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Assessment of Raw Leachate Characteristics and Its Pretreatment by Lime

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The aims of this research are to determine heavy metals (Ni, Cd, Cr, Zn and Cu) and COD concentration in municipal solid waste leachate in Isfahan city (Iran) and to examine the application of precipitation process for pretreatment of raw leachates. Jar-test technique was employed in order to determine the optimum dosages and pH for the removal of COD and heavy metals. Lime was tested as precipitant. The results showed that leachate pH was 4.2-6.8 mgL^{-1} and the average was 5.25 ± 0.53 mg L^{-1}. The mean concentration of COD, total solids, Cd, Cr, Cu, Zn and Ni in raw leachate samples was 40157 ± 6052, 41025 ± 5985, 0.63 ± 0.64, 1.22 ± 0.91, 2.15 ± 1.71, 7.42 ± 5.78 and 2.22 ± 1.48 as mg L^{-1}, respectively. The concentration of measured pollutants was more than effluent standard limits of Iran EPA. The results of precipitation tests in optimum conditions showed that the removal efficiencies of heavy metals and COD were 79-88 % and 25 %, respectively. Also the residues of heavy metals after treatment get to under of guideline limits. The results have indicated optimum pH was 9.5. Also the effective coagulant dosage was 2.4 g L^{-1}. So, lime may be used as a useful pre-treatment step, especially for fresh leachates.

Key Words: Precipitation, Leachate treatment, Pretreatment, Solid waste.

INTRODUCTION

Leachate may be defined as liquid that has percolated through solid waste and extracted dissolved or suspended materials. The chemical composition and quantity of leachate may vary greatly depending on the solid waste composition, age of landfill and time of sampling[1]. Leachate is highly variable and heterogeneous[2]. Leachate produced in the early stages of decomposition of waste is typically generated under aerobic conditions producing a complex solution with near neutral pH. This stage generally only lasts a few days or weeks and is relatively unimportant in terms of leachate quality. As decomposition processes develop, waste becomes anaerobic. At the early anaerobic stage, leachate develops high concentrations of

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soluble degradable organic compounds and a weak to strong acidic pH. Metal concentrations also rise during this phase. Even small quantities of this high-strength leachate can cause serious damage to surface water receptors. After several months or years, methanogenic conditions are established and leachate becomes neutral or slightly alkaline, of lower overall concentration but still containing significant quantities of some pollutants[3].

Leachates from municipal solid waste landfill sites are classified as hazardous waste water because it contains a large number of compounds (organic and inorganic constituents such as heavy metals)[4], some of which can be expected to create a threat to health and nature if released into the natural environment. Therefore, the leachate must be treated before discharging. The treatment process or processes selected will depend to a large extent on the contaminants to be removed. In general, inorganic constituents are removed from leachate first, before the organic constituents. This protects the biological, absorption and stripping processes from problems caused by the metal's toxicity, corrosives and scaling. Because of the large fluctuations in leachate composition, the typical leachate treatment process always begins with equalization and followed by precipitation. Precipitation process is the most common method of removing soluble metals and many anionic species. In this process, the metals are precipitated as hydroxides, sulfides and carbonates by adding appropriate precipitant and adjusting the pH to favour insolubility. Although, sulfite precipitation can be had better removal efficiencies, 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 dosages, pH and rapid mix requirements is determined by laboratory test jar studies[5].

Several studies have been reported on the examination of precipitation for the treatment of landfill leachates. Aluminum and iron salts as well as lime were commonly used as coagulants. For old landfill leachates, coagulation and flocculation can be expected to remove between 10 and 25 % of COD and TOC[6]. Another study showed that alum removed 23-27 % of COD from leachate[7].

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[6,8]. Lime as a precipitating agent can reduce colour up to 85 % and remove metals through precipitation. Researchers reported that precipitation using lime could remove organic matter with high molecular weight greater. Nevertheless, the precipitation process has been mainly investigated by using stabilized landfill leachates for removal of organic matter and solids. Authors have investigated efficiency of alum and ferric chloride in raw leachate treatment in previous research[5]. However, there is limited information on the efficiency of lime for leachate pretreatment before discharging and applying in agricultural, when applied for the removal of pollutants from raw leachates.

There are four large transfer stations in Isfahan city of Iran that collect and transport municipal solid wastes to composting plant and landfill site. The transfer stations are the common applications in management of municipal solid wastes. One of main problems of transfer station is leachate production during collection, transfer and transport processing due to biological and chemical activity. These leachates enter to reservation and septic tanks and then transfer to agricultural farms by tanker vehicles. The discharge of municipal solid waste 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[9,10]. Therefore, the main aims of the present work are to investigate the raw leachate quality in the four main transfer stations in Isfahan city of Iran and pretreatment through precipitation using lime, especially for organic matter and heavy metals removal. More specifically, the aim is the determination of precipitation optimum conditions (optimum dosage and pH).

