A Comparative Study of Anoxic Limestone Drain and Open Limestone Channel for Acidic Raw Water Treatment

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***Abstract* - This study presents the performance of an anoxic limestone drain in comparison to an open limestone channel for treating acidic water. The anoxic limestone drain was designed to enhance limestone dissolution and alkalinity generation thus minimizing the potential of armouring which may decrease the rate of acid neutralization. Actual raw water from two different locations within Sg. Bekok catchment that is highly acidic with low pH value (~ pH 2.5) was used in the experiment. The anoxic limestone drain was found to perform better than the open limestone channel with respect to pH increase, acidicy decrease and alkality production. Iron was removed at relatively higher rate in open limestone channel but resulted in the armouring of limestone surfaces thus limiting further generation of alkalinity.**

***Index Term* - Acidic water; Anoxic limestone drain; Alkalinity production; Open limestone channel**

I. INTRODUCTION

As experienced at Sg. Bekok, Batu Pahat River catchment in recent years, intensive agricultural drainage activities in the riparian lowland between Bekok Dam and the town of Yong Peng have resulted in the deterioration of the river water quality, especially in term of pH, iron and aluminium content. The water supply intakes within Batu Pahat district have been unable to provide sufficient supply of raw water which has lead to water shortages problem. This is a result of water quality problems undergone by Sg. Bekok with high concentration of iron (110 mg/L) and aluminium (290 mg/L) and pH values as low as 2.5 which exceed the limits set out by the National Water Quality Standard for Class II rivers [1]. This has significantly caused interruptions in the operation of Yong Peng 2 & 3, Sri Gading and Parit Raja water treatment plants in producing sufficient potable water for the district's needs. This study was carried out to investigate the viability of limestone treatment in treating acidic raw water prior to being used for water supply consumption.

Financial support for this study was partly funded by SAJ Holdings Sdn. Bhd., and was jointly supported through UPM RUGS/9330700, FRGS grant/5524261 and TWAS-Comstech joint research grants.

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In specific, anoxic limestone drains (ALD) which operate at low oxygen concentration level were studied. The study aims to compare the performance of an anoxic limestone drain and open limestone channel in relation to their respective pH adjustment, acidity reduction, alkalinity generation, and removal of iron.

Acid sulphate soil is a frequently encountered soil type in most of the Sg. Bekok catchment. In some of the sub-catchments, acid sulphate soils are the only soil type that can be found. Overall acid sulphate soil covers 116.4 km^2 of the total 279 km^2 which represents about 41.7% of the whole catchment area (from the Bekok Dam to Sri Gading) [2]. The soil is typically formed in low lying portions of the terrain, where the ocean has recently withdrawn and deposited pyrite, which when oxidized releases acid and sulphate. The cause of the problem is believed to be due to the acidification process of soil by oxidation of pyrite in the soil within the river [3]. Pyrite exposed to the environment through intensive agricultural drainage reacts with oxygen and water to form sulfuric acid, resulting in acidic water condition.

Dissolution of calcite ($CaCO_3$) can neutralize acidity and increase pH and concentration of alkalinity ($HCO_3^- + OH^-$) and Ca^{2+} in acidic water [4, 15]. As the pH increases to near-neutral value, concentrations of Fe^{3+}, Al^{3+} and other metals can decline owing to their precipitation or adsorption [5, 16, 21, 24]. Metal acidity due to high concentrations of Fe^{3+}, Al^{3+}, Mn^{2+} and other solutes in acidic water can be lowered through limestone treatment of metal precipitation [17, 18, 19, 22]. Thus, it is the aim of this study to investigate the conditions under which acidity decreases, pH increases, and metal is removed in an anoxic limestone drain.

II. MATERIALS AND METHODS

A. Sampling and Experimental Materials

Water samples from two different sources of Bekok Intake and Semberong Lagoon were used for the experimental work. An approximately 80 liters of water sample were collected at the respective sites for the experimental purposes. The limestone used to treat the acidic water was of 30 mm in size and were used up to 112 kg (28 kg in each of the anoxic limestone reactor). The chemical reagent used for the determination of total iron was FerroMo iron reagent powder pillow. The 0.1N NaOH solution for acidity test was prepared using 4 g of NaOH to be dissolved in 1L of distilled water. As for alkalinity test, the 0.02N HCl solution was prepared by diluting 200 mL of 0.1N HCl to 1L of deionized water. The analyses of the raw and treated water were being evaluated based on their respective pH, acidity, alkalinity, iron and aluminium. Both the alkalinity and acidity for the samples were titrated with HCl and NaOH to pH 4.5 and 8.3 endpoints, respectively based on Standard Methods for the Examination of Water and Wastewater [6]. Iron was measured in the laboratory using atomic absorption spectroscopy (AAS).

