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SHORT COMMUNICATION

Electrochemical peroxidation of contaminated aqueous leachate

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Abstract The landfill process for disposal of domestic waste produces a large volume of contaminated aqueousleachate. This study was aimed at investigating the feasibility of using electrochemical peroxidation(ECP) for the treatment of this leachate. ECP is a process by which aqueous, or suspended organicmatter, is oxidised by the action of hydroxyl free radicals, produced using hydrogen peroxide and castiron or mild steel electrodes.The effectiveness of the ECP process was quantified by measuring reductions in leachate biologicaloxygen demand (BOD) and chemical oxygen demand (COD) as a result of treatment. Optimisation ofthe process was carried out by varying electrode voltage, polarity switching rate, leachate pH andhydrogen peroxide concentration. This resulted in an observed BOD reduction of 36% and CODreduction of 52%, which was achieved by adjusting the pH to 4.0, applying an electrode voltage of 1.9Vand switching speed of 5 cycles per minute. The optimum hydrogen peroxide concentration was foundto be 100ppm. In addition to reductions in BOD and COD, reductions in chloride and ammonium levelswere measured and found to be 15% and 18% respectively. The results of the investigation indicate that the ECP process is effective in the treatment of landfillleachate, and suggest that with further optimisation, ECP may serve as an attractive alternative tocurrent biological leachate treatment methods.

Keywords Fenton's reagent · Landfill leachate · Remediation · Electrochemical peroxidation

1 Introduction

Landfill leachate contains a wide variety of different pollutants which must be treated before it can be discharged into a waterway or disposed of by some other means. Biological treatment methods, such as trickling filtration and activated sludge, can be costly and may also require additional steps to remove inorganic materials and heavy metals. Such treatment systems are also susceptible to toxic shock, are seldom portable and usually slow to set up. Physical or chemical treatment systems may offer similar remedial capabilities, but without the inherent disadvantages [1]. Current practices include filtration, chlorination and ozonation, but these are often costly and insufficiently effective. Electrochemical peroxidation (ECP) offers a possible alternative to biological treatment, which produces a similar standard of remediation, but which is portable, does not suffer from problems with sensitivity, and requires little pre-treatment.

ECP was first described by Scrudato and Chiarenzelli [2] and involves the oxidation of aqueous or suspended organic matter by the action of hydroxyl free radicals, produced from hydrogen peroxide and ferrous ions, which are electrochemically generated from cast iron or mild steel electrodes. The resultant product is known as Fenton's Reagent. The source of ferrous ions for Fenton's reagent is traditionally an iron (II) salt such as ferrous sulphate or ferrous chloride [3],

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which introduces an additional contaminant, which must often be removed. In addition, large amounts of hydrogen peroxide are often required due to hydroxyl radical scavenging by reactions with hydrogen peroxide and ferric iron, rather than via the oxidation of the organic material present. It is also possible to initiate the process using ultraviolet light activation [4]. This has been used to treat landfill leachate [5]. However, a drawback of this process is that its efficacy is inhibited by the turbidity of the sample.

ECP augments the oxidative powers of Fenton's Reagent, by producing the ferrous ions in situ, which minimises free radical scavenging and consequently the amount of hydrogen peroxide required [6]. It also possible to electrochemically recycle the ferric ions, into ferrous ions much more efficiently than with the conventional Fenton's Reagent process, which minimises amount of ferric hydroxide formed.

When a voltage is applied to the steel electrodes, ferrous iron is produced (Eq. 1):

$$Fe^0(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad (1)$$

In the presence of hydrogen peroxide, this leads to the formation of hydroxyl radicals (Eq. 2):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{o}OH \quad (2)$$

A major advantage of ECP process is that the ferric ions can be recycled into ferrous ions (Eq. 3), so that they behave rather like a catalyst.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Hydroxyl free radicals are second only to fluorine in their oxidative power, which makes the process extremely effective. These radicals react with organic matter (RH or R) to produce organic radicals, as shown in Eqs. 4 and 5, or they may be scavenged by ferrous ions [7], as shown in Eq. 6.

