

Enhancing the use of waste activated sludge as bio-fuel through selectively reducing its heavy metal content

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Abstract

Power plant or cement kiln co-incineration are important disposal routes for the large amounts of waste activated sludge (WAS) which are generated annually. The presence of significant amounts of heavy metals in the sludge however poses serious problems since they are partly emitted with the flue gases (and collected in the flue gas dedusting) and partly incorporated in the ashes of the incinerator: in both cases, the disposal or reuse of the fly ash and bottom ashes can be jeopardized since subsequent leaching in landfill disposal can occur, or their “pozzolanic” incorporation in cement cannot be applied. The present paper studies some physicochemical methods for reducing the heavy metal content of WAS. The used techniques include acid and alkaline thermal hydrolysis and Fenton’s peroxidation. By degrading the extracellular polymeric substances, binding sites for a large amount of heavy metals, the latter are released into the sludge water. The behaviour of several heavy metals (Cd, Cr, Cu, Hg, Pb, Ni, Zn) was assessed in laboratory tests. Results of these show a significant reduction of most heavy metals.

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1. Introduction

Heavy metals are present in urban wastewater as a result of domestic, road run-off and industrial inputs to the urban wastewater collection system [1]. Industrial contributions are the primary source of heavy metals in urban wastewater and represent up to 50% of the total metal loads in sewage sludge [1]. The pollution usually derives from electroplating, plastics manufacturing, fertilizer, pigment, mining, and metallurgical processes [2]. Common contaminants of industrial wastewater are zinc, copper, chromium, nickel, cadmium and lead. Domestic sources are mainly associated with leaching from plumbing materials (Cu and Pb), gutters and roofs (Cu and Zn) and galvanized materials, the use of detergents and washing powders containing Cd, Cu and Zn, and the use of body care products containing Zn. Tap water itself also contains considerable amounts of metals [1,3,4].

Many studies have shown that an activated sludge process removes substantial quantities of metals from influent wastew-

ater [5,6]. Insoluble metals or metals adsorbed onto settling particles are removed during primary settling [7], finely suspended or dissolved metals are adsorbed on the sludge flocs during secondary treatment and thus removed during secondary settling [7–9].

The considerable amounts of heavy metals in sewage sludge pose however major constraints on the sludge disposal. Many countries have indeed imposed legal restrictions concerning the heavy metal content when using sludge for land application (e.g. as fertilizer or soil conditioner) in order to prevent heavy metal accumulation in the cultivated soils.

When choosing co-incineration as disposal route, the release of heavy metals to the environment is one of the major problems, since their volatility is enhanced at high temperatures. The formation and subsequent emission of particles enriched with toxic metals which can be inhaled as well as gaseous emissions during incineration processes have indeed been the subject of several studies [10,11]. Moreover, the ashes generated during combustion contain significant amounts of heavy metals. Since sludge has a high mineral content (usually about 40–50% on a dry solids basis) large quantities of ashes are generated [12]. From the perspective of re-utilisation or even towards landfill disposal, the

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environmental compatibility of these residues must be guaranteed, notably their heavy metal content and their resistance to leaching.

Heavy metals are primarily adsorbed onto sludge flocs by rapid ion-exchange mechanisms [13]. The extracellular polymeric substances (EPS, also referred to as biopolymers) which are present in sludge flocs in considerable concentrations, act as ion exchangers and offer both anionic and cationic binding places. The inclusion of heavy metals in the intracellular structures of the sludge micro-organisms is of limited importance only [8].

Several authors have reported both chemical and biological methods for reducing the heavy metal content in sludge. The chemical methods are mostly based on the use of inorganic or organic acids to solubilise the metals [8,14,15]. Also chelating agents as EDTA [16] or inorganic chemicals like FeCl_3 [17] are used. Biological methods include the solubilisation of the metals by the metabolic action of micro-organisms [18]. The removal rates of heavy metals using the above methods are however rather low.

Based on previous findings, some advanced sludge treatment (AST) techniques seemed to be usable for reducing the heavy metal content of waste activated sludge. These methods were originally developed for enhancing the mechanical dewaterability of the sludge and include thermo-chemical processes (i.e. acid and alkaline thermal hydrolysis) and chemical oxidation using hydrogen peroxide [19–21]. It was shown [22] that they selectively degrade EPS structures within the sludge floc. Hence, the heavy metals which are bound on these EPS will be released in the sludge water. Moreover, the solubilisation of metals is further enhanced through the change of physicochemical properties like pH and ionic strength.