EXPERIMENTAL

Leachate sampling and analytical method: The raw leachate used in this study was collected from municipal transfer stations of Isfahan city. Leachate samples were regularly collected ten times (monthly), transported to the laboratory in 20 L plastic carboys and stored at 4 ºC. The following parameters were systematically monitored: Chemical oxygen demand (COD), total solids (TS), total suspended solids (TSS) and volatile suspended solids (VSS) (according to the methodology described in APHA), pH and heavy metals (Zn, Cr, Cu, Ni, Pb). The leachate samples were digested according to standard methods to release its heavy metal contents and analyses were carried using atomic absorption spectrophotometer. The analytical procedures used in this study were also those recommended by APHA in standard methods for water and wastewater[11].

Precipitation process tests: As stated, lime [$Ca(OH)_2$] was used as precipitating agent. The laboratory jar test apparatus with 6 beakers was used for precipitation processes. Processes included rapid mixing (for 3 min at 120 rpm), slow mixing or flocculation (for 15 min at 20 rpm) and followed by the settling for 45 min. 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 lime was added into the beakers and the pH values were immediately adjusted to the desired levels by the addition of appropriate amounts of acidic or base solutions. The experimental process consisted of three subsequent stages as mentioned[5,12]. In order to determination of optimum dose of lime on removal efficiency, different concentrations (0 to 200 % of initial dosage at stable pH) such as 0, 1.2, 2.4, 4.8, 7.2, 9.6 g/L of lime were added to 1 L leachate sample. The pH was adjusted between 7 and

11 for determination of the optimum pH or pH effect on the efficiency process prior to tests. After the settling period, the supernatant was withdrawn from the beaker and was used for chemical analysis. The supernatant was analyzed for consi-dered parameters. All chemical agents used for the analytical determinations were of analytical grade.

RESULTS AND DISCUSSION

The results have been compiled into four groups: (i) Raw leachate characteristics; (ii) Influence of pH on precipitation process; (iii) Influence of coagulant dosage on precipitation process and (iv) heavy metals content in treated leachate.

Raw leachate characteristics: The survey showed that the total average amount of solid waste collected in Isfahan and its suburb municipality was estimated to 800 tons daily. These solid wastes were generated from residential and commercial sources. An average and range value of leachate characteristics is presented in Table-1. Organics concentration (expressed as COD) varied between 23850 and 56450 mg/L with a mean value of 40157 ± 6052 mg L^{-1} mg/l, which is significantly higher than what has been reported in previous studies[3,13,14]. pH values in leachate showed a nearly acidic phase with variation between 4.2 and 6.8 and average value was 5.25 ± 0.53. Investigated heavy metals were high concentration. For example, Cd had the minimum concentration with 0.63 ± 0.64 mg L^{-1} and Zn had the maximum concentration with 7.42 ± 5.78 mg L^{-1}. The contents of heavy metals in this particular leachate were already upper local wastewater discharge standards.

TABLE-1
COMPOSITION OF THE INVESTIGATED SOLID WASTES LEACHATE

Parameter*	Minimum (mg L^{-1})	Maximum (mg L^{-1})	Average (mg L^{-1})	Standard deviation
pH	4.2	6.8	5.25	0.53
Chemical oxygen demand (COD)	23850	56450	40157	6052
Total solids (TS)	21275	48924	41025	5985
Total volatile solids (TVS)	12200	33780	24589	4330
Total fixed solids (TFS)	7230	23964	16436	4296
Cadmium	0.06	2.10	0.63	0.64
Total chromium	0.16	4.11	1.22	0.91
Copper	0.22	7.12	2.15	1.71
Zinc	0.57	39.27	7.42	5.78
Nickel	0.37	7.87	2.22	1.48

*Units in mg L^{-1} except pH without unit.

The variation of leachate characteristics were attributed to variations in the composition of deposited solid wastes, moisture and decomposition. This result indicated that sources of Zn in solid wastes are more than Cd and the others. So, this leachate displayed high concentrations of contaminants and classified as fresh or raw leachate[1,5]. Comparing the results of this study with parameters previously identified as characteristic for the acid and the methanogenic transformation phases of municipal landfills indicates that the samples were collected in this study representing the beginning acid phase[13]. However, similar values reported in leachate from new site[2]. Similar relative abundances and heavy metal concentration levels have also been reported by other investigators[15,16]. The study in the landfill leachate of Sant'Agostino landfill, in Italy showed the Cr, Zn and Pb concentrations were equal to 0.13-0.36, 0.1-0.5 and 0.05-1 mg L^{-1}, respectively[17]. Ehrig[18] showed that freshly produced landfill leachates are usually high-strength wastewaters, characterized by low pH values (5 ± 6), high BOD_5 (4000 ± 13,000 mg L^{-1}) and COD (10,000-60,000 mg L^{-1}) values, as well as by the presence of several other toxic/hazardous compounds.

