found in fly ashes [17]. Changes in chloride, dissolved solids and organic contents of fly ash leachate were insignificant. As expected, addition of lime increased the pH, alkalinity, hardness, and conductivity of both DW and TW, probably due to the release of hydroxyl ions. Small reductions in Ortho-P and TOC by lime can also be noticed from Table 3.

Phosphorus removal by fly ash

Experiments with the jar test were conducted by fixing the operating parameters normally adopted for lime treatment. The rapid and slow mixing, and sedimentation times were 2, 18 and 30 minutes, respectively. The results of the tests conducted over a one week period are summarized in Table 4. Reported values represent the mean concentrations for five data sets obtained by testing trickling filter effluents collected

Table 3. Some important characteristics of fly ash and lime leachates[a] (1000 mg/l of each lime and fly ash)

Sample	pH	Alkalinity[b]	Hardness		Turbidity (NTU)	Conductivity (μS/cm)	Ortho -P	TOC	Cl^-	SO_4^-
			Ca^{++}	Total						
DW	6.8	–	–	–	0.6	2.2	0	–	–	–
DW + FA	10.1	55	32	32	18.0	150	0.69	–	6.0	2.5
DW + Lime	11.8	730	660	720	21.5	3600	0	0.20	4.0	–
TW	7.9	36	96	116	1.5	475	0.14	0.40	90	86
TW + FA	9.4	64	132	144	14.2	550	0.56	0.55	98	90.5
TW + Lime	11.6	448	460	492	11.4	2250	0	0.30	86	82

DW = Distilled water TW = Tap water FA = Fly ash

[a] Concentrations are in mg/l, except for pH, and where stated otherwise.

[b] Alkalinity and Hardness in mg/l as $CaCO_3$.

Table 4. Summary of jar test experimental results for fly ash and lime[a]

Dosage	pH	Alkalinity[b]	Hardness Ca^{++}	Hardness Total	Turbidity (NTU)	Conductivity (μS/cm)	Ortho-P	COD
0	7.2	48	210	261	5.4	1075	5.08	32
Fly ash								
1000	8.0	59	215	264	28	1075	3.75	26
1500	8.6	62	224	269	11	1075	2.86	23
2000	8.9	68	222	267	5.7	1075	2.03	19
2500	9.1	73	228	275	5.3	1075	1.56	18
3000	9.3	80	240	276	3.7	1100	1.17	18
4000	9.6	92	253	295	4.5	1100	0.95	18
Lime								
100	10.4	99	243	265	3.2	1150	0.48	24
150	10.7	106	257	272	3.2	1250	0.40	20
200	10.9	142	279	297	4.5	1400	0.29	16
300	11.2	198	309	324	4.8	1650	0.29	14
400	11.5	266	312	327	5.3	2150	0.33	14

[a] Concentrations are in mg/l, except for pH, and where stated otherwise.

[b] Alkalinity and Hardness in mg/l as $CaCO_3$.

on five different days. An overall average of 4000 mg/l of fly ash was needed to reduce phosphorus concentration to less than 1.0 mg/l from mean secondary effluent level of 5.1 mg/l as P. However, even a fly ash dosage of 2500 mg/l was sufficient for some effluents containing low initial phosphorus concentrations. On the contrary, a lime dosage of even 100 mg/l was enough to reduce the phosphorus concentrations to less than 1.0 mg/l (see Table 4).

Figure 1 shows the relationship between fly ash dosage and the mean percentage of ortho-P reduction. The relation appears to be linear between dosages of 1500-3000 mg/l and approaches asymptotically above 3000 mg/l. This indicates that 100% removal of phosphorus from wastewater effluents by fly ash may not be feasible under the experimental conditions studied. Moreover, phosphorus was found to leach from the fly ash in the previous leaching experiment, as also shown by other investigators [17]. The removal of phosphorus from the effluents by fly ash may be mainly due to a combination of adsorption and precipitation reactions with calcium (Ca), aluminium (Al), iron (Fe) or other clay minerals present in fly ash. This phenomena of phosphorus removal is also reported in the literature for sand and natural wetland systems [18-20].

