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Subcritical water treatment of landfill leachate: Application of response surface methodology

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ABSTRACT

Context: Leachate is the liquid formed when waste breaks down in the landfill and water filters through that waste. This liquid is highly toxic and can pollute the land, ground water and water ways. It is mandatory for landfills to protect against leachate in most countries worldwide. Controlling the pollutant loading, means reducing its quantity by containing or treating the waste to comply with certain discharge characteristics which are compatible with the receptor medium.
Objective: This paper describes the reduction of the organic load of a mature landfill leachate using a novel experimental set-up that employs hydrogen peroxide under subcritical conditions and aims to establish this method as an effective alternative to currently used options. Response surface methodology was applied to optimize the treatment process and determine which of the following there parameters – temperature, residence time and hydrogen peroxide concentration – played the most important role.
Method: The method employed is based on the use of laboratory-scale, stainless steel reactors, filled with the leachate and appropriate quantities of hydrogen peroxide. Under subcritical conditions (temperature in the range of 100–374 °C and enough pressure to maintain the liquid state of water), hydrogen peroxide produces hydroxyl radicals which are highly reactive and oxidize the organic molecules of the leachate.
Results: The highest COD decrease of 85% was experimentally observed at 300 °C, 500 mM H_2O_2 and 180 min residence time. It was determined that the combination of oxidant concentration and temperature is the rate-determining factor, whereas residence time has a lesser effect on the process.
Conclusions: A simple, quick, effective and environmentally-friendly method for the treatment of the organic load of landfill leachate was developed and optimized at laboratory scale.

1. Introduction

Landfill leachate can be defined as the liquid produced from the decomposition of solid waste and infiltration of rainwater in a landfill. It contains heavy metals, salts, nitrogen compounds and various types of organic substances (Schiopu and Gavrilescu, 2010). Generation of leachate occurs when moisture enters the solid waste in a landfill, dissolves the contaminants into liquid phase and produces moisture content sufficient to initiate liquid flow. This leachate is a high-polluting strength wastewater that has a major impact and influence on landfill design and its operation. Leachate composition varies from one landfill to another, and over space and time in a particular landfill with fluctuations that depend on short and long-term periods due to variations in climate, hydrogeology and waste composition (Keenan et al., 1984).

Generally, leachate possesses high concentrations of ammonia and organic contaminants (measured in terms of chemical oxygen demand COD and biochemical oxygen demand BOD), halogenated hydrocarbons and heavy metals. In addition, leachate usually contains high concentrations of inorganic salts (mainly sodium chloride, carbonate and sulphate) and is dependent on the

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composition of landfilled waste. The main environmental problems at landfill sites are the infiltration of leachate and its subsequent contamination of the surrounding land and aquifers. Improvements in landfill engineering are aimed at reducing leachate production, collection and treatment prior to discharge (Farquhar, 1989). The risks to human health and the environmental impact of landfill leachate contamination of ground- and surface water have been well documented (Slack et al., 2005; Macklin et al., 2011; Kwasniewska et al., 2012; Toufexi et al., 2013). An excess of 200 organic compounds have been identified in municipal landfill leachate, with more than 35 of them having the potential to cause harm to the environment and human health (Slack et al., 2005).

Leachate needs to be pre-treated on site to meet the standards for its discharge into the sewer or its direct disposal into surface water. Leachate management is a complex task due to the highly variable nature of waste landfilled, type and design of the landfill site, its age, and climatic and seasonal variations in different regions. Hence, it is difficult to recommend treatment options merely based on leachate age but it is often necessary to consider each case individually. Treatment systems in recent years are sophisticated, reliable and able to consistently treat leachate to keep in line with specific discharge standards. Generally, high organic and ammonia loads are the key factors in leachate treatment. The feasibility of treating leachate to COD levels lower than 1000 mg/L is uncertain, since at these values COD is primarily composed of humic and fulvic acids. The effect of these substances on aquatic life of receiving waters is dependent extensively on specific cases. While developing a treatment sequence for leachate to be discharged into a river, Robinson et al. (2002) reported that COD levels of about 500 mg/L consisting of humic and fulvic acids did not adversely affect aquatic life.

