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The application of novel coagulant reagent (polyaluminium silicate chloride) for the post-treatment of landfill leachates

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ABSTRACT

Relatively "old" (stabilized) landfill leachates are a special category of wastewaters, which are difficult to treat further, mainly due to their bio-refractory organic content (humic substances). In this study, coagulation–flocculation was examined as post-treatment method for the biologically pre-treated stabilized leachates. The purpose was to examine the coagulation performance of alternative coagulant agents, i.e. the composite coagulant polyaluminium silicate chloride. Composite coagulants with different Al to Si molar ratio and different preparation methods were tested. Their efficiency was evaluated by monitoring from turbidity and phosphate content, other parameters strongly correlated with the presence of organic matter, such as UV absorbance at 254 nm, COD and colour. The results suggest that the silica-based coagulants exhibit better coagulation performance, than the relevant conventional coagulant (alum) or simple pre-polymerized coagulants (PACl). Polyaluminium silicate chloride has greater tolerance against pH variation than alum or PACl, whereas this novel coagulant works better at pH values between 7 and 9. Coagulation–flocculation has proved to be an efficient post-treatment method for the biologically pre-treated leachates, promoting the removal of the refractory humic substances, while the treatment efficiency of coagulation can be improved by the application of the new coagulant agent.

1. Introduction

Municipal solid waste (MSW) landfilling is still widely applied, despite the encouragement of alternative waste treatment methods, such as recycling, composting or incineration. The economical benefits are mainly due to the lower cost and simpler operation, when compared to the alternative MSW treatment methods, and these are still an obstacle against the European Union policy of landfill ban (European Union Landfill Directive 1999/31/EC) (Rivas et al., 2005).

As the landfill matures, the organic fraction in the leachate becomes dominated by refractory (non-biodegradable) compounds, such as humic substances (HS) (Renoua et al., 2007).

According to Kang et al. (2002), the HS of leachate usually comprise from smaller and less aromatic molecules, when compared to commercial humic acid, especially the HS of "fresh" leachate. They also observed that with increasing landfill age, the aromaticity and the molecular size of HS tend also to increase. Despite the differences from HS derived from other sources, those of leachates still preserve the characteristic of refractory organic matter hence they are considered as hardly biodegradable. Regarding that the HS content can vary from 30% (Christensen et al., 1998) up to >70% (Nanny and Ratasuk, 2002) of leachate DOM from "old" landfill sites, the need for an effective treatment method becomes obvious.

The efficient treatment of leachates usually means the appropriate combination of two or more different treatment methods (Renoua et al., 2007). Several publications exist in the literature regarding the assessment of coagulation–flocculation as pre- or post-treatment method for the remediation of landfill leachates, aiming to the optimization of treatment parameters (e.g. coagulant dose, pH, appropriate addition of polyelectrolyte, etc.) (Amokrane et al., 1997; Trebouet et al., 2001; Tatsi et al., 2003; Rivas et al., 2004; Galvez et al., 2005; Ntampou et al., 2006). The coagulants mostly applied are the conventional and the simple pre-polymerized metal salts, i.e. in the case of aluminium the aluminium sulphate (alum) and the polyaluminium chloride (PACl). Regarding the post-treatment of biologically pre-treated leachates with coagulation, Tatsi et al. (2003) observed maximum COD removal of 56% with alum (dosage of 0.5 g Al l^{-1}) at fixed pH 7. Ntampou et al. (2006) applied another relevant commercial product (PACl-18) for the treatment of biologically pre-treated stabilized leachates and found up to 62% COD removal for the optimum dosage of 0.365 g Al l^{-1}, although the target value of 180 mg l^{-1} COD could not be reached, according to the respective legislation limit for the discharge of treated wastewaters (Local Government Executive Order for the Protection of the Aquatic Environment, No. 22374/

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94). Colour and UV absorbance at 254 nm (Abs UV_{254}) removal was 98% and 75%, respectively.

Although various combinations of different methods have been found in the literature for the treatment of landfill leachates, it seems that coagulation–flocculation is widely used in these treatment schemes, mainly due to its simplicity and cost-effectiveness. The increase of the performance of coagulation–flocculation stage seems to be a key factor for the improvement of the overall leachates treatment efficiency, an increase which could be achieved by the use of alternative, more effective coagulation reagents. Zouboulis et al. (2004) noticed that the application of a bioflocculant resulted similar COD removal, but with significant lower dosage than alum.

In recent years, the relevant research in the coagulation–flocculation field has focused mainly to the production of improved coagulation reagents, with the introduction in the structure of pre-polymerized coagulants (such as PACl) of other components, either organic or inorganic (Zouboulis et al., 2007). A novel coagulation reagent that is under intensive investigation during the last few years is polyaluminium silicate chloride, the outcome of polymerized silica addition into PACl. It should be noted that it is rather a new category of coagulants in comparison with the conventionally used specific reagents, as from different Al/Si and OH/Al molar ratios various products can be derived.

