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Removal of Heavy Metals from Solid Wastes Leachates Coagulation-Flocculation Process

M.A. Zazouli and Z. Yousefi
Department of Environmental Health, School of Public Health and Environmental Health Research Center,
Mazandaran University of Medical Sciences, Sari, Iran

Abstract: The main objectives of present research were to determine heavy metals (Ni, Cd, Cr, Zn and Cu) and COD concentration in raw leachate in Esfahan (Iran) composting plant and to examine the application of coagulation-flocculation process for the treatment of raw leachates. Jar-test experiments were employed in order to determine the optimum conditions (effective dosage and optimum pH) for the removal of COD and heavy metals. Alum (aluminum sulphate) and Ferric chloride were tested as conventional coagulants. Ten times had taken sampling from leachates as standard methods in the composting plant prior to composting process. The results showed that Leachate pH was 4.3-5.9 and the average was 4.98±0.62. The concentration of Leachate pollutants were more than effluent standard limits (Environment protection Agency). And also the results indicated, Cd and Zn with concentration 0.46±0.41 and 5.81±3.69 mg L^{-1}, had minimum and maximum levels, respectively. The results of coagulation and flocculation tests showed that in optimum conditions, the removal efficiency of heavy metals and COD by using alum were 77-91 and 21%, respectively. While removal of heavy metals and COD by ferric chloride were 68-85.5% and 28%, respectively. Also the residues of heavy metals after treatment get to under of standard limits of Iran EPA. The results have indicated optimum pH of two coagulants for leachate treatment was 6.5 and 10 and also effective coagulant dosages were 1400 and 1000 mg L^{-1} for alum and ferric chloride, respectively. In view of economical, ferric chloride is cost benefit. The physico-chemical process may be used as a useful pretreatment step, especially for fresh leachates.

Key words: Landfill leachate, heavy metals, coagulation, composting, solid wastes management

INTRODUCTION

Esfahan is one of the most crowded cities in the central of Iran. Esfahan and its suburb municipality have to manage approximately 800 tons of solid waste generated from residential and commercial sources. In Esfahan, composting and then landfilling are the common applications in management of municipal solid wastes. There is a central composting plant receiving commingled solid waste every day. One of main problems of solid wastes is Leachate production in collection, transfer and transport processing and composting and also disposal of solid wastes due to biological and chemical activity. These leachates enter to reservation and septic tanks and then transfer to agricultural farms by tanker vehicles. Increasing of population, progressing technology and rising of living quality are increasing of solid waste per capita and leachate production (Zazouli *et al*., 2001). Leachate contains various pollutants such as a large amount of organic matter (both biodegradable and non-biodegradable carbon), ammonia-nitrogen, heavy metals and chlorinated organic and inorganic salts (Wang *et al*., 2002a). The discharge of landfill leachate can lead to serious environmental problems, as they may percolate through soils and sub soils, causing extensive pollution of ground and surface waters if they are not properly treated and safely disposed and should be treated before discharge in an on-site treatment plant or discharged to a sewage system for treatment (Amuda, 2006; Aktas and Cecen, 2001). Leachate treatment techniques can be classified as: combined treatment with domestic sewage, biological treatment and physico-chemical methods (Berrueta *et al*., 1996). Selections of the most appreciate method for leachate treatment is very important but often difficult because of the highly variable quantity and quality of landfill leachates (Aktas and Cecen, 2001). Although some of pollutants in leachate can be removed by biological treatment, but heavy metals and non-biodegradable parts of organic matter pass the biological processes. The coagulation/precipitation is the most common method of removing soluble metals. In precipitation reactions chemicals are added to transform dissolved constituents to form insoluble precipitates. Metals are precipitated as hydroxides, sulfides and

Corresponding Author: Z. Yousefi, Department of Environmental Health,
School of Public Health and Environmental Health Research Center,
Mazandaran University of Medical Sciences, Sari, Iran Tel: +98-1513543081-7 Fax: +98-151-3543237

carbonates by adding appropriate precipitant and adjusting the pH to favor insolubility. Precipitation can be used to remove most metals (arsenic, cadmium, chromium III, copper, iron, lead, mercury, nickel, zinc) and many anionic species (phosphates, sulfates, fluorides). Better removal efficiencies can be achieved with sulfite precipitation, but hydroxide precipitation, using lime or caustic, is more practiced. This is due to the fact that sulfide precipitation is more expensive and may produce H_2S gas and hydroxide precipitation is cheaper and less dangerous. The selection of the best precipitant, flocculants, pH, rapid mix requirements and dosages is determined by laboratory jar test studies. Several studies have been reported on the examination of coagulation/flocculation for the treatment of landfill leachates. Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate were commonly used as coagulants. Iron salts were proved to be more efficient than aluminum ones, resulting in sufficient Chemical Oxygen Demand (COD) reductions (up to 56%), whereas the corresponding values in case of alum or lime addition were lower (39 or 18%), respectively (Amokrane *et al*., 1997; Tatsi *et al*., 2003).

