

LIMESTONE-BASED CLOSED REACTOR FOR PASSIVE TREATMENT OF HIGHLY ACIDIC RAW WATER

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Abstract

Limestone has been widely used in the treatment of acidic water due to its potential of neutralising acid and removing metals in water. In this study, the efficiency of a laboratory-scale limestone-based closed reactor was evaluated for treatment of highly acidic raw water. The treatment reactor was basically designed to enhance limestone dissolution and alkalinity generation under anoxic condition thus minimising the potential of armouring which may decrease the rate of acid neutralisation. Actual raw water from two different sources that is highly acidic with very low pH was used in the experiment, treated with 30 mm diameter of 112 kg of limestone. The conditions under which the pH increases, acidity decreases, alkalinity produced and metals were removed in the closed limestone reactor have been determined in comparison to open limestone channel performance. pH was significantly increased from 3.27-4.09 to 6.49-6.67 after flowing through the reactor in 10 minutes of contact with the limestone. Acidity was reduced from 73-99 mg/L as CaCO₃ to 17-19 mg/L as CaCO₃ as pH were raised to reach near neutral levels. Iron and aluminium were also found removed in the closed limestone reactor.

Keywords: acidic water treatment; alkalinity generation; pH rise; limestone-based closed reactor

1. INTRODUCTION

There has been increasing river water quality deterioration over the country in recent years. The deteriorating trend of river water quality has prompted the water authority to look into more effective means of improving them in a holistic manner so as to sustain their beneficial uses and demands. As experienced at Bekok River, Batu Pahat, Malaysia 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 terms of pH, iron and aluminium contents.

The water supply intakes within Batu Pahat district have been unable to provide sufficient supply of raw water leading to water shortages problem. This is a result of water quality problems encountered at Bekok River

with pH value as low as 2.5 which exceeds the limit set out by the National Water Quality Standard (NWQS) for Class II rivers (SAJ Holdings, 2005). 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. In specific, a limestone-based closed reactor that operates at low oxygen concentration level was studied. The study aims to provide efficient on-site treatment system as an alternative solution to acidic raw water problem of Bekok River, Batu Pahat by means of diversion prior to entering the water treatment plant.

Acid sulphate soil is a frequently encountered soil type in most of the Bekok River catchment. In some of the sub-catchments, acid

sulphate soil is the only type of soil that can be found. Overall, acid sulphate soil covers 116.4 km² of the total 279 km² which represents about 41.7% of the whole catchment area (from the Bekok Dam to Sri Gading) (Asia Water, 2005). The soil is typically formed in low lying portions of the terrain, where the ocean has recently withdrawn and deposited pyrite, which when oxidised 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 (Katimon et al., 1999). Pyrite that is exposed to the environment through intensive agricultural drainage reacts with oxygen and water to form sulphuric acid, resulting in acidic water condition. This results from the action of bacteria, which generate their energy by using oxygen to oxidise ferrous iron (Fe²⁺) to ferric iron (Fe³⁺). The ferric iron in turn reacts with pyrite to produce ferrous iron and sulphuric acid which is then available for oxidation by the bacteria. The cycle continues until the pyrite is exhausted which can take up to more than 100 years (Kalin et al., 2005). The chemical reactions governing the oxidation of pyrite and acid generation are given in Eq. 1-4 (Younger et al., 2002):

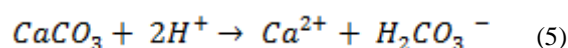
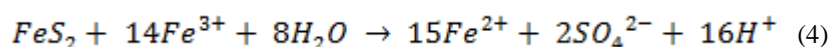
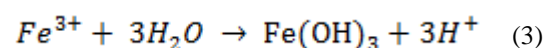
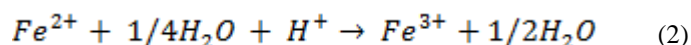
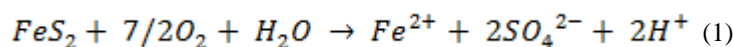
Limestone is a sedimentary rock composed of 50 to 90% mineral calcite (calcium carbonate, CaCO₃). Impurities in limestone generally consist of silica, alumina, and iron oxide (Lewis and Boynton, 1995). Pure limestone is typically white or almost white; however, because of impurities, many limestones exhibit different colours especially on weathered surfaces.