$$RH + {}^{o}OH \rightarrow R^o + H_2O \quad (4)$$

$$R + {}^{o}OH \rightarrow (OH)R^o \quad (5)$$

$$Fe^{2+} + {}^{o}OH \rightarrow Fe^{3+} + OH^- \quad (6)$$

Scavenging of hydroxyl radicals is undesirable since it reduces the number present for reaction with the organic matter and it also reduces the amount of ferrous ions for reaction with hydrogen peroxide [8]. Further reactions may then occur (Eqs. 7, 8, 9).

$$R^o + Fe^{3+} \rightarrow Fe^{2+} + \text{oxidised product} \quad (7)$$

$$R^o + R^o \rightarrow \text{dimer product} \quad (8)$$

$$R^o + Fe^{2+} \rightarrow Fe^{3+} + RH \quad (9)$$

The constant supply of hydroxyl radicals will, theoretically, cause the complete mineralisation any organic matter present into carbon dioxide and water, as shown in Eq. 10.

$$RH + H_2O_2 \rightarrow H_2O + CO_2 \quad (10)$$

Oxidation of halogenated compounds by ECP can also be performed [9], resulting in the formation of chloride and hydrogen ions as shown in Eq. (11).

$$RHX + H_2O_2 \rightarrow H_2O + CO_2 + H^+ + X^- \quad (11)$$

The original application of ECP involved remediation of water, using a pilot-scale system, on a petroleum spill site in New York [10]. However, applications have been shown to be much broader than this. In tests, so far, ECP has been shown to degrade many organic compounds, including: volatile organic carbon compounds (VOCs), benzene, toluene, ethylbenzene, and xylene (BTEX compounds), dyes and chlorinated solvents [11]; atrazine [12]; polychlorinated biphenyls (PCBs) [13]; and nitrophenols [14].

2 Experimental

All reagents were supplied by Fisher Chemicals (Loughborough, UK) unless stated otherwise. Landfill leachate was obtained from the Stewartby (Bedfordshire, UK) Landfill Site.

An electrochemical peroxidation unit, which consisted of a Perspex tank, capable of holding 6 L of leachate and containing a number of mild steel electrodes and a hydrogen peroxide injection system, was designed and built. The design was kept as simple as possible, to allow easy construction, but was versatile to allow changes to the electrode spacing and number.

Previous work [2] (Scrudato et al. 2000) suggests a preferable electrode separation of 0 to 1.5 inches, so an initial spacing of 2.5 cm (approximately 1 inch) was chosen. With these dimensions, it allowed room for a total of 10 interdigitated electrode plates (F). The electrodes in each bank were held in position and electrically connected by two threaded mild-steel bars, such that the polarity of each bank could be alternated between anodic and cathodic voltage under the control of a voltage switching unit. The plate separation and their number could be varied by altering the width and number of plastic spacers which were threaded over the steel bars between the electrode plates. The plates can be removed for cleaning if necessary by unscrewing the steel bars and withdrawing them for the unit. The leachate inlet was positioned near the top of the unit and the outlet was positioned at the other end of the unit, close to the base.

In order to minimise fouling and also maximise the efficiency of the process, the polarity of the electrodes can be intermittently switched, using a simple electronic switching unit, which was designed constructed for the task. The timer circuit allows the selection of six different switching speeds, between 5 and 120 cycles min^{-1}, selected by a rotary switch. Full details of the circuit were previously published by Freeman [11].

The general electrochemical peroxidation experimental procedure is shown schematically in Fig. 1. A small bench-top laboratory power supply was used to supply the appropriate voltage.

Initial experiments were performed batch-wise on 2 L of leachate, circulated through the system at a rate of approximately 1.5 L min^{-1}, using a small submersible pump. A 1% solution of hydrogen peroxide was added to the medium, over a period of approximately 1 min, using a pipette to distribute the solution between the electrode plates and into the reservoir. The volume of the added hydrogen peroxide was varied in order to achieve the desired concentration.

