Enhanced heavy metals removal without phosphorus loss from anaerobically digested sewage sludge
A. Ito, K. Takahashi, J. Aizawa and T. Umita

ABSTRACT
Heavy metals removal without phosphorus loss from anaerobically digested sewage sludge was investigated by conducting batch experiments using hydrogen peroxide and/or iron sulphate under acidified conditions at pH 3. The addition of hydrogen peroxide to the sludge improved the elution efficiencies of As, Cd, Cu and Zn with phosphorus loss from the sludge. The optimum initial concentrations of hydrogen peroxide were, respectively, 0.1% for As, Cd, Mn and Zn and 0.5% for Cu and Ni. The combined process of 0.1% hydrogen peroxide and 1 g Fe/L ferric sulphate enhanced the initial elution rate of Cu and Cr compared to the addition of either ferric sulphate or hydrogen peroxide, indicating that oxidants stronger than hydrogen peroxide were produced in the sludge. Furthermore, the combined process immobilised phosphorus in the sludge due to co-precipitation with ferric hydroxide or precipitation as ferric phosphate. It was concluded that there is a possibility that the combined process could remove heavy metals effectively without phosphorus loss from anaerobically digested sewage sludge.

Key words | ferric sulphate, heavy metals removal, hydrogen peroxide, phosphorus immobilisation, sewage sludge

INTRODUCTION
Recovery of biogas such as methane from sewage sludge through anaerobic digestion has become widespread because biogas is regarded as carbon-neutral energy. Owing to the existence of nutrients and organic matters, the use of the digested sludge as a raw material of fertiliser or soil conditioner is a reasonable recycling system. Especially, phosphorus present in the sludge should be beneficially reused because of a potential depletion risk. However, toxic substances such as heavy metals and endocrine disrupting chemicals in sewage are concentrated into the sludge through sewage treatment processes (Oliver & Cosgrove 1974; Stephenson & Lester 1987) and the subsequent anaerobic digestion of the sludge (Giger et al. 1984; PWRI Japanese Ministry of Construction 1993). Land application of the sludge without reducing the contents of toxic substances could potentially cause environmental pollution. Therefore, it is necessary to develop an efficient process to remove toxic substances without phosphorus loss from the sludge.

It has been reported that chemical or biological acidification of sewage sludge eluted heavy metals from the sludge and the elution efficiencies of heavy metals were increased with a decrease in the pH value of the sludge (Oliver & Carey 1976; Jenkins et al. 1981; Blais et al. 1992; PWRI Japanese Ministry of Construction, 1994; Kitada et al. 2001). Ito et al. (2000) showed that the addition of approximately 1 g Fe/L ferric sulphate (Fe₂(SO₄)₃) enhanced the elution efficiencies of heavy metals present as sulphide forms in anaerobically digested sewage sludge. Yoshizaki & Tomida (2000) proposed that the application of 2% hydrogen peroxide (H₂O₂) improved the elution of Cu bound organically in the sludge. On the other hand, it has been reported that the application of the Fenton reaction process for sewage sludge can improve the
dewaterability (Mustranta & Viikari 1993) and releases heavy metals from the sludge into water phase (Neyens et al. 2002; Dewil et al. 2007). Therefore, a combination of iron sulphate and H2O2 has the possibility of enhancing heavy metals elution from the sludge and preventing phosphorus loss from the sludge due to co-precipitation with ferric hydroxide (Fe(OH)3) or precipitation as ferric phosphate (FePO4). However, no comparison between H2O2, ferrous or ferric ion and their combination has been conducted as yet for simultaneous heavy metals removal and phosphorus immobilisation.

The purpose of this study was to clarify the effectiveness of iron sulphate and H2O2 combination on enhanced removal of heavy metals from anaerobically digested sludge and immobilisation of phosphorus into the sludge.

**METHODS**

The anaerobically digested sewage sludge used in this study was taken in the Tonan sewage treatment plant in Iwate Prefecture, Japan, where sewage is treated by a conventional activated sludge process, and then preserved in the refrigerator at 4°C in our laboratory. Table 1 details the heavy metals and phosphorus contents of the sludge. Heavy metals and phosphorus were separately analysed with an inductively coupled plasma mass spectrometer (Yokogawa Analytical Systems, HP-4500) and a spectrophotometer (Shimadzu, UV-1600) after pretreatment (Japan Sewage Works Association 1997).