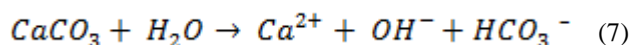
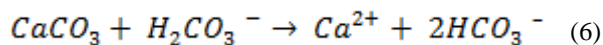
Dissolution of calcite can neutralise acidity and increase pH and concentration of alkalinity (HCO₃⁻ + OH⁻) and Ca²⁺ in acidic water (Cravotta III and Trahan, 1999).

Limestone generates alkalinity through the following reactions (Eq. 5-7):

Metal acidity due to high concentrations of Fe³⁺, Al³⁺, Mn²⁺ and other solutes in acidic water can be lowered through limestone treatment. As the pH increases to near-neutral value, concentrations of Fe³⁺, Al³⁺ and other metals can decline owing to their precipitation or adsorption (Blowers and Ptacek, 1994). Precipitation of ferric hydroxide (Fe(OH)₃) and aluminium hydroxide (Al(OH)₃) occurs where dissolved ferric iron and aluminium are present. Additionally, ferrous iron and aluminium may precipitate as carbonates, (FeCO₃) and (AlCO₃), although the kinetics governing precipitation of metal carbonates from a supersaturated solution may be slow (Hedin and Watzlaf, 1994). However, it is generally known that limestone armouring is inevitable. The armoured limestone will slowly decrease the neutralisation efficiency (Ziemkiewicz et al., 1997; Cravotta and Trahan, 1999; Younger et al., 2002; Huminicki and Rimstidt, 2008).

There has been limited research on the use of limestone for on-site treatment of acidic water in this country. It has been reported that limestone treatment could be an effective means of neutralising acidic water (Mokhtar, 2006). The preliminary study revealed that limestone has a significant potential in enhancing pH of acidic water, which in turn has resulted in the removal of metals (Fe and Mn) from the raw water, in a lab-scale oxalic limestone reactor. Limestone is also capable of removing heavy metals such as Cu, Zn, Cd, Pb, Ni, Cr, Fe and Mn from landfill leachate of up to 90% and was potentially useful as an alternative leachate treatment system at a relatively low cost (Aziz et al., 2004).





2. MATERIALS AND METHODS

2.1 Water Sampling and Analysis

Water samples from two different sources of Bekok Intake and Sembrong Lagoon were used in the experiment. Approximately 80 L of water samples were collected at the respective sites for the experimental purposes (collected in each 20 L bottle and acidified with 1% by volume nitric acid). Samples were kept cool at 4°C until the experimental run. The limestones used to treat the acidic water were obtained within the vicinity of the river catchment, i.e. 30 mm in size and were used up to 112 kg (28 kg in each of the limestone reactor). The analyses of raw and treated water were carried out for their respective pH, acidity, alkalinity, and content of iron and aluminium. pH was measured using Orion 3-Star pH meter (to a precision of ± 0.01). Both the alkalinity and acidity for the samples were determined by titration with 0.02 N HCl and 0.1 N NaOH, to pH 4.5 and 8.3 endpoints, respectively according to APHA (1999). Iron and aluminium were measured using atomic absorption spectroscopy (AAS).

2.2 Laboratory-scale reactor development

The study comprised of an experimental limestone treatment using a laboratory-scale limestone-based closed reactor. The raw acidic water used in the experiment was obtained from the two sources of Bekok Intake and Sembrong Lagoon as mentioned earlier. The efficiency of the limestone-based reactor was assessed in relation to pH adjustment, acidity reduction, alkalinity generation, and removal of iron and aluminium.

