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Effect of anoxic transformation processes in municipal wastewater on pH and oxidation reduction potential

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Abstract
This paper presents findings of an investigation into the relationships between nitrate utilization rate (NUR), pH and oxidation reduction potential (ORP) during anoxic transformation processes in municipal wastewater. The study utilized municipal wastewater obtained from a wastewater treatment plant located within Shah Alam, Malaysia. Denitrification was observed by monitoring the change in nitrate and nitrite concentrations in a bench-scale reactor during anoxic transformation processes. It was found that the decrease in nitrate concentration was correlated with the increase of pH. The nitrite concentration gradually increased at the onset of the experiment and reached an optimum value of approximately 3 mg/L before it was reduced and removed from solution at approximately 5 hours of residence time. It was clear that the ORP reduced as the experiment progressed indicating a parallel relationship between ORP and denitrification. These results showed that pH increased while the ORP decreased during denitrification of municipal wastewater. It was established that the optimum pH and ORP for denitrification was from 6.5 to 8.5 and -40mV to -160mV respectively.

Keywords
Anoxic condition; Municipal wastewater; Oxidation reduction potential; pH

INTRODUCTION

The sewerage system is important to preserve public health, environment and the living standards of a community. Microbial processes generally occur in sewerage systems under three conditions (Nielsen *et al*., 1992) and they are elucidated in the following. In the beginning, degradation of fresh sewage occurs under aerobic condition. Subsequently, anoxic condition prevails when nitrate (NO_3) or nitrite (NO_2) is present in the absence of oxygen (O_2). The last condition occurs when degradation of sewage becomes anaerobic with harmful hydrogen sulphide (H_2S) being released when dissolved oxygen (DO) and NO_3/NO_2 are absent.

Anaerobic condition in sewage leads to the formation of hydrogen sulphide (H_2S) which is detrimental to the environment and human being. As such, studies on anoxic condition, particularly on nitrate/nitrite utilization are vital since it is capable of suppressing anaerobic conditions, thus prevents the formation of hydrogen sulphide.

Studies on anoxic transformation processes under sewer conditions had been conducted by Abdul-Talib *et al.* (2002). A model enabling nitrate dosing rates into sewers, based on observed nitrate and nitrite utilization rates in sewers had been proposed by Abdul-Talib *et al.* (2005).

Investigations on anoxic oxidation of sulphide had been reported by Nielsen (2004) and Yang (2005). Much of these investigations focused on transformations of sulphur and nitrogen compounds in municipal wastewater under sewer conditions. It has been established that sulphide can undergo biological anoxic oxidation resulting in elemental sulphur and intermediates such as thiosuphate and sulphite.

While reports relating pH and oxidation reduction potential (ORP) to anoxic transformation processes of municipal wastewater in sequencing batch reactors are available (Chang and Hao, 1995; Lee *et al.,* 2001; Akm and Ugurlu, 2005) very few reports are available on relationship between denitrification, pH and ORP under sewer conditions. These relationships are important as they could affect the bio-chemical processes which in turn affect denitrification rates in sewers. The main objective of this study was to investigate the relationships between NUR, pH and ORP during anoxic processes in Malaysian municipal wastewater.

MATERIALS AND METHODS

Municipal wastewater samples were taken from a wastewater treatment plant in Section 23, Shah Alam, Malaysia. The treatment plant received wastewater from residential and commercial premises. The study was conducted using two/three batch reactors. Detail of the reactor is shown in Figure 1. The volume of the reactor is approximately 2 litres. All reactors were fitted with pH and Oxidation Reduction Potential (ORP) electrodes.

Two experimental setups were used in this study and their schematic diagrams are presented in Figure 2. The first experimental setup was used to monitor pH and ORP while the second setup was used to investigate the effect of varying pH on the denitrification process. The reactors were filled with 1.5L of wastewater sample each and magnetic stirrer for each reactor was turned on. Wastewater temperature in the reactors was kept constant at 25°C via the circulating water throughout the coil from the water bath.