Initial experiments by the present authors confirmed that the heavy metals of the sludge were affected by the selected techniques of advanced sludge treatment. Therefore, the research was extended to multiple experiments, and by varying the reaction conditions during treatment, i.e. the pH and the dosage of the chemicals. The influence on the release of heavy metals was hence studied under a wide variety of conditions. This paper reports on these extensive laboratory-experiments using thermal hydrolysis and Fenton's peroxidation for reducing the heavy metal content of sewage sludge.

2. Experimental lay-out and procedures

2.1. Sludge characteristics

Activated sludge samples, taken from the full-scale wastewater treatment plant of Deurne-Schijnpooort (located in Flanders, Belgium), were used in the experiments. All experiments were repeated three times, and average results are further reported.

The mineral fraction of the raw sludge was 30.2%. The sludge samples were collected and settled in the laboratory for about 4 h. The supernatant was thereafter poured off. The resulting dry solids content was about 3 wt.%.

2.2. Hydrolysis

Hydrolysis (acid or alkaline) of the sludge implies a treatment at moderate to high temperature. For the experiments, the sludge was treated in a batch reactor, built as a pressure vessel with an electrically heated shell. The temperature of the sludge mixture was kept constant during treatment. Samples of 300 ml of sludge were batch treated.

For the acid thermal hydrolysis, sulphuric acid (from a solution containing 1.75 kg $\text{H}_2\text{SO}_4/\text{l}$) was gradually added to the sludge in the reactor until the desired pH (i.e. 3 or 5) was reached. The reactor was thereafter closed and the sludge mixture inside was heated to a temperature of 120 °C. Due to the temperature rise, the pressure inside the reactor increased to approximately 3 bar, also the pressure set for the pressure relief valve. The temperature was kept constant for 1 h, during which the reaction took place. After this period, the reactor was opened and the mixture was left to cool to ambient temperature. The sludge was subsequently neutralised by adding $\text{Ca}(\text{OH})_2$ (from a suspension containing 50 g $\text{Ca}(\text{OH})_2/\text{l}$).

For the alkaline thermal hydrolysis, $\text{Ca}(\text{OH})_2$ (from a suspension containing 50 g $\text{Ca}(\text{OH})_2/\text{l}$) was gradually added to the sludge in the reactor until the desired pH (i.e. 9 or 11) was reached. The reactor was thereafter closed and the sludge mixture inside was heated to a temperature of 100 °C. Due to the temperature rise, the pressure inside the reactor increased to approximately 3 bar. The temperature was kept constant for 1 h, during which the reaction took place. After this period, the reactor was opened and the mixture was left to cool to ambient temperature. The sludge was subsequently neutralised by adding sulphuric acid (from a solution containing 1.75 kg $\text{H}_2\text{SO}_4/\text{l}$).

2.3. Fenton's peroxidation

The Fenton peroxidation is carried out in a reactor at ambient temperature and pressure. About 500 ml of sludge was introduced into the reactor. Firstly, the pH was adjusted to the desired value (i.e. 3, 5, 7) using H_2SO_4 . Fe^{2+} from FeSO_4 (1.5 g $\text{FeSO}_4/\text{kg DS}$) was added as a catalyst. The H_2O_2 (from a solution containing 390 g/l) was subsequently added. During treatment the sludge mixture was gently stirred (at 200 rpm). The oxidation releases reaction gases (mostly CO_2 , H_2O and small organic molecules) and the time of reaction is considered as the time until the gas production is stopped. This time is about 60 min (depending on the DS-content of the sludge and the amount of H_2O_2 added).

After reaction, the sludge mixture was neutralised using $\text{Ca}(\text{OH})_2$.

2.4. Sludge dewatering and heavy metal analysis

Since the main target of this study is to improve the release of heavy metals from WAS during sludge dewatering, this mechanism was studied by dewatering the treated and blank sludge on lab scale.