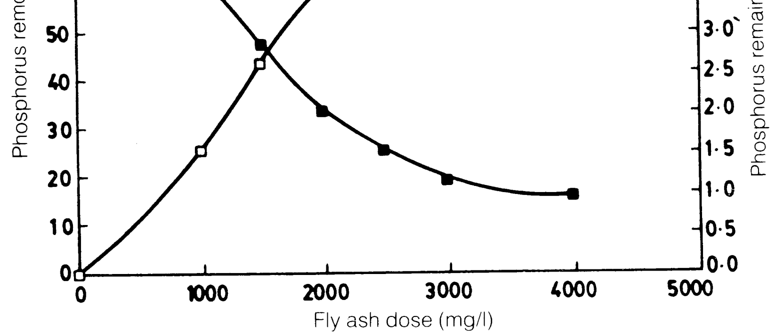

Fig. 1. Removal of phosphorus as a function of fly ash dose

The addition of fly ash increased the pH, alkalinity and calcium content of the secondary trickling filter effluents (Table 4), as was previously observed in the case of distilled and tap water experiments. According to Table 4, the fly ash dosage should be greater than 4000 mg/l in order to be able to raise the pH above 10.0; the optimum value for phosphate removal by lime [1]. The changes in effluent pH values due to the addition of varying fly ash dosages are shown in Fig. 2. The alkalinity and calcium concentrations increased with increasing fly ash dosage, but to a much lesser extent than observed in the case of leaching in tap water. This indicates the possible consumption of both alkalinity and calcium in the precipitation reactions.

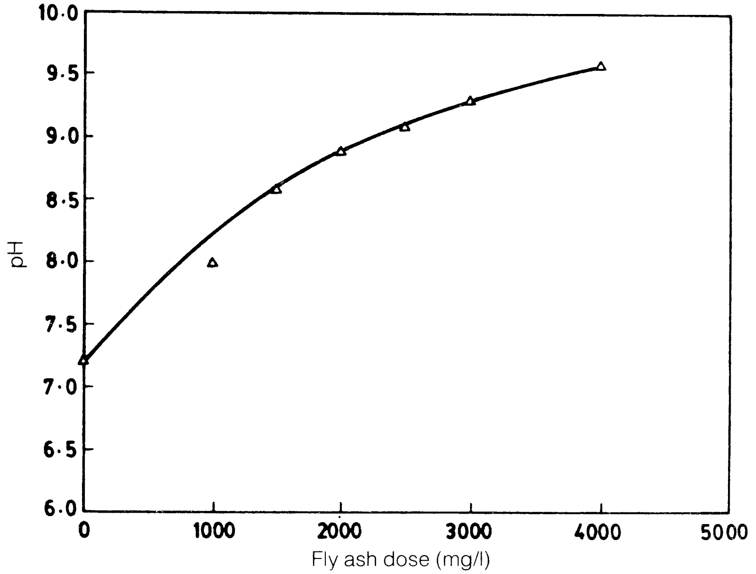

Fig. 2. The change in effluent pH values as a function of fly ash dose

The turbidity was very high (Av. 28 NTU) for 1000 mg/l fly ash dose for all the experiments. The optimum dosage of fly ash was around 3000 mg/l which gives the lowest turbidity of 3.7 NTU. There was no appreciable change in the conductivity of the trickling filter effluents with changing fly ash dosage, indicating low solubility of fly ash. A reduction of up to 44% in the dissolved organic content measured as COD can be noticed from Table 4. The removal of COD can be attributed to two processes; adsorption of non-polar and higher molecular weight organics onto fly ash [7] and enmeshment of organics in the precipitates ($CaCO_3$, hydroxyapatite, etc.) and subsequent settlement.