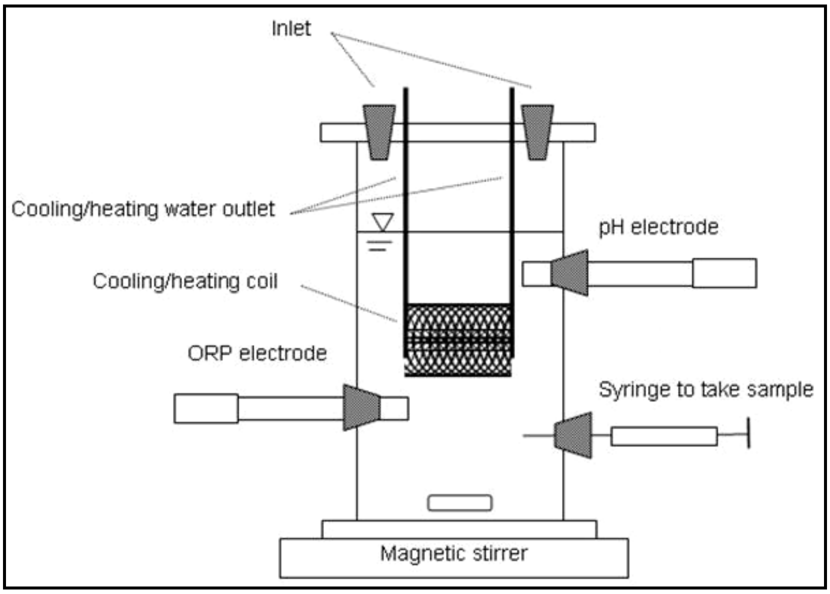

Figure 1. Batch reactor.

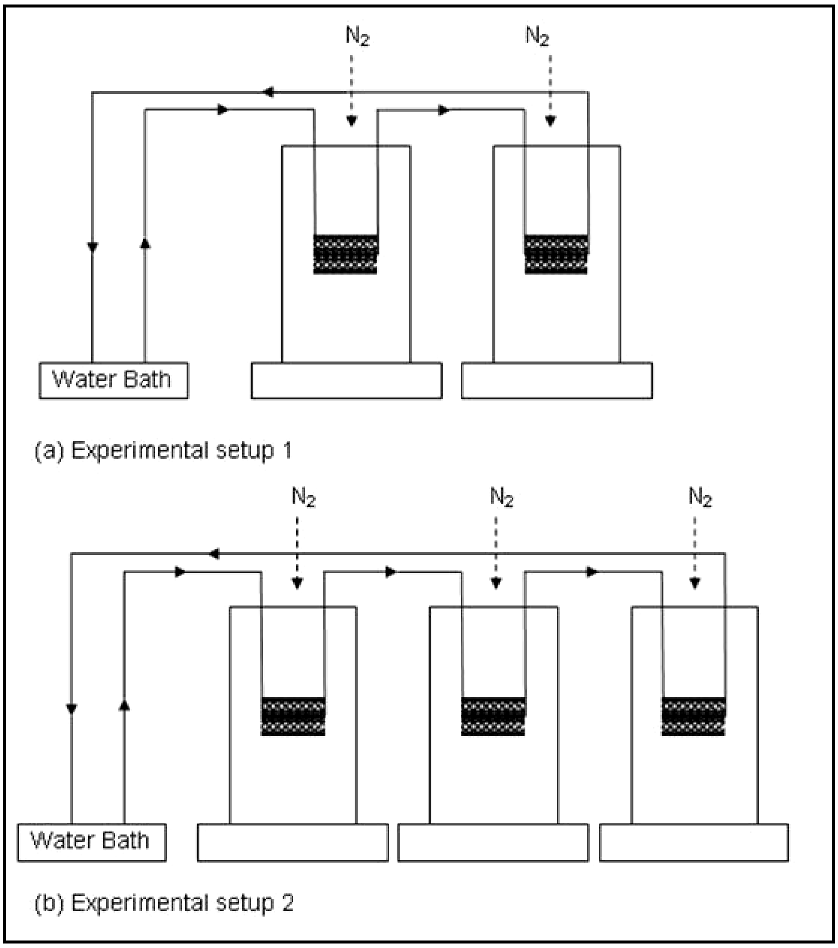

Figure 2. Experimental setups 1 and 2.

Nitrogen gas was transmitted into the reactors for 5 minutes in order to purge dissolved oxygen in the wastewater. Sodium acetate and sodium nitrate were added into the reactors to create anoxic conditions. Once nitrogen gas supply was stopped, the first samples were taken and the pH and ORP were measured. Subsequently samples were taken every 20 minutes. pH and ORP readings were recorded at the same time interval. For the second experimental setup, the pH value was maintained constant by addition of HCL or NaOH throughout experiment.

Chemical oxygen demand (COD) of the wastewater samples was measured via American Public Health Association (APHA) Standard Method (1992). Nitrate and nitrite concentrations were determined using an ion chromatograph unit (Metrohm 790 IC). The unit was equipped with 5µm particle size column packing of polyvinyl alcohol with quaternary ammonium groups and required an effluent to be used as a carrier. The effluent consisted of 3.2 mmol/L NaCO3 and 1.0 mmol/L NaHCO3. The flow rate adopted was 0.7 mL/min. The unit was calibrated using a standard with a concentration of 6 mg/L for nitrate and nitrite.

RESULTS AND DISCUSSION

Effect of denitrification on pH and ORP

Figures 3 and 4 show the effects of denitrification on pH and ORP respectively. It is evident the pH increases from approximately 7.5 to a plateau of 7.9 during the denitrification process.