In the literature, there have been reported a considerable variation in the quality of leachate produced from different landfills in the world. In previous studies, it is concluded that leachate from young landfill is characterized by high COD, even several thousands of mg/L, while in leachate from old landfill COD concentrations are below a few hundreds mg/L[2].

Influence of pH on precipitation process: The aims of the precipitation process were to remove organic compounds and heavy metals from the raw leachate and determining the optimum conditions. Before determining of the best pH and coagulant dosages, an initial dosage of lime has been denoted based on pre-tests by jar test apparatus. An initial dose denoted by adding lime while observed to formed floc. Dosage that floc observed to select the initial dosage. The initial dosage of lime was be obtained 4.8 g L^{-1}. The first series of experiments was devoted to examine the effect of the pH values on the precipitation efficiency. 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[5]: (1) between H^+ and metal hydrolysis products for interaction with organic ligands and (2) between OH^- and organic anions for interaction with metal hydrolysis products. At low pH values, H^+ 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 by co-precipitation[8]. Bila *et al.*[19] observed that the pH is the parameter that most influences the coagulation/flocculation process, since for high pH, COD removal was more. 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.

The results obtained have been plotted in Fig. 1. The pH of initial samples was varied between 7.0 and 11.0. As shown in Fig. 1, the removal efficiency of precipitation is as a function of pH. Removal percent of COD varied from 10 to 25 %. The same observation was reported by other workers[7,8,15,19,20]. Amokrane *et al.*[6] reported that precipitation of older leachates can be expected to remove between 10 and 25 % of COD by using alum[6] and Silva *et al.*[7] reported 23-27 % of COD removal. Generally, most researchers were reported that the removal efficiency of COD varying from 10 to 25 %[7,8,15,19,20]. In practice, Fig. 1 indicates that the optimum pH for the best removal of COD and heavy metal was 9.5. 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[20]. Besides, precipitation of flocs at this pH was more and better than the other pH. Therefore, pH 9.5 was optimum pH for leachate pretreatment with lime.

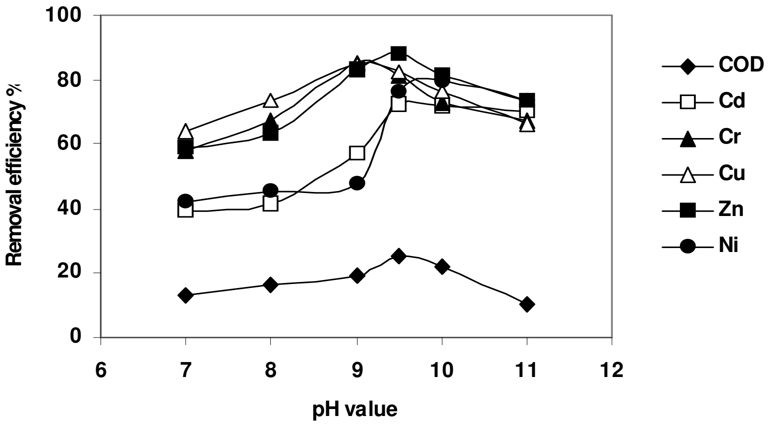

Fig. 1. Influence of pH on the leachate treatment using lime with 4.8 g L^{-1} initial concentration

Influence of coagulant dosage on precipitation process: The influence of different dosages of lime on the removal of COD and heavy metals by precipitation is shown in Fig. 2. The removal of COD and heavy metals increased with increasing concentration of lime. It was observed that when the dose of lime was greater than 2.4 g L^{-1}, the removal increased slowly. Thus, the optimum dose was 2.4 g L^{-1} for the highest removal of heavy metals in optimum pH from fresh leachate. These results are mainly due to the fact that the optimum precipitant 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 restability of flocs can be happened in this cases. The similar trend and results reported in the literature[15,16,19,20]. 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 previous studies. For example, Salem *et al.*[3] reported that the lime dose of 2.5 g/L is sufficient to provide the best effectiveness of lime precipitation not only for metals removal but also for the colour. They suggested chemical