Effect of mixing time

For fly ash dosages above 1500 mg/l, the particles and precipitates in the jars were settling down soon after the rapid mix period (approx. 2-3 min), leaving a clear supernatant at the top. In order to find the effect of mixing time one additional set of experiments with prolonged mixing time (20 min. rapid mix, 10 min. slow mix and 20 min settling) was run simultaneously with the normal set. The results of the two sets are shown in Table 5. There was an overall improvement in the characteristics of the effluent, in the case of the longer mixing period. Longer rapid mixing achieved 0-24% more reduction of phosphorus than the shorter rapid mix period. The organics removal (measured as COD) was also enhanced (see Table 5). This increased reduction may be due to slow precipitation and adsorption, which takes place apart from the fast reactions [18].

Effect of dissolved oxygen

Secondary effluents from activated sludge treatment plants normally have more dissolved oxygen (DO) than trickling filter effluents. Hence, an experiment was conducted in which one sample of trickling filter effluent was aerated to increase the DO concentration to 6.8 mg/l. Jar tests were run on both aerated and unaerated samples using a long mixing time of 20 min. and a fly ash dosage of 2500 mg/l, which was found effective in the previous experiment. The results are presented in Table 6. As can be seen from the table, phosphorus removal was 82.2% for the aerated sample as compared to 71.8% in case of the unaerated sample. This indicates that DO has a positive effect on the removal of phosphorus from wastewater effluents by fly ash.

Effect of solution pH

pH of the solution plays an active role in the precipitation/adsorption of phosphate by various coagulants, such as salts of aluminium, iron or lime. Reactions with lime occur mainly under alkaline conditions, while reactions with aluminium and iron salts predominate in acid to neutral conditions [1;18]. Hence, an additional test was conducted in which 1g each of fly ash was mixed with 100 ml portions of trickling filter effluent. High dosage of fly ash was selected to raise the solution pH to higher levels. The solutions were also adjusted to initial pH values of 4.0, 7.0 and 10.0 with the addition of dilute sodium hydroxide or sulphuric acid solutions.

The effluent was also spiked with phosphate solution to increase the concentration to approximately 15.0 mg/l as P. The contents were mixed thoroughly for one hour, filtered using 0.45μm membrane filter and analyzed. The results of these runs are shown in Table 7.

Table 5. Jar test results of fly ash for two different experimental conditions[a]

Experimental conditions	Fly ash dose	pH	Alkalinity[b]	Calcium hardness	Turbidity (NTU)	Ortho-P	COD
Rapid mix 20 min.	0	7.2	51	212	3.2	5.89	25.6
Slow mix 10 min.	1000	8.2	61	228	6.8	4.44	17.6
Settling 20 min.	1500	8.6	61	232	1.8	3.11	–
	2000	8.8	64	240	1.4	1.89	12.8
	3000	9.3	77	248	2.2	0.67	11.2
	4000	9.8	97	272	3.8	0.33	11.2
Rapid mix 2 min.	1000	8.1	61	224	47	4.44	16.0
Slow mix 18 min.	1500	8.4	65	224	27	4.22	12.8
Settling 30 min.	2000	8.6	68	224	10	3.22	16.0
	2500	8.9	69	228	7.8	2.44	–
	3000	9.1	75	240	4.8	1.78	16.0
	4000	9.4	84	248	5.2	1.03	16.0

[a] Concentrations are in mg/l, except for pH, and where stated otherwise

[b] Alkalinity and Hardness in mg/l as $CaCO_3$

Table 6. Effect of DO on phosphorus removal by fly ash[a]

DO (mg/l)	Ortho-P (mg/l)	Removal (%)
4.0	6.4	–
4.0	1.82	71.8
6.8	1.10	82.2

[a] Fly ash dosage = 2500 mg/l

Table 7. Effect of pH on phosphorus removal by fly ash[a]

Initial pH	Final pH	Ortho-P (mg/l)	Removal (%)
7.5	7.5	15.2[b]	–
4.0	8.6	3.3	78.3
7.0	9.6	0.8	94.7
10.0	12.2	0.3	98.0

[a] Fly ash dosage = 10,000 mg/l
[b] Spiked sample

As seen from the Table, greater phosphorus removal occurred at high pH values. The phosphorus removal was 78.3, 94.7 and 98.0% for final solution pH values of 8.6, 9.6, and 12.2 respectively. This indicates that neutral to alkaline conditions favor the precipitation of phosphorus by lime present in the fly ash.