The closed limestone reactor was constructed in series (a sequence of four limestone channels), operated under anoxic condition. The experiment was conducted on a continuous mode of flow. It received the inflow from a holding tank of 30 L acidic raw water. The water from the tank flowed through the

On the other hand, many studies on limestone treatment outside this country have been associated with treatment for acid mine drainage (AMD). A closed limestone-based reactor, often called anoxic limestone drain (ALD) has been applied for AMD treatment in many instances particularly in the USA (e.g. Hedin et al., 1994; LaBar et al., 2008; LaBar and Nairn, 2009; Cravotta, 2010; Denholm et al., 2010; Zipper and Skousen, 2010; Genty et al., 2012). In theory, owing to the reaction between AMD and limestone (CaCO_3), the pH and concentration of alkalinity increase asymptotically with detention time in the ALD (Genty et al. 2012). The dissolution of calcite and precipitation of metal compounds have also been studied to evaluate on the processes affecting neutralisation of acidic mine drainage within limestone-based closed reactor (e.g. Robbins et al., 1999; Nuttall and Younger, 2002; Hallberg and Johnson, 2003; Cravotta, 2003; Huminicki and Rimstidt, 2008; Green et al., 2008; Palmer et al., 2012). Nevertheless, a study by Santomartino and Webb (2003) suggested that ALDs would not be effective for AMD with pH <1.5 and iron content of > 2 mg/L (Younger et al., 2002; PIRAMID, 2003). Even though ALD is not always the best option for AMD, but given the nature of acidic water encountered in our local situation, similar concept of treatment may be adopted. While it is known that a so-called reducing and alkalinity-producing system might be a better option for acidic, metal-containing mine water (e.g. Clyde et al., 2010; Genty et al., 2012), the simplicity of ALD treatment could be useful especially when the raw water is to be used for drinking water purposes (as in the case of Bekok River). Moreover, the highly acidic raw water is of greatest concern in addition to presence of iron and aluminium.

limestone reactor via gravity to reach the effluent point at several contact times i.e. 10 minutes, 20 minutes, 30 minutes and 60 minutes. The dissolved oxygen level within the reactor was monitored to ensure that the anoxic condition in the water was achieved prior to the start of experiment. Oxygen was displaced from the reactor by nitrogen gas until the O₂ content was < 0.5 mg/L, which was considered anoxic (Santomartino and Webb, 2003).

Each of the limestone channel was of 20 cm in diameter with a length of 0.67 m and depth of 14 cm. The channel 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 channel liner prior to place in the 28 kg of 30 mm limestone. The liner was wrapped over the top of the limestone to minimise O₂ 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 channel outlet. pH was monitored at the inlet and outlet of each channel. Samples were taken at the outlet of final channel and analysed for acidity, alkalinity, Fe and Al.

3. RESULTS AND DISCUSSION

3.1 Effect of limestone amount and contact time on pH rise

The results of limestone treatment in the closed limestone reactor for Bekok Intake and Sembrong Lagoon are shown in Table 1. The pH of the acidic water increased rapidly when first contacted with the limestone at the amount of 28 kg. This might be due to higher limestone dissolution rate at lower pH (pH ~ 4) since the rate of limestone dissolution is directly proportional to the activity of H⁺ (Plummer et al., 1978; Huminicki and Rimstidt, 2008). The pH of Bekok Intake sample reached a near neutral level (pH 6-7) after contacting with 28 kg of limestone, whereas the Sembrong Lagoon sample needed 56 kg to raise its pH to the near neutral range. It was also found that influent water of pH 3.27 was neutralised slightly faster than influent water of pH 4.09 (Fig. 1(a) and 1(b)). This agrees with Plummer et al. (1978) and Huminicki and Rimstidt (2008) that the greater the state of initial disequilibrium between

calcite, CaCO₃ and the solution, the greater the rate of reaction to reach equilibrium.