Nevertheless, the coagulation/precipitation process has been mainly investigated by using stabilized landfill leachates for removal of organic matter and solids. However, there is limited information on the efficiency of this process for heavy metals removal, when applied for the removal of pollutants from raw leachates. Therefore, the objectives of present research were the study of leachate quality in the composting plant (Esfahan composting plant, Iran) and survey of coagulation-precipitation process efficiency for the treatment of fresh or raw leachates, especially in terms of organic matter and heavy metals removal. More specifically, the aim was the determination of most appropriate coagulant type and dose, the examination of pH effect on removal capacity and the identification of optimum experimental conditions for the efficient application of this process.

MATERIALS AND METHODS

Leachate sampling: The raw leachate samples were obtained directly from Esfahan composting plant before composting process (Esfahan, Iran), the area where fresh solid wastes were deposited. The samples had collected ten times monthly. This study was conducted in the 2006.

Sample analyses: The samples were taken to the laboratory in 20 L plastic carboys, stored at -4°C before analyses. Parameters such as the initial pH of the samples, heavy metals concentration (nickel, cadmium, total chromium, zinc and copper), solids concentration such as Total Solids (TS), Volatile Solids (VS) and Fixed Solids (FS) and also the Chemical Oxygen Demand (COD) were determined according to the standard methodology (APHA, 1998).

All chemicals used for the analytical determinations were of analytical grade.

Coagulation and flocculation tests: The conventional jar-test apparatus, in equipped with 6 beakers of 1 L volume, was employed for coagulation/flocculation and precipitation processes. Chemicals reagents used as coagulants included alum ($Al_2(SO_4)_3 . 18H_2O$) and ferric chloride ($FeCl_3 . 6H_2O$). Leachate samples were thoroughly shaken, for re-suspension of possibly settling solids and the appropriate volume of sample was transferred to the corresponding jar test beakers. A Jar test was set up at room temperature for each trial. The coagulant was added into the beakers and the pH values were immediately adjusted to the desired levels by the addition of appropriate amounts of NaOH and HCl solutions. The experimental process consisted of three subsequent stages: the initial rapid mixing stage took place for 3 min at 120 rpm, the following slow mixing stage for 15 min at 20 rpm, while the final settling step lasted for another 45 min (Eckenfelder, 1989).

In order to determination of coagulant dosage (optimum dose) on removal efficiency, different concentrations (0 to 200% of initial dosage at stable pH) such as 0, 350, 700, 2100 and 2800 mg L^{-1} of alum and 0, 500, 1000, 2000, 3000 and 4000 mg L^{-1} of ferric chloride were added to 1 L leachate sample. pH was adjusted between 4 and 8 for determination of the optimum pH or pH effect on the efficiency process for alum coagulant and between 3 and 11 for ferric chloride prior to tests. After the settling period, the supernatant was withdrawn from the beaker and was used for chemical analysis. The supernatant was digested using standard methods to release its heavy metal contents and analyses were carried using atomic absorption spectrophotometer. Results were analyzed based on Excel software.

RESULTS AND DISCUSSION

Leachate characteristics: The composition of the investigated leachate is shown in Table 1. Taking into account the high concentration of heavy metals, the pH value (4.98±0.62) and the high contents of total solids (38815±6488 mg L^{-1}) and COD (38563±5771 mg L^{-1}), the leachate was classified as fresh or raw leachate (Frank, 1994). So, this leachate displayed high

Table 1: Composition of the investigated solid wastes leachate

Parameter*	Value Mean±SD**	Range
pH	4.98±0.62	4.3-5.9
Chemical oxygen demand (COD)	38563±5771	25762-45500
Total solids (TS)	38815±6488	26474-46000
Total volatile solids (TVS)	22596±3082	15714-26219
Total fixed solids (TFS)	16210±4997	10760-23964
Cadmium (Cd)	0.46±0.41	0.06-1.31
Total chromium (Cr)	1.27±0.88	0.35-2.61
Copper (Cu)	1.21±0.73	0.34-2.34
Zinc (Zn)	5.81±3.69	1.26-12.66
Nickel (Ni)	2.38±1.17	0.72-4.01