This effect is most likely attributed to the anoxic process in which nitrate is used as electron acceptor to form nitrogen. The following equation indicates this process:

Organics (with C, H and O elements) + NO_3^- + H^+ $\rightarrow$ N_2 + CO_2 + H_2O (1)

The equation shows that hydrogen ion is used, thus increasing the relative OH^- concentration in the solution leading to the observed increase in pH.

The opposite, however, was observed for ORP in which ORP gradually reduces from about -10 mV to -180 mV after 8 hours of denitrification process. This reduction is expected due to the absence of oxygen coupled with mass substrate consumption which induce reduction reactions in the process. In this case, it is theorized that there is existence of two types of organic substrates, namely, fast and slow hydrolyzable organic substrates (Vollertsen and Hvitved-Jacobsen, 2002).

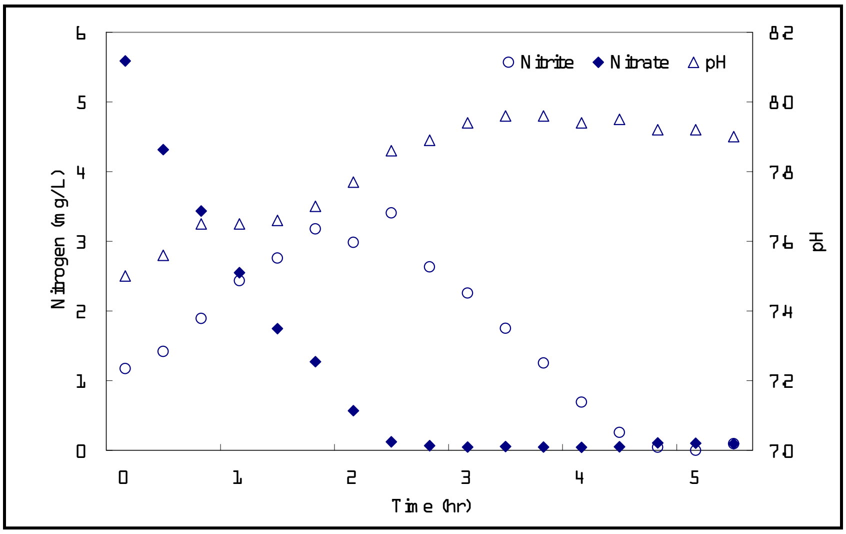

Figure 3. Effect of denitrification on pH

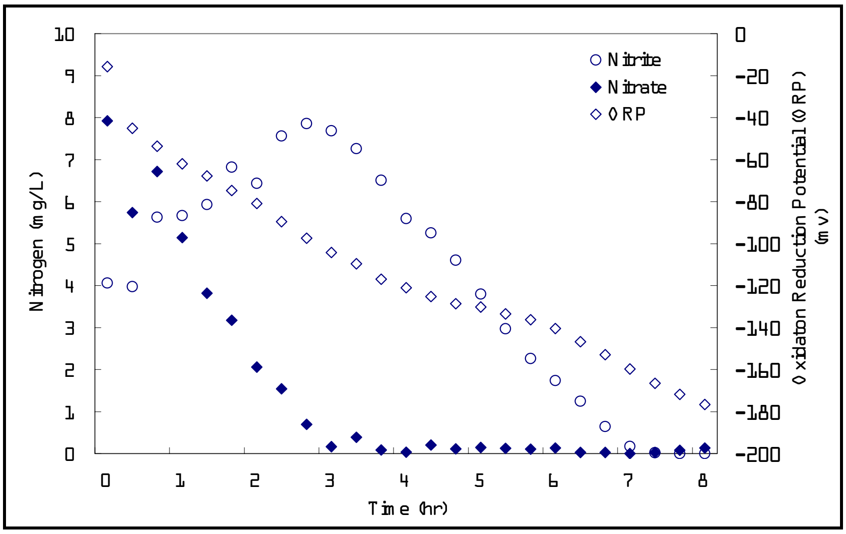

Figure 4. Effect of denitrification on ORP

The difference in redox potential between the fast hydrolyzable organic substrate (smaller substrate) and nitrate is more as compared to slow hydrolyzable organic substrate (larger substrate) and nitrate. As such, at the start of substrate degradation, most of the fast hydrolyzable substrates are being degraded rapidly resulting in a relatively less negative ORP. Eventually, all of these fast hydrolyzable substrates are degraded and this marks the start of slow hydrolyzable substrate degradation which results in further decrease in ORP.

The nitrite concentration gradually increased at the onset of the experiment and reached an optimum value of approximately 3 mg/L before it was reduced and removed from solution at approximately 5 hours of residence time.