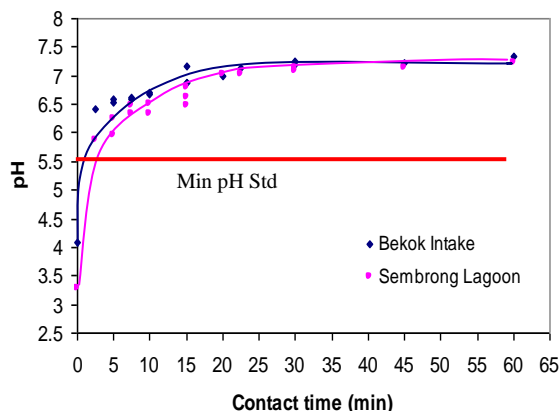


Figure 2. Effect of contact time on pH rise

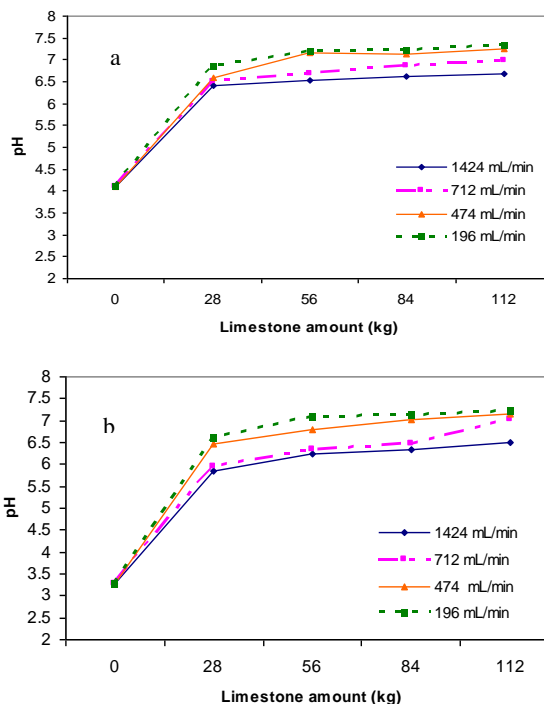


Figure 1. Effect of limestone amount on pH rise (a) Bekok Intake (b) Sembrong Lagoon

The rate of pH rise in relation to contact time is shown in Fig. 2. As obtained from the

experiment, pH increased with increasing contact time, depending on the initial pH of the raw water. As the water flowed through the limestone, pH increased due to the dissolution of limestone to reach near neutral level after 10 minutes of contact with the limestone. Initial pH of 4.09 for Bekok Intake rose to 6.67 in 10 minutes, whereas Sembrong Lagoon pH rose from 3.27 to 6.61 after 15 minutes of contact time. After 15 minutes, no significant increase of pH was observed indicating that calcite reaction has reached its equilibrium with the solution. Similar trend was also found by Genty et al.

(2012) in their batch experiment under anoxic condition that after certain reaction time pH showed no significant increase. Their experiment was then continued for an extended hours under aerobic condition to promote oxygenation and precipitation of iron hydroxide. Effect of detention time is also associated with the velocity of the flow, i.e. slower velocity may provide a longer time for reaction and therefore greater amount of neutralisation and degree of treatment may be achieved (Huminicki and Rimstidt, 2008; Kusin et al., 2012, Kusin, 2013).

Table 1. pH rise for Bekok Intake and Sembrong Lagoon

Source of sample	Contact time (min)	Flowrate mL/min	Initial pH	Limestone amount (kg)			
				28	56	84	112
Bekok Intake	10	1424	4.09	6.41	6.53	6.63	6.67
	20	712	4.09	6.49	6.69	6.87	6.98
	30	474	4.09	6.58	7.16	7.14	7.24
	60	196	4.09	6.87	7.18	7.23	7.33
Sembrong Lagoon	10	1424	3.27	5.86	6.24	6.34	6.49
	20	712	3.27	5.96	6.33	6.47	7.01
	30	474	3.27	6.48	6.79	7.03	7.15
	60	196	3.27	6.61	7.09	7.13	7.22

Table 2. Results of acidity reduction for Bekok Intake and Sembrong Lagoon

Source of Sample	Contact time (min)	pH	Acidity (mg/L as CaCO ₃)	% Reduction of acidity	% Increase in pH
Bekok Intake	0	4.09	73	0	0
	10	6.67	57	21.92	63.08
	20	6.98	35	52.05	70.66
	30	7.24	24	67.12	77.02
	60	7.33	17	76.71	79.22
Sembrong Lagoon	0	3.27	99	0	0
	10	6.49	60	39.39	98.47
	20	7.01	43	56.57	114.37
	30	7.15	21	78.79	118.65
	60	7.22	19	80.81	120.8

increased. Initial acidity of Bekok Intake of 73 mg/L as CaCO₃ was reduced to 17 mg/L as

3.2 Relationship between acidity and pH

The results of pH increase for Bekok Intake and Sembrong Lagoon in relation to acidity are given in Table 2. The profile of acidity reduction with respect to contact time is shown in Fig. 3. As anticipated, the acidity reduced significantly as the contact time

CaCO₃ after 60 minutes of contact with the limestone. For Sembrong Lagoon, the acidity reduced from 99 to 19 mg/L as CaCO₃ in 60 minutes.