The discussion presented above is based on a preliminary study. But the results provide a crude estimate of the quantity of fly ash needed to remove phosphorus from the effluents. The fly ash dosages required (2500-4000 mg/l) are very high when compared to the normal lime dosages of 150-400 mg/l used in wastewater treatment. This may create serious sludge handling problems. The cost of fly ash has not been evaluated but it is expected to be very low in comparison to the cost of lime.

Conclusions

The conclusions drawn from this study, which was conducted to evaluate the removal of soluble phosphorus from trickling filter effluents by fly ash, are as follows:

- Fly ash is effective in removing phosphorus from up to 5.9 mg/l to less than 1.0 mg/l. However, the dosages required (2500-4000 mg/l) to accomplish the task are very high.
- High solution pH values favour the precipitation reactions between phosphorus and fly ash. The phosphorus reduction was 78.3, 94.7 and 98.0% for reaction pH values of 8.6, 9.6 and 12.2, respectively.
- The DO concentration of the effluent has an appreciable effect on the removal of phosphorus by fly ash. Increasing DO resulted in increased phosphorus removal. This indicates that fly ash is expected to be more efficient for the removal of phosphorus from activated sludge effluents.
- A prolonged rapid mix period enhanced phosphorus reduction; hence the optimum rapid mix period for maximum phosphorus reduction should be determined.
- The high dosage of fly ash necessary to reduce the phosphorus concentration is more likely to create sludge handling problems, which requires serious consideration.

Recommendations

- More detailed studies need to be conducted to understand the mechanisms of phosphorus and other pollutants removal from wastewaters by fly ash.
- Methods of treatment which consume less fly ash dosages should be sought.
- Possible incorporation of fly ash addition to suspended growth processes, such as activated sludge treatment, is expected to have significant advantage and should be investigated.
- The removal and addition of heavy metals of concern in wastewater effluents should also be considered and evaluated.

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إزالة الفوسفور من مياه الصرف المعالجة بالمرشّحات الحيويّة باستخدام الرماد المتطاير

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(استلم في ١٧/١١/١٩٩٣م؛ قبل للنشر في ٢٠/٣/١٩٩٤م)

ملخص البحث. لقد تمّ خلال هذه الدراسة تقويم كفاءة الرماد المتطاير في إزالة الفوسفور من مياه الصرف المعالجة بوساطة المرشّحات الحيويّة، وتّم مقارنته مع كفاءة الجير الذي يستخدم تقليديًّا في إزالة الفوسفور من مياه الصرف. وبإستخدام تجارب اختبار الدوارق تّم تحديد الجرعة المثاليّة من الرماد المتطاير اللازمة لتخفيض نسبة الفوسفور الذائب من حوالي ٩,٥ملجم/ لتر إلى أقل من ١ ملجم/لتر، حيث بلغت الجرعة اللازمة من الرماد المتطاير بين ٢٥٠٠ إلى ٤٠٠٠ ملجم/ لتر بالمقارنة بجرعة ١٠٠ ملجم/ لتر من الجير. وقد لوحظ أنّ زيادة زمن الخلط السريع يحسّن إلى حد جيد من نسبة إزالة الفوسفور بوساطة الرماد المتطاير، كما أن ارتفاع الرقم الهيدروجيني وتركيز الأوكسجين الذائب يزيد إلى حد كبير من نسبة إزالة الفوسفور.