*Units in mg L^{-1} except pH without unit, **Average±Standard deviation

concentrations of contaminants. Similar relative abundances and heavy metal concentration levels have also been reported by other investigators in literature (Trebouet *et al*., 2001; Slack *et al*., 2005). The chemical composition of the landfill leachate (Sant'Agostino landfill, in Italy) showed that an important content of heavy metals can exhibit considerable temporal variation. The Cr, Zn and Pb concentrations were reported equal to 0.13-0.36, 0.1-0.5 and 0.05-1 mg L^{-1}, respectively (Dimitra and Carmela, 2006). The variation of leachate characteristics were attributed to variations in the composition of deposited solid wastes, moisture and decomposition. From this table, it can be deduced that fresh leachates corresponded to the acidic phase of decomposition.

In addition, the comparison of the average values of heavy metal concentrations in the leachate with the guidelines from Iranian Environmental Protection Agency (for effluent discharge in the sewer) and USEPA (according to water irrigation and agricultural standards) show that, the concentration of heavy metals in leachate exceed the maximum values allowed. The minimum and maximum concentration of heavy metals was 0.46±0.41 and 5.81±3.69 mg L^{-1}, related to Cd and Zn, respectively. This result indicated that sources of Zn in solid wastes are more than Cd and the others.

Efficiency of coagulation and flocculation: pH and coagulant dosages has been observed to significantly affect to efficiency of coagulation and flocculation process. So, the best conditions for coagulation and flocculation tests on COD and heavy metals removal are evaluated and optimized (pH and coagulant dosage) by a jar test technique. The first, effect of pH values and then, coagulant dosages on the efficiency was evaluated. Initial dosages of alum and ferric chloride were 1400 and 2000 mg L^{-1} as based on pre-tests, respectively.

Effect of pH: The results of effect of pH values on the coagulation efficiencies and removal of heavy metals and COD in the leachate are presented in Fig. 1. The pH of

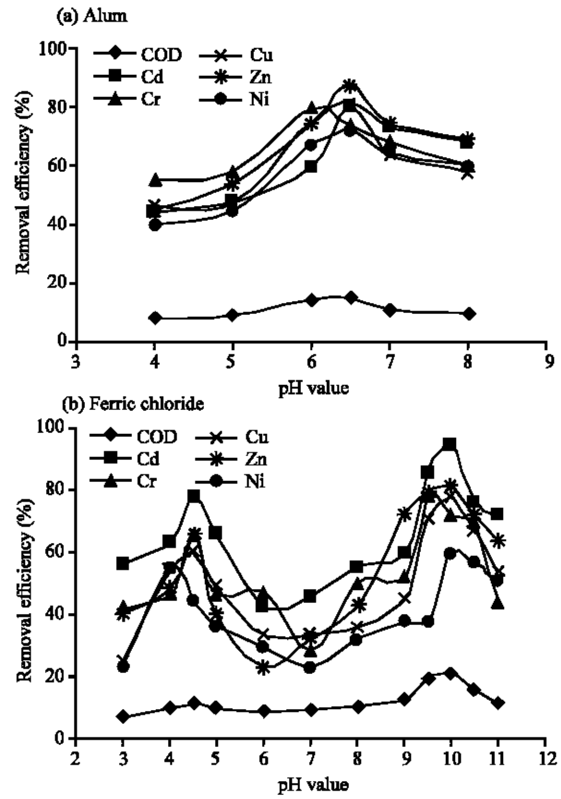

Fig. 1: The effect of pH on the removal efficiencies of heavy metals and COD in the leachate, (a) Alum with initial dosage = 1400 mg L^{-1} and (b) ferric chloride with initial dosage = 2000 mg L^{-1}

initial samples was varied between 3 and 11 for ferric chloride and 4 and 8 for alum. As shown in Fig. 1, the removal efficiency of coagulation is as a function of pH. Removal percent of COD varied from 7 to 15% for alum and from 7 to 20% for ferric chloride. The same observation was reported by other workers (Trebouet *et al*., 2001; Wang *et al*., 2002b; Tatsi *et al*., 2003; Silva *et al*., 2004; Bila *et al*., 2005). In general, they were reported that the removal efficiency of COD varying from 10 to 25%.