Effect of pH on nitrate utilization rate

The nitrate utilization rate (NUR) was calculated as an indicator for measurement of the denitrification process. Concentration of nitrogen was determined by Equations 2 and 3:

For nitrate-nitrogen;

$$\left[NO_3^- - N\right] = \frac{\left[NO_3^-\right]}{M\left(NO_3^-\right)/M(N)} \quad (2)$$

For nitrite-nitrogen;

$$\left[NO_2^- - N\right] = \frac{\left[NO_2^-\right]}{M\left(NO_2^-\right)/M(N)} \quad (3)$$

where *M* is the molar weight of nitrogen.

Figure 5 shows the effect of pH on NUR. The curve is clearly bell-shaped with an optimum pH range for NUR (denitrification) from 6.5 to 8.5. Figure 6 shows the effect of pH on the rate of change in ORP.

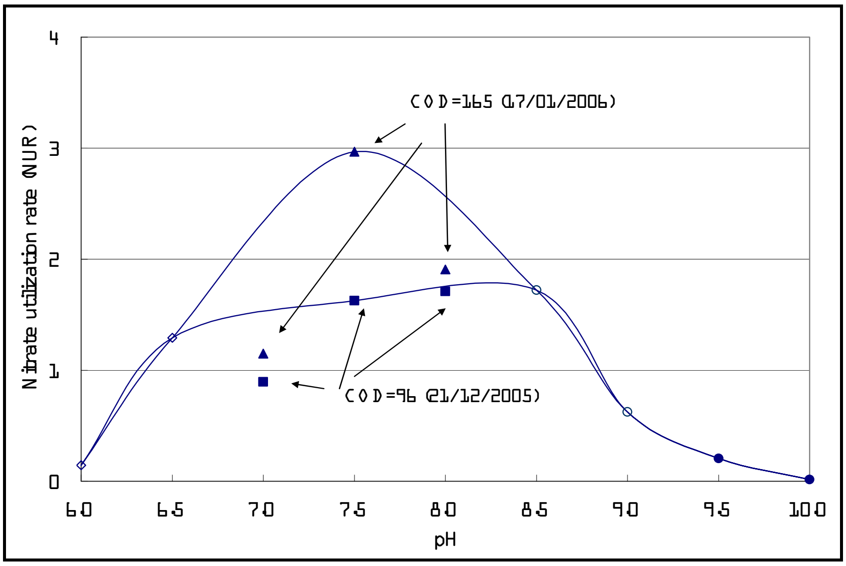

Figure 5. Effect of pH on NUR.

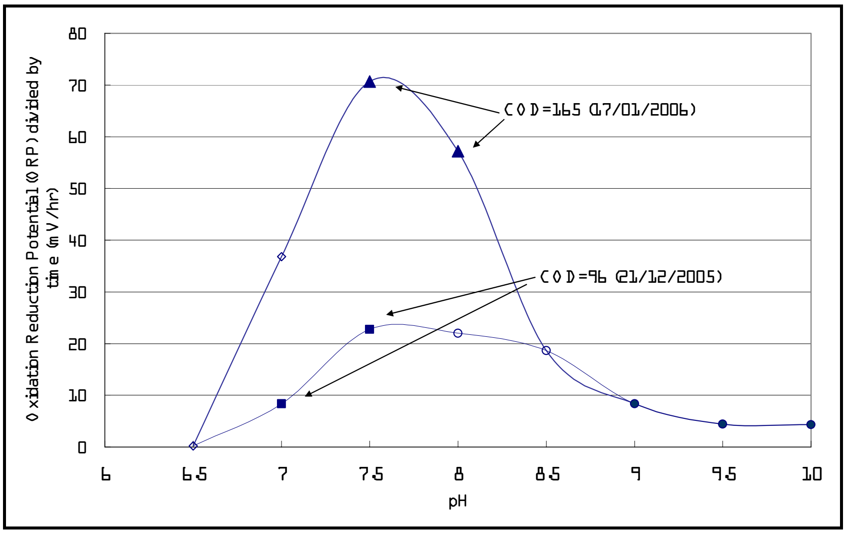

Figure 6. Effect of pH on Rate of change in ORP

Similarly, the curve is bell-shaped with optimum pH range from 7 to 8.5 As such, it is deemed that the microbes which are present in the wastewater are biologically active in the optimum pH range of 6.5 to 8. It was also observed that for wastewater with higher COD value, the recorded NUR and ORP are higher. This is due to the presence of higher quantity of substrates in wastewater with higher COD value.

CONCLUSIONS

The relationships between nitrate utilization rate (NUR), pH and oxidation reduction potential (ORP) during anoxic processes in wastewater were investigated in this study. The pH increased while the ORP decreased during denitrification of the municipal wastewater. It was determined that the optimum pH and ORP for denitrification was from 6.5 to 8.5 and -40mV to -160mV respectively.

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