As observed in the experiment, acidity of the raw water reduced with increasing pH level as illustrated in Fig. 4(a). It was due to the

dissolution of calcite, the principle component of limestone which can neutralise acidity and increase pH and alkalinity (Cravotta and Trahan, 1999). As shown in the figure, reduction of initially high acidity could significantly result in greater pH enhancement to reach near neutral pH. However, after pH about 6.5, reduction of acidity resulted in only small percentage of pH rise.

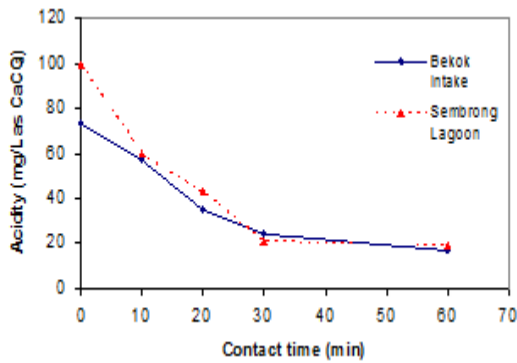


Figure 3. Acidity reduction of the raw water in relation to contact time

Fig. 4(b) demonstrates the percentage of acidity reduction in relation to percentage of pH increase. The higher the reduction of the acidity, the greater the increase in pH was. It was found that the percentage of pH increase for both raw water sources differed greatly depending on their initial pH and acidity.

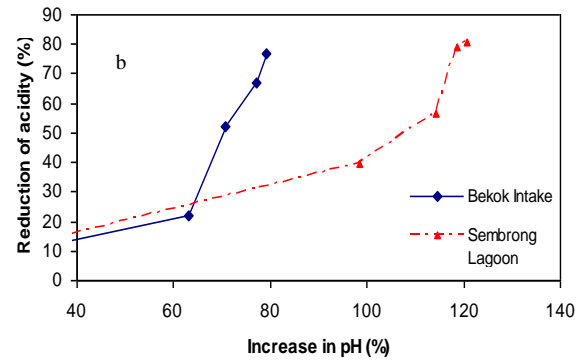
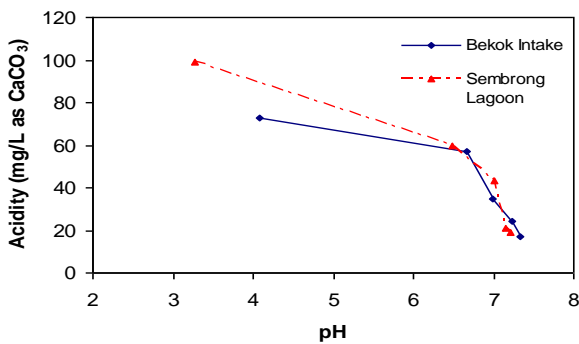


Figure 4. Reduction of acidity (a) Acidity in relation to pH (b) Percentage of acidity reduction

3.3 Effect of alkalinity on pH

The profile of alkalinity increase with respect to contact time is shown in Fig. 5(a). Two distinct stages of alkalinity increase can be observed. A greater increase of alkalinity generation was found to take place during the early stage. Alkalinity was then increased with increasing contact time. Fig. 5(b) meanwhile demonstrates the profile of pH rise with respect to alkalinity generation as a result of calcite dissolution and alkalinity production. When carbonic comes into contact with limestone, dissolution of limestone takes place (Appelo and Postma, 1993). pH increased as the alkalinity was being generated to reach near neutral level in 10 minutes of contact time. It was also found that the alkalinity was significantly increased relative to low pH rise after it reached near neutral pH, which was also evidenced by Palmer et al. (2012). It is because dissolution takes place until a saturated solution of calcite is achieved at which point equilibrium pH have been reached (Nuttall and Younger, 1999). The increase of alkalinity in an anoxic reactor was also influenced by several factors such as the characteristics of water (i.e. pH, concentration of iron and sulphate) and the type and size of the limestone used (Genty et al., 2012). It was found that finer limestone could initiate higher pH rise and that the calcite had greater neutralising potential compared to dolomite rock.