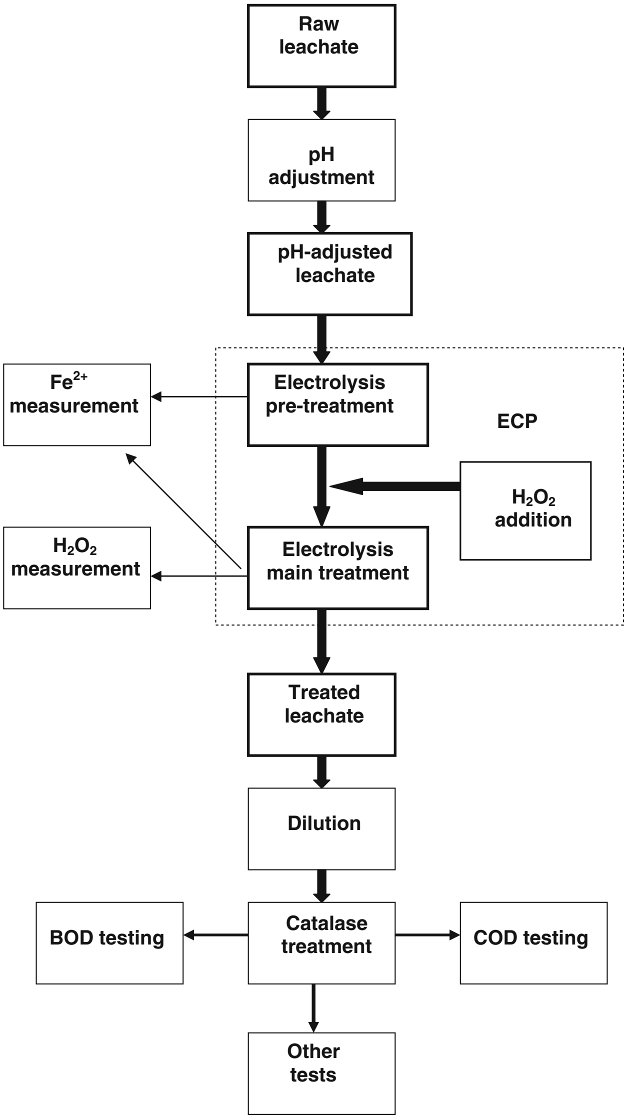

Fig. 1 Flow diagram of electrochemical peroxidation experimental procedure

Hydrogen peroxide and ferrous ion concentrations were measured using a Merck (Nottingham, UK) Reflectoquant test meter with the appropriate test strips. Samples were extracted from the reservoir using a 1 mL pipette and diluted with RO water, if required, before measurement.

The initial pH of the leachate was adjusted using concentrated sulphuric acid or sodium hydroxide to a value of 4.0, which has the added benefit of enhancing trace metal solubility and increasing the conductivity of the solution.

Biological oxygen demand (BOD) and chemical oxygen demand (COD) were monitored in order to give an indication of the strength of the leachate and the efficacy of treatment. Prior to measurement of these parameters, each sample was treated with catalase in order to remove any residual hydrogen peroxide which might affect the final COD or BOD reading. Samples of the leachate were diluted 1:3 with RO water to a final volume of 100 mL and 10 μL of catalase was added, which was found to achieve complete removal of any residual hydrogen peroxide. Catalase was added to every sample, including the untreated controls, as the catalase has a small COD/BOD of its own.

COD measurements were performed using the potassium dichromate method [15] with a spectrophotometer and 0–150 ppm range COD test vials (Hach, Salford, UK). BOD measurements were performed using the standard BOD5 (ATU) method and a dissolved oxygen probe.

3 Results and discussion

The effect of the voltage polarity switching rate on initial ferrous ion concentration was investigated by oscillating the polarity at 120, 24, 5 and 0 cycles min^{-1}. With an applied potential of 2.0 V and pH adjusted to 4.0, hydrogen peroxide was added to give an initial concentration of 100 ppm. The ferrous ion concentrations were found to be inversely proportional to the switching rate (Fig. 2). At 5 cycles min^{-1}, the highest reduction of COD was found, so this was chosen for further studies.