The sludge concentrated by centrifugation was distributed into 2 L shaking flasks and was acidified to the pH value of 3 with dilute sulphuric acid, and then different amounts of H2O2 were added to the acidified sludges to clarify the effect of H2O2 concentrations on heavy metals elution from the sludge under acidic conditions. The initial concentrations of H2O2 were, respectively, 0.1, 0.5, 1 and 2%, and the control without H2O2 addition was also tested. In addition to the conditions described above, ferrous sulphate (FeSO4) or Fe2(SO4)3 solution was added to the sludge before addition of H2O2, and controls without H2O2 addition were respectively tested as well. The concentrations of H2O2 and iron added were, respectively, 0.1% and 1 g/L in the sludge.

In all conditions the sludge concentration was adjusted to 20 g dry solid/L, and the flasks containing the sludge were kept mixing with a shaker at 120 rpm and 25°C. The sludge pH and ORP were measured with a pH meter (Horiba, F-12) and an ORP meter (TOA, HM-5S), respectively. Part of the sludge in the flasks was taken in plastic tubes and was centrifuged at 10,000 rpm. The supernatant was filtered using an Advantec membrane filter with a pore size of 1 μm for dissolved heavy metals and phosphorus measurements as described above. Ferrous ion in the filtrate was analysed by the phenanthroline method using a spectrophotometer (Japan Sewage Works Association 1997).

**RESULTS AND DISCUSSION**

**Effect of initial hydrogen peroxide concentrations on heavy metals elution from sludge**

Figure 1 shows the variations of elution efficiencies of (a) Cd, (b) Cu, (c) Mn and (d) Zn from the sludge with time at different initial H2O2 concentrations. The initial concentration represents the value before acidification of the sludge without the addition of H2O2. In the control, Mn was rapidly eluted from the sludge and Cd and Zn was gradually eluted, whereas Cu elution was very slight. Addition of H2O2 accelerated the initial elution rate of Cd, Cu and Zn and resulted in higher elution efficiencies after 24 hours than with no addition, although the elution rate of Cu was slower than those of other metals.

Figure 2 shows the maximum elution efficiencies of heavy metals from the sludge at different initial H2O2 concentrations. The maximum elution efficiencies were higher than 95% for Cd, Mn and Zn, 88% for As, 76% for Cu, 73% for Ni and 5% for Cr. It was found that the optimum H2O2 concentrations were 0.1% for As, Cd, Mn and Zn and 0.5% for Cu and Ni, and were much lower than the optimum value (2%) reported by Yoshizaki & Tomida (2000).

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<th>Metals contents of sludge used in this study</th>
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*Units are mg/kg dry solid for As, Cd, Cu, Mn, Ni and Zn, and g/kg dry solid for Fe and P.*
Figure 3 shows the variations of (a) ferrous ion concentration and (b) ORP value with time at different initial H$_2$O$_2$ concentrations. The initial ORP values were measured immediately after the start of the experiment. When no H$_2$O$_2$ was added to the sludge, ferrous ion concentration reached approximately 240 mg/L and then gradually decreased. This increase in the concentration means that acidification of the sludge resulted in the elution of ferrous iron from the sludge. The addition of H$_2$O$_2$ inhibited a rise in ferrous ion concentrations in the first few
hours. This will be due to rapid oxidation of ferrous ion eluted from the sludge by H$_2$O$_2$. At H$_2$O$_2$ concentration of 0.1%, ferrous ion concentration was gradually increased after 12 hours. On the other hand, additions of H$_2$O$_2$ significantly elevated the ORP values compared to no addition. At an H$_2$O$_2$ concentration of 0.1%, the ORP value was once increased and then was decreased after 6 hours. In general, H$_2$O$_2$ reacts with ferrous ion or ferric one to produce hydroxyl radical (OH$^-$) or hydroperoxyl radical (HO$_2^-$) under acidic condition (Neyens & Baeyens 2003):

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{OH}^- + \text{Fe}^{3+}$$  \hspace{1cm} (1)

$$\text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{HO}_2^- + \text{H}^+ + \text{Fe}^{2+}$$  \hspace{1cm} (2)

It is likely that some oxidant derived from Equations (1) and (2) was produced in the sludge and that the oxidant and residual H$_2$O$_2$ were consumed to oxidise the reduced substances, such as organic matters, in the sludge when the H$_2$O$_2$ concentration was 0.1%. However, no decreases in the ORP values was observed at concentrations higher than 0.1%. This result, and no increase in ferrous ion concentrations, would suggest that H$_2$O$_2$ remains in the sludge when added at higher concentrations.