After the reaction and neutralisation of the treated sludge, an appropriate amount of polyelectrolyte (Ciba® ZETAG 7878

FS40) was added and the sludge was subsequently dewatered using a vacuum-assisted Buchner filtration at a vacuum pressure of 0.5 bar, assessed for a 100 ml sample during a set time of 5 min. The filter cake was removed from the filter paper and analysed for heavy metals. Cr, Cu, Ni, Zn, Cd and Pb were measured by ICP-OES. Hg was determined by cold vapour AAS. Prior to the analysis, the sludge samples were submitted to a high pressure microwave destruction method.

3. Results and discussion

3.1. Generalities

Heavy metals are bound in the sludge flocs by different means [13,23]: exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter and residual. The exchangeable fraction is likely to be affected by changes in water ionic composition, as well as by sorption and desorption processes. The carbonate fraction is sensitive to changes in pH, while the reducible fraction, which consists of iron and manganese oxides, is thermodynamically unstable under anoxic conditions. The organic fraction can be degraded, leading to a release of soluble metals in an oxidising environment. The residual fraction, containing mainly primary and secondary minerals, holds metals within its crystal structure. The metals that are associated with the residual fraction are normally not expected to dissolve.

Obviously the bond strength of metals depends on the nature of the metal. With respect hereto reference is frequently made to the Irving–Williams series [24], which defines the relative orders of metal–organic chelate bond strengths. This series orders the metal–organic bond strengths as follows: $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd}$. The greater the metal–organic bond strength, the less soluble is the complex.

3.2. Hydrolysis

Acid as well as alkaline thermal hydrolysis significantly reduce the concentration of most heavy metals in the sludge cake as is shown in Table 1.

Dewatering the untreated sludge has no statistical significant effect on the heavy metal content (on a DS basis). This obser-

vation confirms the strong bond strengths of the metals in the sludge flocs.

Using acid thermal hydrolysis, the highest removal rates are observed for Ni and Zn; Cd and Cr are moderately released; for Cu, Pb and Hg only a small or no reduction at all is observed. A lower pH enhances the release for all metals.

These results follow roughly the order of the Irving–Williams series explained above: the acid hydrolysis succeeds in overcoming the weaker metal–organic chelate bond strengths of Ni, Zn and Cd, but fails to break the stronger Cu–organic complex. Cr is generally considered to be present in the sludge as an inorganic precipitate or in a weakly chelated form [25]. These forms are known to react and therefore attain solubilisation equilibrium much more rapidly than strongly complexed organic–metal chelates.

At lower pH a competition between metals and protons for binding sites on the sludge will moreover start occurring. Heavy metals which are absorbed on the sludge flocs are hereby exchanged by protons [14]. A decrease in pH also dissolves metal–carbonate complexes and hence releases the metals as free ions into the water phase [26].

It was seen that the treatment did not solubilise Pb and Hg from the sludge. Oliver and Cosgrove [7] however reported a solubilisation of 40% of lead from anaerobically digested sludge when decreasing the pH to 3 using hydrochloric acid. The very low solubilisation in the present study is therefore explained by the low solubility of lead sulphate ($K_S(\text{PbSO}_4) = 1.6 \times 10^{-8}$) and mercury sulphate ($K_S(\text{Hg}_2\text{SO}_4) = 7.4 \times 10^{-7}$) which is formed by the addition of sulphuric acid [17]. All other metal sulphates are indeed soluble.

The elevated temperature increases the rate of reaction since the diffusivity of ions increases with increasing temperature [14].

On the contrary, alkaline thermal hydrolysis effectively removes the major part of Cu and Pb from the sludge, although its removal capacity for the other metals is lower than when using acid thermal hydrolysis. It is also observed that a higher value of the pH corresponds with a higher release for all metals.