Keeping other parameters the same as above, potentials of 1.0, 1.5 and 2.0 V were applied and the COD reduction and initial and final ferrous ion concentrations were measured. The COD and ferrous ion concentrations of untreated leachate were also recorded. These values are shown in Fig. 3. The maximum COD reduction, of 46%, occurred at an applied potential of 2.0 V, which was the maximum obtainable voltage for the power supply used. The peak COD reduction coincides with the highest initial ferrous ion concentration, suggesting that the high availability of ferrous iron is maximising the reaction with hydrogen peroxide

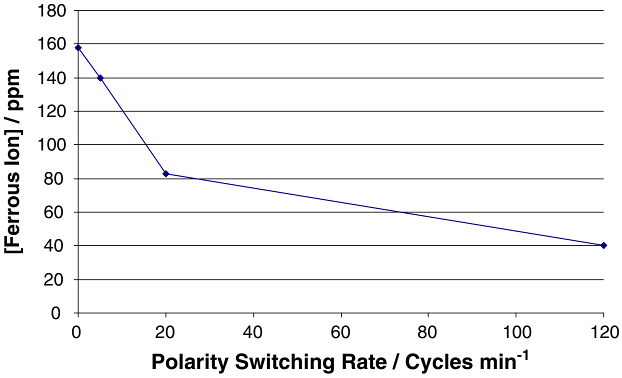

Fig. 2 Effect of switching rate on initial ferrous ion concentration

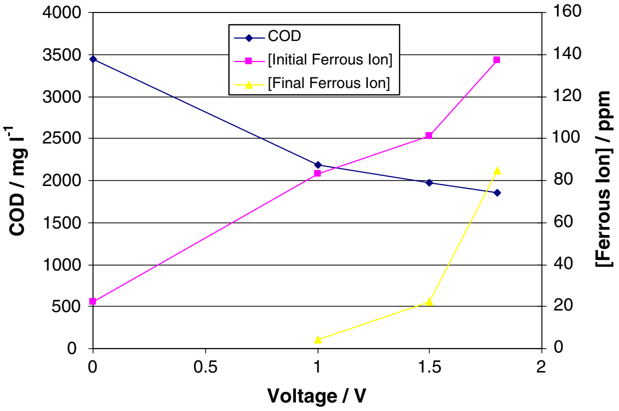

Fig. 3 Effect of voltage on the initial and final ferrous iron concentration and COD reduction of the leachate

to produce hydroxyl radicals which oxidise the components of the leachate. Interestingly, at voltages 1.0 and 1.5, the relatively high values of the final Fe^{2+} concentration are accompanied by a final peroxide concentration of zero, indicating that all the hydrogen peroxide had been consumed. It was, therefore, postulated that that adding more peroxide and continuing the ECP treatment for longer could result in further reductions in COD.

The initial concentration of hydrogen peroxide of 100 ppm, in the work reported above, was obtained by a single addition of hydrogen peroxide at the beginning of the experiment. The effect of varying hydrogen peroxide concentration was studied by adjusting the initial concentration to 50, 100 and 200 ppm, by addition of the necessary amount of concentrated hydrogen peroxide at the beginning of the treatment, with duplicate amounts added half way through the treatment. The voltage was set at 2.0 V and the pH adjusted to 4.0, as in previous experiments. Both COD and the more time-consuming BOD measurements were also performed.

COD reduction was found to be almost directly proportional to peroxide concentration. However, a maximum reduction of approximately 52% (COD was reduced from 3,825 to 1,820 mg/L) was observed at a peroxide concentration of 200 ppm. This limit could be due to the oxidation proceeding to its maximum potential, beyond which remaining compounds are recalcitrant to further degradation by hydroxyl radicals. The other explanation could be that there is a ferrous ion concentration limiting factor. The latter appears more likely, since there was residual hydrogen peroxide found when the initial concentration of 200 ppm was used.

BOD reduction was very similar for the three concentrations of hydrogen peroxide used during treatment. In each case, a reduction of 30–36% was seen, a drop from 655 to 421 mg/L in the best case.

Since chloride and ammonium concentrations are often measured in such leachates, these were also monitored. Under the conditions that produced the highest COD reduction, ammonium and chloride levels were reduced by 15% (4,089–3,478 mg/L) and 18% (4,794–3,917 mg/L) respectively. It should be noted, however, that the ECP process had been optimised to achieve maximum COD removal reduction for this particular leachate and that it might be possible to achieve higher efficiency of removal of these species using different conditions. In the case of chloride removal, higher concentrations of ferrous ions are known to enhance the process in conventional Fenton's reagent reactions [16], so a different electrochemical procedure could be adopted to enhance this, if required.

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