In practice, Fig. 1 indicates that the optimum pH for the best removal of COD and heavy metal was 6.5 and 10 for alum and ferric chloride, respectively. However, as reported by other authors, this value can greatly fluctuate according to the class of pollutants and to the matrix effect in complex leachate (Wang *et al*., 2002a, b; Lopez *et al*., 2004). Besides, precipitation of flocs at this pH was more and better than the other pH. Therefore, pH 6.5 and 10 were optimum pH for lechate coagulation with alum and ferric chloride, respectively. The pH influences the nature of produced polymeric metal species that will be formed as soon as the metal coagulants are dissolved in water. The influence of pH on chemical coagulation/flocculation may be considered as a balance of two competitive forces: (1) between H^+ and metal hydrolysis products for interaction with organic ligands and (2) between hydroxide ions and organic anions for interaction with metal hydrolysis products. At low pH values, hydrogen ions out compete metal hydrolysis products for organic ligands, hence poor removal rates occur and some of the generated organic acids will not precipitate.

At higher pH values, hydroxide ions compete with organic compounds for metal adsorption sites and the precipitation of metal-hydroxides mainly occurs mainly by co-precipitation (Tatsi *et al*., 2003).

Effect of coagulant dose: The effect of different dosages of alum and ferric chloride is as shown in Fig. 2. The removal of COD and heavy metals increased with increasing concentration of coagulants. It was observed that when the dose of alum and ferric chloride was greater than 1400 and 1000 mg L^{-1}, respectively, the removal increased slowly. Thus, the optimum dose of alum and ferric chloride was 1400 and 1000 mg L^{-1} for the highest removal of heavy metals in optimum pH from fresh leachate, respectively. These results are mainly due to the fact that the optimum coagulant dosage produced flocs that have a good structure and consistency. But in dosages lower and higher than optimum dosages, the produced flocs are small and influence on settling velocity of the sludge. In addition, small size of flocs and re stability of flocs can be happened in this cases. The similar trend and results reported in the literature (Trebouet *et al*., 2001; Wang *et al*., 2002a, b; Rivas *et al*., 2004; Bila *et al*., 2005). However, in some studies, effective dose was less and efficiency was higher than this research, in the reason that leachate used in this study had more pollutants than leachates used in previously studies. For example, Wang *et al*. (2002a,b) reported that effective dose of ferric chloride for the removal of COD in landfill leachate was 500 mg L^{-1} (Wang *et al*., 2002a, b). Amuda (2006) observed that the removal of COD increased with increasing concentration of $FeCl_3$. The highest value (37 %) of COD was obtained using a Fe^{3+} dosage of 1000 mg L^{-1} (Amuda, 2006).

A comparison between alum and ferric chloride for removal of COD and heavy metals in optimum conditions revealed that the removal efficiency of heavy metals and COD by alum were 77-91 and 21%, respectively. While by ferric chloride were 68-85.5 and 28%, respectively. Also residues of heavy metals after coagulation with Alum and ferric chloride get below standard limits of Iran EPA.

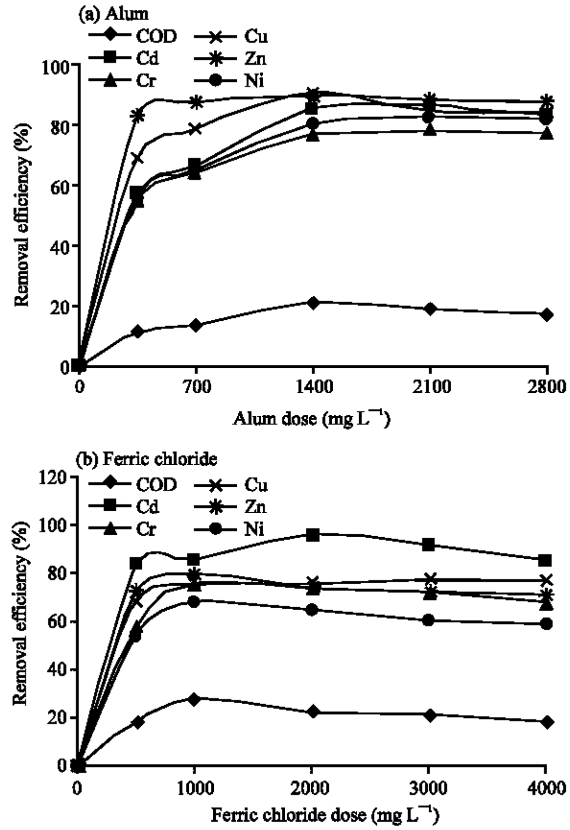

Fig. 2: The effect of coagulant dosages at optimum pH on the removal efficiencies of heavy metals and COD in the leachate. (a) Alum at pH = 6.5 and (b) ferric chloride at pH = 10