B. Experimental Procedures

The anoxic limestone drains were constructed in series to receive the inflow from a holding tank of 30 liters of acidic raw water. Water from the tank flowed through the anoxic drain via gravity to reach the effluent point at several contact times i.e. 10 minutes, 20 minutes, 30 minutes and 60 minutes. Each of the limestone drain was of 20 cm in diameter with a length of 0.67 m and depth of 14 cm. The drain was made of PVC pipe in a semicircular form and was constructed with a slope of 1:50-100. A cling wrapper was used as the drain liner prior to place in the 28 kg of 3 mm limestone. The liner was wrapped over the top of the limestone to minimize O_2 from taking part in the treatment process. The flow rate was measured by recording the time to collect a known volume of water as it reached the drain outlet. pH was monitored at the inlet and outlet of each drain. Samples were taken at the outlet of final drain and analyzed for acidity, alkalinity, and Fe. Prior to experiment, oxygen was displaced from the drain by nitrogen gas until the O_2 content was < 0.5 mg/L which was considered anoxic [7]. The open limestone channel was provided without the purging of nitrogen gas and by removing the cling wrapper so that the water is exposed to the atmosphere.

III. RESULTS AND DISCUSSION

Performance of anoxic limestone drain and open limestone channel were compared for a contact time of 30 minutes. These include the comparison of both systems with respect to pH rise, acidity reduction, alkalinity generation and removal of iron.

A. pH Rise

Results of pH increase for both systems are as presented in Table I. It was discovered that pH rise in open limestone channel was slightly slower as compared to anoxic limestone drain. However, both systems were capable of enhancing the initial pH of 4.09 and 3.27 for Bekok Intake and Sembrong Lagoon, respectively to reach near neutral pH level.

As illustrated in Fig. 1(a), initial pH of Bekok Intake of 4.09 was increased to 6.58 by the anoxic limestone drain when first contacted with 28 kg of limestone compared to 5.69 by the open channel. This showed a significant difference between anoxic limestone drain and open limestone channel in affecting pH rise of the water at the initial stage of the treatment. However, final pH achieved by both systems was almost the same. As the water flowed through the drains, pH increased with increasing limestone amount to finally reach 7.24 and 7.22 by the anoxic limestone drain and open limestone channel, respectively. The trend showed that the open limestone channel was capable of enhancing pH level as effective as the anoxic limestone drain despite its slower pH rise.

TABLE I.
pH RISE IN ANOXIC LIMESTONE DRAIN AND OPEN LIMESTONE CHANNEL

Source of sample	**Treatment type**	**Initial pH**	**Limestone amount (kg)**			
			28	**56**	**84**	**112***
Bekok Intake	Open Drain	4.09	5.69	6.07	6.78	7.22
	Anoxic Drain	4.09	6.58	7.19	7.16	7.24
Sembrong Lagoon	Open Drain	3.27	5.24	6.29	6.33	6.87
	Anoxic Drain	3.27	6.48	6.79	7.03	7.16

*30 minutes contact time

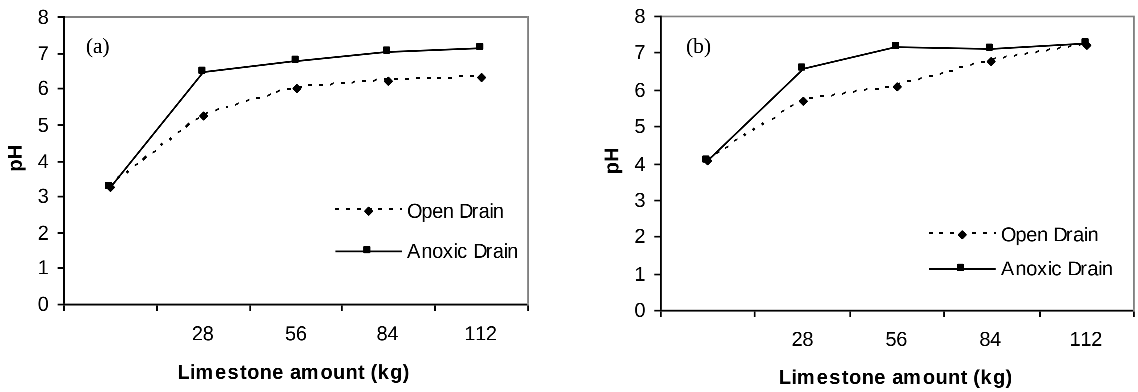

Fig. 1. Difference between anoxic drain and open channel pH rise (a) Bekok Intake (b) Sembrong Lagoon

As for Sembrong Lagoon, initial pH of 3.27 was raised to 6.48 by the anoxic limestone drain and 5.24 by the open limestone channel at the initial stage after contacted with 28 kg of limestone as shown in Fig. 1(b). Final pH after 30 minutes contact time was found as 7.16 and 6.87 by the anoxic limestone drain and open limestone channel, respectively. The final pH for both systems was found in the near neutral range even though the rate of pH rise in open limestone channel was slightly slower.