This is in line with previous findings of Hsiao and Lo [27], who demonstrated that the higher affinity for organics a metal has in unlimed sludge, the more unstable this metal is in

Table 1

Concentration of heavy metals (in mg/kg DS) in the untreated (blank) sludge and in the sludge cake after dewatering for untreated (blank) sludge and sludge subjected to hydrolysis

	Blank	Blank dewatered	Acid thermal hydrolysis		Alkaline thermal hydrolysis	
			pH 3	pH 5	pH 9	pH 11
Cd	3.4	3.5	2.1	2.4	3.0	2.8
Cr	30	31	16.3	18.9	21.9	20.1
Cu	441	443	402	421	150	102
Hg	0.9	0.9	0.9	0.9	0.9	0.9
Pb	96	111	82	86	71	45
Ni	9	11	2.1	4.3	8.7	8.2
Zn	629	626	203	225	567	532

Table 2
Concentration of heavy metals (in mg/kg DS) in the untreated (blank) sludge and in the sludge cake after dewatering for untreated (blank) sludge and sludge subjected to Fenton's peroxidation

H ₂ O ₂ -dose (g/kg DS)	Blank	Blank filter cake	[0,4-12]Fenton's peroxidation								
			[0,4-6]pH 3			[0,7-9]pH 5			[0,10-12]pH 7		
			0	0	10	25	50	10	25	50	10
Cd	3.4	3.5	1.2	1.2	1.1	1.5	1.4	1.4	2.0	1.8	1.7
Cr	30	31	28.2	24.1	23.1	28.5	26.2	24.9	29.1	28.1	27.2
Cu	441	443	251	202	176	290	225	220	330	298	287
Hg	0.9	0.9	0.9	0.9	0.8	0.9	0.9	0.9	0.9	0.9	0.9
Pb	96	111	92	94	95	91	92	89	93	96	91
Ni	9	11	7.1	5	4.5	7	6.1	6	8.1	6.9	6.3
Zn	629	626	231	121	115	301	269	233	410	367	279

lime-stabilised (Ca(OH)₂) sludge. The very strong Cu–organic bond is thus destabilised to a large extent and the metal is released.

Leita and Nobili [28] attributed the higher solubility of the heavy metals at alkaline pH to the enhanced formation of organic matter–metal complexes.

Moreover, hydroxyl ions can act as a ligand with an affinity for the central metal ion and compete with other (organic) ligands. When the pH (and thus the hydroxyl ion concentration) is increased to a level at which the other ligands can no longer compete, the metal will precipitate from solution as an insoluble metal hydroxide [5].

3.3. Fenton's peroxidation

Fenton's peroxidation comprises the activation of H₂O₂ by Fe(II)-salts. These salts act as a catalyst and promote the dissociation of H₂O₂ in two highly reactive hydroxyl radicals, being stronger oxidants than H₂O₂ itself [29]. These radicals specifically oxidise organic components in the sludge, hence destroying the EPS in the sludge flocs [22].

The activity of the peroxidation can easily be monitored by measuring the oxidation–reduction potential (ORP) of the tested samples.

The experimental results when applying Fenton's peroxidation are presented in Table 2.

These results show a significant reduction of Cd, Cu, Ni and Zn in the cake. The reduction increases with decreasing pH and increased dosage of the H₂O₂.

The release of Cu is explained by the degradation of organic matter by the H₂O₂. Cu, having a strong affinity for organics [8], is hence released. The same is true for Zn. The removal of Zn is moreover enhanced by the oxidation of insoluble zinc sulphides into soluble sulphates and, at low values of pH, by the increased solubility of the carbonatic phase. Also Cd was solubilised.

The concentrations of Pb and Hg are not significantly altered by the peroxidation. These metals may however be released by the degradation of organic matter, but subsequently be re-precipitated under forms of lead and mercury sulphate (which are highly insoluble).

4. Conclusions

Heavy metals are present in significant amounts in waste activated sludge. Cr, Cu, Pb and Zn are present in high concentra-

tions. These high concentrations can jeopardize the sustainable disposal of the sludge. Methods for reducing the heavy metal content of the sludge could hence enhance the ultimate disposal options. In this framework, the current paper evaluates some advanced sludge treatment methods with respect to their capability of reducing the heavy metal content of waste activated sludge. Acid thermal hydrolysis effectively reduces the concentrations of most heavy metals, with exception of Cu and Pb, while alkaline thermal hydrolysis is most effective in solubilising these two metals. Fenton peroxidation releases Cd, Cu, Ni and Zn to a large extent. It cannot be used however for a reduction of Pb and Hg.

These findings illustrate the usefulness of the proposed methods in reducing the heavy metal content of waste activated sludge, hereby reducing the toxicity and enhancing the disposal options of the sludge. In combination with their capability of enhancing the dewaterability of the sludge [19–21], their use on full-scale is economically favourable.

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