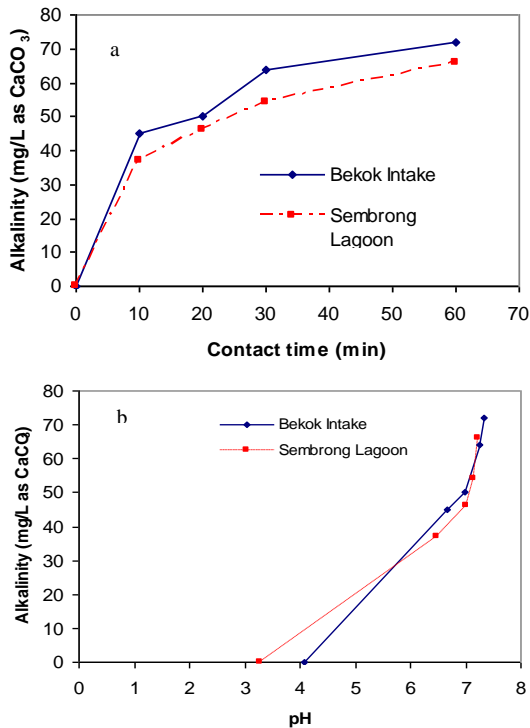


Figure 5. Factors affecting alkalinity generation of the raw water (a) contact time (b) pH

The increase of alkalinity in relation to acidity reduction is given in Fig. 6. As observed, there was a strong correlation between acidity reduction in generating alkalinity in the raw water as given by the R² values. Sample of Sembrong Lagoon indicated a greater acidity reduction for a particular increase of alkalinity than that of Bekok Intake raw water. This was probably due to low initial pH and higher acidity of Sembrong Lagoon raw water which tends to fasten the neutralisation rate as the dissolution of limestone is proportional to the activity of H⁺. This also corresponds with the mechanism of acidity removal and addition of alkalinity as given by the following reactions (Eq. 8).

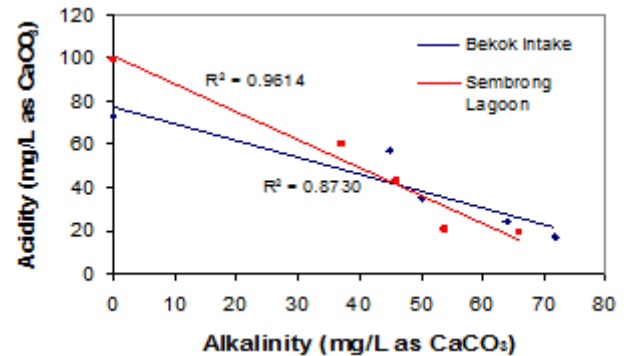
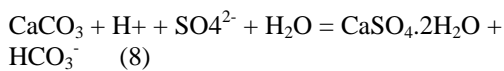


Figure 6. Acidity reduction in relation to alkalinity production

3.4 Metal removal

Initial iron concentrations of Bekok Intake and Sembrong Lagoon were found to be 0.433 mg/L and 0.571 mg/L, respectively, values of which are still below the standard limit of NWQS (Fig. 7). Despite this, the concentrations of iron for both samples were found reduced up to 69.52% and 71.28%, respectively even though oxygen levels within the reactor were very low. Iron was removed due to precipitation at increased pH (pH ~ 6) as a result of neutralisation reaction between limestone and the raw water. Iron precipitation occurred as the water was being rapidly neutralised, reflecting the fact that iron precipitation is greatly accelerated at pH > 4.5 (Singer and Stumm, 1970). In fact, for iron precipitation to occur under anoxic condition, neutralisation to pH ~ 6 is required (Santomartina and Webb, 2003). Excluding O₂ from contact with the acidic water in a closed, anoxic reactor minimises the potential for precipitation of Fe(OH)₃, which otherwise can result in armouring of the limestone surface reducing its efficiency (Ziemkiewicz et al., 1997; Cravotta and Trahan, 1999).