Worldwide, the issue of leachate treatment has been thoroughly investigated, but a universal solution has not yet been established. Therefore, there is a need to develop reliable and sustainable options to manage leachate generation and treatment effectively. While designing a treatment system, the process train must include techniques or unit operations to treat leachate produced from the landfill over a longer period. The most widely used treatment processes and their combinations have been thoroughly reviewed (Kjeldsen et al., 2002; Renou et al., 2008; Abbas et al., 2009; Foo and Hameed, 2009; Schiopu and Gavrilescu, 2010; Li et al., 2010; Oller et al., 2011; Ahmed et al., 2012).

Subcritical water is hot water (>100 °C) under enough pressure to maintain the liquid state. It is an environmentally friendly and inexpensive solvent that exhibits a wide range of properties that render it very effective in solvating and decomposing moderately polar or non-polar organic substances from a wide range of environmental matrices. Several studies have shown that subcritical water can decompose naturally-occurring substances and materials, such as complex amino acids, proteins and carbohydrates (sucrose, fructose, sorbose) and brown coal to produce more valuable and useful products. Additionally, subcritical water has been proven to decompose hazardous organic substances and materials such as residual reactive dyes (Daskalaki et al., 2011), fluorochemicals (Hori et al., 2008), explosives (Hawthorne et al., 2000; Kalderis et al., 2008), pentachlorophenol (Benedictus, 2007), dioxins (Hashimoto et al., 2004) and polyvinyl chloride (Takeshita et al., 2004).

The scope of this work is to reduce the organic load of a mature landfill leachate using a novel experimental set-up that employs hydrogen peroxide under subcritical conditions and therefore establish this method as an effective alternative to currently used options. Using subcritical water, with or without oxidants is an effective way of degrading various environmental pollutants. Such subcritical water set-up has not been used for the treatment of landfill leachate before. Compared to the studies mentioned earlier, this time the process aims at a highly complex wastewater consisting of a large number of organic and inorganic constituents of diverse nature. Hydrogen peroxide is used as an environmentally-friendly oxidant, as it leaves no residues after treatment. In contrast to the dynamic set-ups that require considerable quantities of water and more complicated apparatus, the experiments described here are under static conditions i.e. no flow is required and no additional use of water. Additionally, monitoring of the process is not essential, since the oven can be pre-set at the required temperature and residence time. Finally, no pumping system is needed to maintain the system pressure, since pressure is automatically controlled by the steam/water equilibrium inside the reactor cell.

When applying oxidative methods to decrease the organic load of the leachate, temperature, oxidant concentration and experimental time are the most important factors. Therefore, optimization of the influencing parameters is vital towards designing an effective degradation system. As a result, advanced statistical design has been widely employed for process characterization, optimization and modeling (Alaton et al., 2009; Singh et al., 2010). Experimental design methodologies have become a significant tool that have enabled us to gain a better understanding of a process in terms of the interactions among the parameters that need to be optimized. Response surface methodology (RSM) – a collection of mathematical and statistical techniques – has been found to be a useful aid for studying the effect of several factors that influence the response of a system as well as optimizing the variables of a wastewater treatment process. Furthermore, it is essential to choose an appropriate experimental design method that will evaluate the effects of the major parameters involved in the treatment method and their probable interactions, through the minimum number of experiments. RSM provides a large amount of information and is a more economical approach because a small number of experiments are performed for monitoring the interaction of the independent variables on the response. In conventional optimization, the increase in the number of experiments necessary to carry out the research, leads to an increase in time and expenses as well as an increase in the utilization of reagents and materials for experiments.

Based on the above, the objectives of this study are the following:

- effectively reduce the organic load – as shown in COD measurements – of a mature landfill leachate using hydrogen peroxide in subcritical conditions
- apply a 5-level central composite experimental design (CCD) combined with RSM to optimize the various parameters and obtain maximum response,
- validate the suggested model and determine the optimum operational conditions, based on COD measurements

2. Materials and methods

2.1. Materials

Landfill leachate was obtained from the Chania (Crete, Greece) municipal waste landfilling site with the help of the staff of DEDISA A.E. The sample was followed by an analytical certificate showing the levels of organic and inorganic constituents and other quality parameters (Table 1). The addition of the appropriate quantities of hydrogen peroxide (30% solution, Sigma–Aldrich) was carried out