Trebouet *et al*. (2001) observed that the optimal amount of ferric chloride allowing the best COD removal in stabilized leachate treatment was in the range of 1-1.5 g Fe/l, depending on the sample characteristics. The COD reduction was in the range of 50-55% (Trebouet *et al*., 2001). Bila *et al*. (2005) reported that COD removal for both $Al_2(SO_4)_3$ and $FeCl_3$ reached around 40%. And also they observed that the pH is the parameter that most influences the coagulation/flocculation process, since for high pH, COD removal was around 15% (Bila *et al*., 2005). As a result, coagulant dosages used in leachate treatment processes are controlled by the concentration of pollutants especially organic matter, which is generally higher in fresh leachate samples (Kang *et al*., 2002). Tatsi *et al*. (2003) revealed that the addition of ferric chloride to fresh leachates resulted in low COD removal rates, ranging 20-25%. They were found that the removal of COD was maintained almost constant with the coagulant dosage. And also the addition of alum to leachate samples resulted in COD reduction, when aluminum dosages were in the range of 0.8-1.5 g L^{-1}, whereas for higher dosages, further COD reduction was not observed. The maximum COD reduction was 38% and this was achieved for fresh leachates, using an aluminum dosage of about 1.5 g L^{-1}. However, COD removal capacities were found to be lower for fresh leachates than for stabilized ones (Tatsi *et al*., 2003).

The pH values of treated samples were decreased, when the coagulants were added, towards the value of about 5.0. The explanation for this decrease can be devoted to the acidic character of Fe^{+3} or Al^{+3} cations (both Lewis acids). Under acidic conditions, hydrolysis is taking place, resulting to the formation of metal hydroxide precipitates, with the general formula $Me\ (OH)_3$.

Furthermore, comparing the results of experiments, it can be observed that ferric chloride was more efficient than alum for the removal of COD. However, alum was slightly more efficient than ferric chloride for the removal of heavy metals. Especially at higher pH values, hydrous iron hydroxides are precipitating in greater degree than the corresponding alum flocs, resulting in more efficient removal of pollutants, than that obtained at lower pH values.

The advantages of the proposed coagulation-flocculation method for the treatment of leachates are mainly simplicity, low cost, good removal efficiencies and easy on site implementation. This method could be used for pre- or post-leachate treatment in combination with biological treatment process. As a result of the apparent inability of the method for sufficient pollutant removal, the cost of the high chemical dosages that are required and the associated problems of the chemical sludge that is generated, it could be suggested that no single leachate treatment method, biological or physicochemical, is able to produce an effluent with acceptable quality and that both approaches should be appropriately combined.

Anyhow, the residual heavy metals concentration in treated leachate (supernatant) were below the limit values recommended by Iran EPA guidelines for effluent discharge in the sewer and USEPA guidelines for water irrigation and agricultural standards. But COD concentration exceeds the above guideline values.

CONCLUSIONS

Experiments to treat raw leachate collected from Esfahan composting plant (Iran) by coagulation and flocculation process has been carried out using Jar test technique at ambient temperature. The major findings are as the following: raw leachates were characterized by low pH values and high concentration of heavy metals and COD. The relative abundance of heavy metals in the fresh leachate samples followed the order: Zn <Ni < Cr <Cu <Cd. The concentrations of heavy metals in leachate exceed Iran EPA guideline values for effluent discharge in the sewer and USEPA guideline for water irrigation and agricultural standards.

Treatment of fresh leachate using coagulation and flocculation process was affected by pH and coagulant dosages. The optimum pH of two coagulants for leachate treatment was 6.5 and 10, for alum and ferric chloride, respectively. Also the effective dosages of alum and ferric chloride were 1.4 and 1 g L^{-1}, respectively for the best efficiency of heavy metals and COD removal.

The maximum amount (in the optimum conditions) of COD and heavy metals that could be removed by the ferric chloride was about 68-85.5 and 28% of the initial value, respectively. The maximum amount (in the optimum conditions) of COD and heavy metals that could be removed by the alum was about 77-91 and 21% of the initial value, respectively.

The treated leachate meets the guideline recommended by Iran EPA guideline values for effluent discharge in the sewer and USEPA guideline for water irrigation and agricultural standards in view of heavy metals concentration except COD. Although in view of efficiency of removal, alum was better than ferric chloride, but in view of economic aspects ferric chloride is better.

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