The introduction of silica chains into the structure of PACl has proved increases in the molecular weight (MW) of the coagulants (Gao et al., 2003), thus leading to enhanced aggregating power and bigger and denser flocs' formation (Zouboulis and Tzoupanos, in press). Polyaluminium silicate chloride has shown superior coagulation performance than alum and PACl in water or wastewater treatment (Gao et al., 2003, 2007; Zouboulis and Tzoupanos, in press). Its advantages can be summarized as the better coagulation performance for lower additions of used coagulant and wider effective pH range, than the conventional or pre-polymerized coagulants. Furthermore, the residual aluminium concentration which remains in the treated sample is significantly lower, in comparison with the conventionally applied coagulants.

In this study, coagulation–flocculation was applied as the post-treatment method of biologically pre-treated stabilized landfill leachates. The coagulation efficiency of several polyaluminium silicate chloride coagulant reagents with different Al/Si molar ratios was investigated and compared with the coagulation efficiency of alum and PACl reagents. The main purpose was to define whether the application of new, composite coagulants can exhibit specific advantages for the physico-chemical treatment of leachates and to determine the appropriate Al/Si molar ratio, as well as the respective preparation method, which corresponds to the most efficient product, thus improving the efficiency of coagulation–flocculation.

2. Materials and methods

2.1. Leachate samples and pre-treatment

The pre-treatment stage included the biological treatment of leachates in a Membrane Sequencing Batch Reactor (MSBR). After the pre-treatment, appropriate samples were collected from the sequential operation circles (every 24 h) and mixed together to obtain a homogenous sample. Essential quantitative parameters were determined according to APHA Standard Methods (Clesceri et al., 1989) and the samples were stored at 4 °C for few days until treated. The properties of the biologically pre-treated leachates were: pH 8.5 (initial 8.4), turbidity 4.5 NTU (initial 103), Abs UV_{254} 2.74, COD 450 mg l^{-1} (initial 2456), *ortho*-phosphates 18.2 mg l^{-1} (initial 8.2), and the colour 1813 ADMI values (changed from dark brown to yellow).

It is evident that after the application of biological treatment, significant improvement of major physicochemical properties of leachates occurs. Particularly, the colour changed from dark brown to yellow, COD, total nitrogen and conductivity decreased significantly (82%, 90%, 51% removal, respectively). However, the biological treatment cannot be assigned alone as completely satisfactory, as the intense yellow colour indicates the strong presence of organic matter and particularly of strong coloured organics, such as HS. Furthermore, COD value still remains high as well as UV absorbance at 254 nm. Both parameters are also strongly related with the presence of (residual) organic matter. Finally, during the biological processes in the MSBR, accumulation of phosphorous is taking part rather than removal, with the consequence the treated sample to exhibit greater phosphates concentration than the initial sample. This increment is due to the specific requirements of the MSBR treatment (very large sludge age, resulting in P release from the dead bacterial cells into the treated mixture), and eventually due to the periodically addition of K_2HPO_4 in order to preserve the necessary BOD:N:P = 100:5:1 ratio. Considering these observations, it is clear that further treatment of leachate samples is required, especially for the removal of the remaining refractory organic matter, as well as of increased phosphate content.

2.2. Preparation of coagulation reagents

All used reagents were analytically pure chemicals. Deionized water with conductivity lower than 0.5 μS cm^{-1}, as well as carbonate-free by boiling, was used to prepare all the solutions used for the synthesis of the coagulants.

For comparison reasons, commercially available PACl-18 containing 17.15% Al_2O_3, with basicity 40% and density 1.365 g cm^{-3}, obtained from Phosphate Fertilizers Industry (Greece), as well as aluminium sulphate (alum, $Al_2(SO_4)_3 \cdot 18H_2O$, analytical reagent) were also examined.

The novel coagulants preparation procedure was recently described (Zouboulis and Tzoupanos, in press). 0.5 M $AlCl_3 \cdot 6H_2O$ and 0.5 M NaOH were used as aluminium solution and base solution, respectively. The polymerized silica solution (or polysilicates solution) was obtained by acidifying (with 1 N HCl) a diluted (to 0.5 M SiO_2) water glass solution (initial content 10% NaOH, 27% SiO_2), until the pH of 2. The addition of polysilicates was accomplished according to two procedures: in the first method the silicates were introduced in the Al solution ("co-polymerization", product denoted as PASiC) and then the base was added, whereas in the second method initially the base was added to Al solution and then the silicates solution ("composite polymerization", product denoted as PACSi). Base addition rate was 0.1 ml min^{-1} and the stirring speed 700–800 rpm.

The amount of base was properly calculated in order to achieve hydroxyl to aluminium molar ratio equal to one. The choice of OH/Al = 1 was based upon relevant experience (Zouboulis and Tzoupanos, in press) and preliminary coagulation experiments with synthetic wastewater (data not shown), where it was found that the composite coagulants with OH/Al = 1 worked better in wastewater treatment applications. The amount of polysilicates solution varied, aiming to the preparation of coagulants with different silica content. It was calculated based on the target Al/Si molar ratio in the composite coagulant, i.e. Al/Si = 10 or 15. These ratios were selected based upon the aforementioned preliminary experiments.

The final Al concentration in all laboratory prepared coagulants was fixed to 0.2 M. The coagulants are referred in the text as PASiC 1/10 or PACSi 1/10, where 1 corresponds to OH/Al molar ratio and 10 to Al/Si molar ratio. For comparison purposes, PACl with OH/Al 1 (referred as PACl-1) was also prepared, under the same procedure, but without the addition of silicates.