In practice, the amount of H$_2$O$_2$ added should be minimised from the viewpoint of economic aspect and subsequent sludge process. Therefore, the effect of a combination of H$_2$O$_2$ and iron sulphate was investigated to improve elution of Cu and Cr and immobilise phosphorus under 0.1% H$_2$O$_2$ concentration.

**Effect of combination of iron sulphate and hydrogen peroxide**

Figure 4 shows the variations of the elution efficiencies of (a) Cu and (b) Cr from the sludge with time. In the control and addition of only FeSO$_4$, the elution efficiencies of Cu and Cr were less than 5%. Ferric sulphate played a role in improving the elution of Cu by oxidising the sulphide form of Cu in the sludge as previously reported (Ito et al. 2000) as well as Cr. The addition of both Fe$_2$(SO$_4$)$_3$ and H$_2$O$_2$ accelerated the initial rate of Cu elution compared to that of only Fe$_2$(SO$_4$)$_3$ or H$_2$O$_2$. However, addition of both FeSO$_4$ and H$_2$O$_2$ decreased the initial elution rate compared to that of only H$_2$O$_2$ under the conditions of this study.

Figure 5 shows the variations of (a) ferrous ion concentration and (b) ORP value with time. In all conditions, the ferrous ion concentration before acidification and iron addition was 100 mg/L. In the control, the ferrous ion concentration was once increased to 150 mg/l and then was gradually decreased to 70 mg/L due to the oxidation of ferrous ion with dissolved oxygen. The addition of Fe$_2$(SO$_4$)$_3$ gave rise to higher ferrous ion concentrations than the control after 12 hours. This is due to a reduction of ferric iron added as an oxidising reagent. Additions of H$_2$O$_2$ decreased ferrous ion concentrations as described previously. Especially, most of ferrous ion added was oxidised by H$_2$O$_2$ in the first hour. On the other hand, the ORP value was remarkably increased to 750 mV immediately after the addition of both Fe$_2$(SO$_4$)$_3$ and H$_2$O$_2$. This result would suggest that strongly oxidative substances derived from Fenton and/or Fenton-like reactions as described previously were generated, resulting in higher initial elution.
rates of Cu and Cr. However, the ORP value was rapidly
decreased to 630 mV after 1 hour and its variation was
different from the addition of only H₂O₂. Further enhance-
ment of Cu and Cr elution would be accomplished if high
ORP values could be kept by changing operational
parameters such as iron concentration. The addition of
both FeSO₄ and H₂O₂ resulted in lower ORP values than
that of only H₂O₂ or both Fe₂(SO₄)₃ and H₂O₂. It appeared
that H₂O₂ was consumed by oxidising high concentrations
of added ferrous ion and further the resulting hydroxyl
radicals was also immediately consumed by oxidising
residual ferrous ion (Du et al. 2006).

Figure 6 shows the variation of elution efficiency of phosphorus from the sludge with time. Acidification of the
sludge (control) eluted phosphorus as well as heavy metals.
The addition of H₂O₂ similarly resulted in the elution of phosphorus, although the efficiency was low compared to
the control. However, the additions of H₂O₂ and either
Fe₂(SO₄)₃ or FeSO₄ decreased elution efficiency of phosphorus to less than 5% as well as that of only Fe₃(SO₄)₅.
This is due to co-precipitation of Fe(OH)₃ and phosphorus
compound eluted from the sludge or precipitation of FePO₄.
From these results, it was found that the addition of both
Fe₂(SO₄)₃ and H₂O₂ could immobilise phosphorus into the
sludge in addition to enhanced Cu removal.

CONCLUSIONS

In this study, the effectiveness of iron sulphate and
hydrogen peroxide combination on enhanced heavy metals
removal and phosphorus immobilisation for anaerobically
digested sewage sludge was investigated. The optimum
initial concentrations of hydrogen peroxide were, respec-
tively, 0.1% for As, Cd, Mn and Zn and 0.5% for Cu and Ni.
The combined process of 0.1% hydrogen peroxide and 1 g
Fe/L ferric sulphate enhanced the initial elution rate of
Cu and Cr compared to the addition of either ferric sulphate
or hydrogen peroxide. Moreover, the combined process
immobilised phosphorus in the sludge. It was concluded
that there is a possibility that heavy metals could be
effectively removed without phosphorus loss from anaero-
bically digested sewage sludge by the combined process of
ferric sulphate and hydrogen peroxide.

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