



Treatment of landfill leachate using a combined Coagulation and modify bentonite adsorption processes

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Abstract Sanitary landfilling is the common way to dispose municipal solid wastes. In the operations, leachate treatment is a difficult and expensive process. This experimental study was conducted to investigate the effect Combination of coagulation and with modify bentonite absorbed process in leachate treatment.

This study was conducted experimentally in the lab scale. The results showed that Maximum COD removal rates for 55% in coagulation For the PAC pretreated leachate, the maximum COD removal is 69% using modify bentonite adsorbent with optimum dose of 0.5 g/L. Therefore combination of coagulation and adsorbed is sufficient for treatment of this leachate such as bentonite adsorption should be applied.

Keywords Leachate, coagulation, adsorbent, bentonite, treatment.

Introduction

Landfilling is one of the most important methods for disposal of solid waste in many countries. One of the most obvious problems associated with the landfilling practice is the generation of leachate. Leachate is created while water penetrates through the waste in a landfill, carrying some forms of pollutants. Leachate pollution is the result of biological, chemical and physical processes in landfills combined with waste composition and landfill water regime [1]. Leachate is commonly generated from precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through the landfill [1-2]. It can usually contain both dissolved and suspended material. The characteristics of landfill leachate depend on several parameters such as design of landfill site, climate, and type of decomposed MSW at landfill site, moisture content, landfill age, pH, BOD5/COD ratio and the stage of decomposition in the landfill [2-3].

Solid waste landfills may cause severe environmental impacts if leachate and gas emissions are not controlled. Leachate generated in municipal landfill contains large amounts of organic and inorganic contaminants [4]. Leachate may also have a high concentration of metals and contain some hazardous organic chemicals. The removal of organic material based on COD, BOD and ammonium from leachate is the usual prerequisite before discharging the leachates to the environment [5]. The performance of combined treatment of municipal landfill leachate is reviewed. A combination of two physico-chemical treatments can give optimum results in removal of organic compounds leachate, as reflected by a significant decrease of the COD values after treatment. On the other hand, a combination of physico-chemical and biological treatments is required to achieve effective removal of COD with a substantial amount of biodegradable organic matter. [3]. Air stripping, adsorption, and membrane filtration are major physical leachate treatment methods [6-7]; coagulation flocculation, chemical precipitation, and chemical and electrochemical oxidation methods are the common chemical methods used for



the landfill leachate treatment [7, 8]. Thus combination of these two processes may be a promising technology for the treatment of leachate.

adsorption as a surface phenomenon, operated by a fluid mixture of multi-components absorbed to the surface of a solid adsorbent via physical or chemical styles, is believed to be one of the most efficient and promising approaches for landfill leachate treatment [9], And in the adsorption technologies, the adsorbents are considered to be crucial factors, among which activated carbon, [10, 11], coal fly ash and clays [12], are normally used.

One type of montmorillonitic clay, bentonite, is a 2:1 layered aluminosilicate of smectite-type clay, which is composed of two tetrahedral sheets with Si in the cationic sites sandwiching an octahedral Al sheet. The partial substitution of Al^{3+} for the tetrahedral Si^{4+} and Mg^{2+} makes the layers negatively charged, and thus bentonite interacts electrostatically with some metals and cationic polymers. However, natural bentonite exhibited a low adsorption capacity for anionic pollutants due to its negatively charged layers. To enhance the adsorption capacity of bentonite for anionic pollutants, the positively charged polymers were applied to modify bentonite. It is well established that positively charged polymers, for instance, sulfuric acid can be intercalated in bentonite following cation exchange mechanisms [13]. Consequently, natural bentonite is an ineffective sorbent for nonionic organic compounds in wastewater, with a high surface area [14]. The aim of this study is investigate the Combination of Coagulation and adsorbed Processes for Treatment of Landfill Leachate of Zahedan.

Materials and Methods

The leachate sample was provided from landfill site in Zahedan city .The Zahedan sanitary landfill produced with average 340 tons of waste per day. The types of solid waste at landfill were housing, domestic, commercial, industry, institutions, market and construction. A 50 L leachate sample was obtained from a wastewater pond in the landfill site. Then, the sample was transported to the laboratory in sealed plastic barrels and stored refrigerator at 4 °C in accordance with the Standard Methods [15] before being used and analyzed. The characteristics of the raw leachate (RL) are as shown in Table 1.

Chemicals and Analytical Method

All chemicals used were of analytical grade. COD, biological oxygen demand (BOD5), NH_3-N , total suspended solids (TSS), total kjeldahl nitrogen (TKN) and pH were measured according to the Standard Methods for the Examination of Water and Wastewater [15]. The pH was determined by a pH meter (model MIT65) the sample leachate pH was adjusted by adding HCl or NaOH solution, the COD was determined by the dichromate method, colorimetric method at 600 nm with Hach spectrophotometer (HACH DR/5000), NH_3-N was tested by the Nessler's reagent spectrophotometry and the TSS was determined by gravimetric standard method in 103°C to 105°C. TDS and EC were determined by EC meter (model HACH).