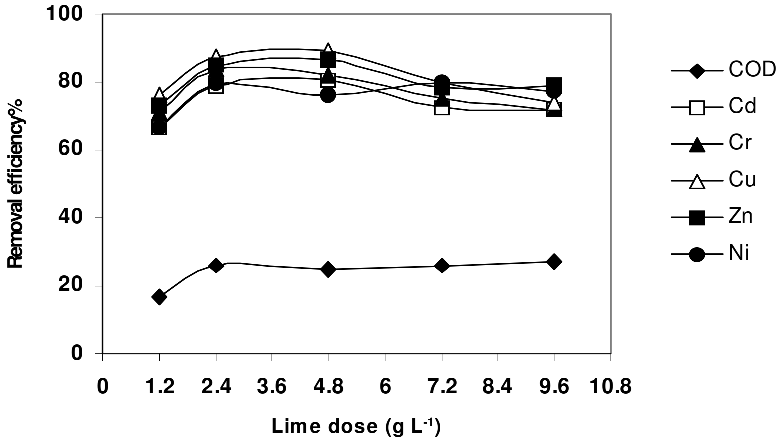

Fig. 2. Influence of lime dosages on the leachate pretreatment (pH = 9.5)

precipitation to avoid metal pollution effects on the future biological treatment plant because of chromium, iron and lead important concentrations. The chemical precipitation for leachate mainly makes use of lime because of its low cost and availability. However, Kurniawan *et al.*[21] showed that 8 g/L of lime was found to be reasonably effective for metal precipitation in stabilized leachate. In addition to lime addition, pH adjustment to 11.0 was suggested as a means to enhance metal precipitation. Amuda[9] observed that the removal of COD increased with increasing concentration of coagulant.

The pH values of treated samples were decreased, when the precipitants were added, towards the value of *ca.* 5.0. The explanation for this decrease can be devoted to the acidic character of Ca^{2+} cations. Under acidic conditions, hydrolysis is taking place, resulting to the formation of metal hydroxide precipitates[5].

Due to its capability, the simplicity of the process and inexpensive equipment employed, chemical precipitation has been employed for the removal of non-biodegradable organic compounds and heavy metals from municipal solid wastes leachate. During chemical precipitation, dissolved ions in the solution are converted to the insoluble solid phase *via* chemical reactions. Typically, the metal precipitate from the solution is in the form of hydroxide. Furthermore, since COD was not significantly removed during the treatment using lime precipitation, biological steps needed to be conducted after precipitation to reduce the organic loading of leachate. In other words, this process could be used for pretreatment 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 physico-chemical, is able to produce an effluent with acceptable quality and that both approaches should be appropriately combined.

Heavy metals content in treated leachate: Comparison of the residual heavy metals concentration in treated leachate (supernatant) in optimum condition of pH and coagulant dose with FAO and Iranian guidelines[22] have been shown in Table-2. It was shown that the residual heavy metals concentration in treated leachate was low. Anyhow, the residual heavy metals concentration in treated leachate were below the limit values recommended by Iran EPA guidelines for effluent discharge in the river, agricultural irrigation and disposal in well. However, in some case was upper the limit values for agricultural irrigation recommended by FAO. From the viewpoint of COD concentration, it exceeds the above guideline values. Thus it doesn't advise to use before biological treatment.

TABLE-2
RESIDUAL HEAVY METALS CONCENTRATION IN TREATED LEACHATE IN OPTIMUM CONDITION AND COMPARED TO GUIDELINES

Heavy metal*	Residual concentration in treated leachate (mg L^{-1})	Maximum level for recommended by Iranian EPA (mg L^{-1}) [Ref. 22]			Maximum level for recommended by FAO (mg L^{-1}) [Ref. 22]
		Agricultural irrigation	Dispose in well	Discharge to rivers	
Cd	<0.06	0.05	0.1	0.1	0.01
Cr	<0.50	2.00	2.0	2.0	0.10
Cu	<0.60	0.20	1.0	1.0	0.20
Zn	<1.20	2.00	2.0	2.0	2.00
Ni	<1.00	2.00	2.0	2.0	–

*It is noted that total chromium measured in treated leachate but standard values only indicate of Cr^{3+}.

Conclusion

From this work, the following conclusions are made:

• The overall conclusion from this study is that lime can be used as good precipitant for metal removal from raw leachate. To avoid metal pollution effects on environment and biological treatment, it is suggested that lime is best and low cost chemical precipitant. The lime dose of 2.4 g/L is sufficient to provide the best effectiveness of lime precipitation for metals removal. The optimum pH was 9.5. Using this process, about 25 % COD and 79-88 % of heavy metals were removed. Present study addressed on metal and COD removal, thus additional researches are required in order to optimize the precipitation process for BOD and TOC removal.

• Municipal solid wastes leachates from transfer stations were characterized by low pH values and high concentration of heavy metals and COD. The concentrations of heavy metals in leachate exceed guideline values for effluent discharge. However, the pretreated leachate by lime meets the guideline values for effluent discharge in view of heavy metals concentration except COD.

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