As shown in the figure, the anoxic limestone drain was capable of enhancing a higher pH rise as compared to open limestone channel. It was because, if CO_2 becomes trapped within the closed anoxic limestone drain, both the partial pressure of CO_2 and the Ca^{2+} concentration will increase, leading to a net rise in pH [8]. When the closed system reaches equilibrium, the pH attained will be higher than that of an equivalent open system [9].

B. Acidity Reduction

Reduction of acidity for both the anoxic limestone drain and open limestone channel are as shown in Table II. As observed, the anoxic limestone drain gave a higher percentage of acidity removal in 30 minutes contact time as compared to the open limestone channel. Fig. 2. illustrates the difference between anoxic limestone drain and open limestone channel with respect to acidity removal after 30 minutes of contact with the limestone.

The acidity of raw water sample of Bekok Intake was reduced to 24 mg/L as $CaCO_3$ by the anoxic drain as compared to 37 mg/L as $CaCO_3$ for the open channel. As for Sembrong Lagoon, initial acidity of 99 mg/L as $CaCO_3$ was reduced to 21 mg/L as $CaCO_3$ by the anoxic drain, as compared to 43 mg/L as $CaCO_3$ by the open limestone channel. The results demonstrated that anoxic drain had a better neutralization rate which tends to remove higher acidity as compared to open channel. The effect has also been observed by Ziemkiewicz [10] that armoured limestone (due to open channel) to be 2 to 45 % less effective in neutralizing hydrogen ion acidity compared to unarmoured limestone (anoxic drain).

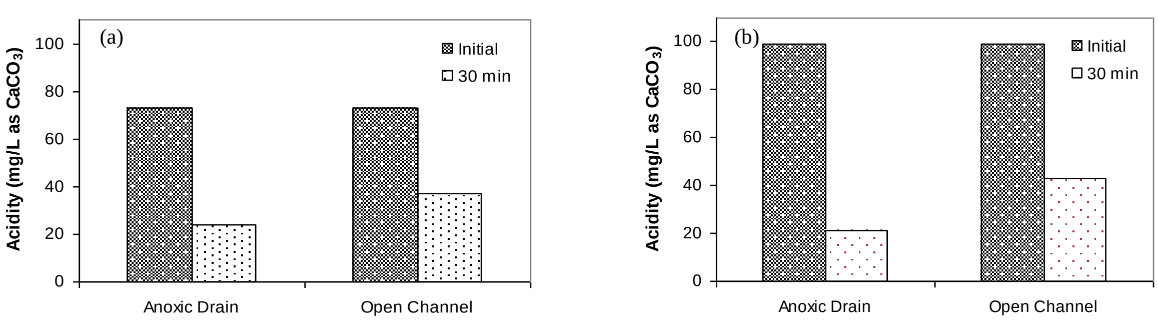

Fig. 2. Acidity reduction in anoxic drain and open channel (a) Bekok Intake (b) Sembrong Lagoon

TABLE II.
ACIDITY REDUCTION IN ANOXIC LIMESTONE DRAIN AND OPEN LIMESTONE CHANNEL

Source of sample	Treatment type	Initial acidity (mg/L as $CaCO_3$)	Acidity*	% Reduction
Bekok Intake	Open Drain	73	37	49
	Anoxic Drain	73	24	67
Sembrong Lagoon	Open Drain	99	43	57
	Anoxic Drain	99	21	79

*30 minutes contact time

C. Alkalinity Generation

The production of alkalinity in both systems is shown in Table III. It was found that the anoxic limestone drain showed a greater increase of alkalinity as compared to the open limestone channel. Anoxic limestone drain which have been designed to avoid armouring, are particularly effective for generation of alkalinity [11]. The rate of alkalinity production for Bekok Intake was found to be increased up to 64 mg/L as $CaCO_3$ as the water flowed through the anoxic drain in 30 minutes of contact with limestone. In contrast, the alkalinity was only generated to a concentration of 47 mg/L as $CaCO_3$ by open limestone channel. Sembrong Lagoon water sample indicated a production of 54 mg/L as $CaCO_3$ of alkalinity for the anoxic drain relative to 43 mg/L as $CaCO_3$ for open limestone channel.