Initial aluminium concentration of Sembrong Lagoon raw water was recorded as 1.136 mg/L, which was higher than the recommended standard limit as shown in Fig. 8. The results indicated aluminium removal of 49.73 % up to 82.04 % due to precipitation of aluminium throughout the anoxic reactor. It can be seen that aluminium was removed as the pH were increased to near neutral level with respect to different contact time since aluminium precipitated best at pH 6-7 (Wei et al., 2005).

However, the outlet aluminium concentrations were slightly higher than the recommended standard of 0.5 mg/L for 10, 20 and 60 minutes contact time. Generally, significant removals of iron and aluminium with respect to low pH (pH 2-4) have also been found in other studies, e.g. Denholm et al, 2010; Clyde et al., 2010, when incorporating limestone-based treatment reactor for such waters.

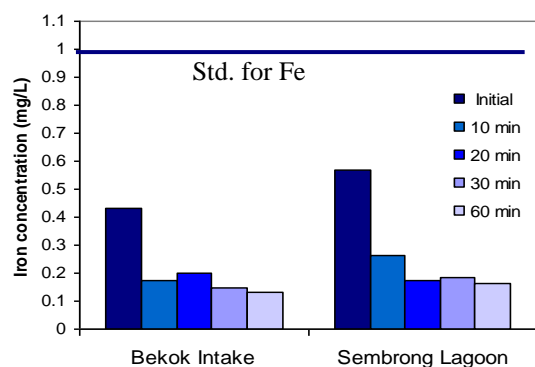


Figure 7. Iron removal with respect to different contact time

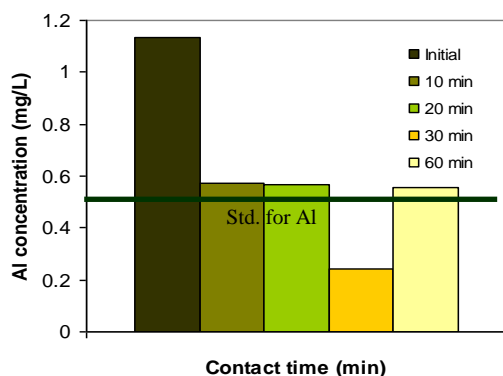


Figure 8. Aluminium removal with respect to different contact time

4. CONCLUSION

The results from the experiment indicated that the limestone-based closed reactor was capable of reducing acidic condition of the raw water at Bekok Intake and Sembrong Lagoon. The required amount of limestone to neutralise acidic water and the contact time needed were much depending on the initial pH and acidity. Initial pH ranging from 3.27-4.09

with acidity of 73-99 mg/L as CaCO_3 have been increased up to 6.49-6.67 as the water flowed through the closed limestone reactor in 10 minutes of contact with the limestone. pH was found to rapidly increase when first in contact with limestone since the dissolution of limestone is proportional to the acidity. Alkalinity increased significantly as the acidity reduced due to higher rate of limestone dissolution. The closed limestone reactor was also found to be effective in removing iron and aluminium (despite present at relatively low concentrations) even though oxygen levels were very low.

Performance of the closed limestone-based reactor was also compared with an open limestone channel. Details of the comparative analysis are presented in Kusin et al. (2013). Generally, the closed limestone reactor was capable of enhancing a higher pH rise compared to the open limestone channel for an equivalent contact time, and was particularly effective for generation of alkalinity. Despite slower precipitation rate in the closed reactor, formation of armouring could be minimised which is important for continuous dissolution of calcite and alkalinity production. Additionally, an open limestone channel may incur a higher cost of treatment per ton of acid water treated whilst indicating lower removal efficiency (Cravotta, 2010).

While it is understandable that clogging may limit the efficiency of the closed, anoxic limestone reactor, such a problem was presumably minimal in this case given the relatively low initial iron and aluminium contents. It is also worth noting that application of multi-steps treatment system would be a good practice incorporating that of the limestone-based closed reactor with other treatment approaches, e.g. open limestone channel, aerobic wetland and/or sulphate-reducing bacteria bioreactor. Successful trial of the closed limestone reactor may be adopted in field application, therefore giving alternative solution to acidic raw water. Further work will aim at evaluating the efficiency of such reactor containing elevated concentration of metals and longevity of treatment performance.

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