Retaining CO_2 within an enclosed anoxic limestone drain can enhance calcite dissolution and alkalinity production [4, 20, 23]. As for an open channel, higher rate of metal ion precipitation could armoured the limestone surface (Fig. 3.), decreasing the rate and extent of limestone dissolution and alkalinity production [12, 13].

Fig. 3. Armouring due to iron precipitation in open limestone channel

TABLE III.
ALKALINITY GENERATION IN ANOXIC LIMESTONE DRAIN AND OPEN LIMESTONE CHANNEL

Source of sample	Treatment type	Initial alkalinity (mg/L as $CaCO_3$)	Alkalinity*
Bekok Intake	Open Drain	0	47
	Anoxic Drain	0	64
Sembrong Lagoon	Open Drain	0	43
	Anoxic Drain	0	54

*30 minutes contact time

D. *Iron Removal*

Results of iron removal for the anoxic limestone drain and open limestone channel are given in Table IV. The results showed that the open limestone channel was capable of removing a higher concentration of iron compared the anoxic limestone drain.

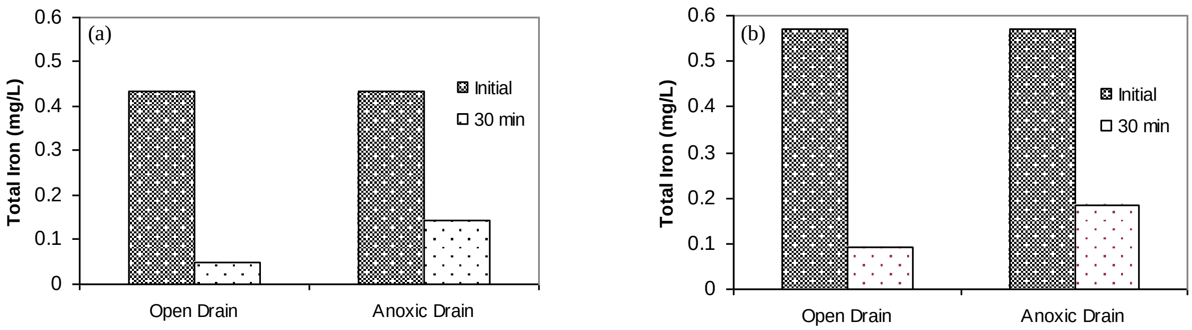

Fig. 4. Iron removal in anoxic drain and open channel (a) Bekok Intake (b) Sembrong Lagoon

TABLE IV.
REMOVAL OF IRON IN ANOXIC LIMESTONE DRAIN AND OPEN LIMESTONE CHANNEL

Source of sample	Treatment type	Initial iron concentration	Iron concentration*	% Removal
Bekok Intake	Open Drain	0.433	0.048	89
	Anoxic Drain	0.433	0.145	67
Sembrong Lagoon	Open Drain	0.571	0.092	84
	Anoxic Drain	0.571	0.185	68

The iron removal in the anoxic limestone drain and open limestone channel is shown in Fig. 4. It was observed that a relatively lower iron concentration was obtained by the open limestone channel for Bekok Intake and Sembrong Lagoon sample of 0.048 mg/L and 0.092 mg/L, respectively after 30 minutes of contact time. It was probably due to higher precipitation rate as the water was exposed to the atmosphere, and solid $Fe(OH)_3$ was produced by the oxidation of iron. In contrast, excluding O_2 from contact with the acidic water in anoxic drain minimizes the potential for precipitation of $Fe(OH)_3$ [4, 14, 23]. Statistically, there was a significant difference between anoxic drain and open channel performance in affecting the pH rise for Bekok Intake and Sembrong Lagoon at 90% (p-value $\leq$ 0.1) and 95% of confidence level, respectively. As described earlier, the anoxic limestone drain was capable of enhancing a higher pH rise compared to open limestone channel due to higher neutralization rate between the calcite and the acidic water.

IV. CONCLUSION

Generally, it was discovered that the anoxic limestone drain was capable of reducing acidic condition of the raw water. The anoxic limestone drain was found to be effective in generating higher pH rise, better acidity reduction and alkalinity production in comparison to open limestone channel. Iron removal was relatively greater in open limestone channel due to higher precipitation rate. However, given the greater precipitation rate for iron in open limestone channel, amouring of limestone surfaces clearly limits its capability of producing more alkalinity and hence slower removal of acidity in the water. Further work will aim at enhancing the performance of the anoxic limestone drain by incorporating the use of compost media and the limestone to compensate any limitations of system performance encountered in this study.

ACKNOWLEDGMENT

The authors wish to thank Syarikat Air Johor (SAJ) Holdings Sdn. Bhd. for providing useful information for the study and for giving permission to use their water treatment plant facilities.

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