Table 1: Zahedan landfill leachate characterisations

Parameter	pH	COD (mg/L)	NH_3-N (mg/L)	BOD5 (mg/L)	TSS (mg/L)	EC ($\mu s/cm$)
Value	6.5	1800	21.5	500	512	13.64

Pretreatment of Leachate by Coagulation Process

Coagulation studies were performed in a conventional jar test apparatus, equipped with six beakers of 1 liter volume. The jar test was carried out: first, pH of samples was adjusted to desired pH (2, 4 ,6, 8, and 10) before the addition Poly aluminum chloride and then the varying coagulant Poly aluminum chloride (PAC) concentrations (50, 150, 200 and 250 mg/L) at room temperature (25 °C) were dosed into 1 L of a leachate sample. The jar test process consists of three steps which is the first rapid mixing stage took place for 3 min at 100 ± 2 rpm; aiming to obtain complete mixing of the coagulant with the leachate to maximize the effectiveness of the destabilization of colloidal particles and to initiate coagulation. Second step is slow mixing for 20 min at 40 ± 2 rpm; the suspension is slowly stirred to increase contact between coagulating particles and to facilitate the development of large flocs. After that, the third step settling stage; mixing is terminated and the flocs are allowed to settle [16]. After that, the supernatant was analyzed for COD concentration according to standard methods [15].



Adsorption Experiments

The clay collected from a zahedan city were washed several times with distilled water .The clay was washed, dried at 105_C for 24 h in drying oven and then screened through a set of sieves to get geometrical size 50–315 mm. The activation was carried out using Sulfuric acid solution, where part of the sample was soaked in Sulfuric acid solution for 24 h. After, the samples were paralyzed in a muffle furnace in absence of air at 600°C for 1 h. The modify bentonite Sulfuric acid used in these experiments can be described structurally as in Table 2. Therefore, the pH of supernatant was first adjusted to 5.5 as suggested by previous study done at the laboratory. The modified bentonite was added into 1000 ml Leachate Then identical mixtures were shaken on orbital shaker at 130 rpm for 60 min. The supernatant was filtered through Wattmann 40 filter paper before COD analysis [17].

Table 2: Chemical analysis of modified bentonite clay with acid

Conc. (% w/w)	Chemical Formula	Combine Name
25	SiO ₂	Cristobalite
29	Al ₂ (SO ₄)16H ₂ O	Aluminum sulfate hydrate
18	SiO ₂	Quartz
9	Na(AL,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ZH ₂ O	Montmorillonite
10.1	Na-Ca-AL-Mg-Si-O-H ₂ O	Hydrated silicate of sodium, calcium, Magnesium, aluminum

The removal efficiency and sorption capacity of the bentonite were determined by Eq. (1) and (2), respectively [18]:

$$Q_e = \frac{(C_0 - C_e)V}{M}$$

$$RE = \left[\frac{C_0 - C_t}{C_0} \right] \times 100$$

Where; R (%) and qe (mg/g) are the removal efficiency and adsorption capacity, respectively. Co (mg/L) is the initial COD concentration, Ce (mg/L) is COD concentration at the equilibrium, m (g) is the mass of the sorbent and V (L) is the volume of the leachate.

Results and Discussion

Alternative I: Pretreatment with Coagulation

The main characteristics of the partially leachate samples studied in this project are presented in Table 1. Treatment of leachate from landfill was more effective using the physic-chemical process [17].

In the chemical coagulation, the important operating conditions including the presence of inorganic and organic substances in the leachate, pH, and coagulant dose. In agreement with our results, a previous Report showed that low pH values were most suitable for treating mature landfill leachates [19]. Coagulation was then performed using various coagulant dosages at the appropriate pH values. The study shows that Polyaluminum chlorides are most effective at pH equal to 6 [20]. Poly Aluminum Chloride is great power in the removal of organic contaminants and COD [21].

Table 3: Results of experiments with PAC (AL₂ (OH)_n Cl₆)

Jar Test No	PAC Dose (mg /L)	pH	COD (mg/ L)		Removal of COD (%)
			Raw sample	Effluent from pretreatment with PAC	
1	50	6	1800	1275	40
2	150	6	1800	925	48.6
3	200	6	1800	882	50
4	250	6	1800	810	55



The data in Table 3 show that the highest COD removal efficiencies of 55% were achieved at pH 6, 0.25 g /L of PAC. As a result, the COD concentration of the leachate was reduced from about 1800 mg/ L to 810 mg/ L in these conditions. COD removal increased with increasing coagulant dosages up to the optimum dosage. This result is mainly due to the fact that the optimum coagulant dosage produced flocs having a good structure and consistency. But in doses lower than optimum, the produced flocs are small and influence the settling velocity of the sludge. In doses higher than the optimum, in addition to the small size of floc, rest ability of floc can happen.

Alternative II: Chemical coagulation +modify bentonite adsorption

Over the last few years, adsorption process, a surface phenomenon by which a multi-components fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes [22]. In most cases, bentonite adsorption has revealed the prominence in removal an essential amount of organic compounds from the leachate samples. Aggregate organic constituents are generally indicated by chemical oxygen demand or COD. **Table 4** shows of COD adsorption on modify bentonite. Removal of COD in the pretreated leachate by PAC coagulation (COD = 810 mg/L; pH = 6) has been carried out by adsorption process using modify bentonite from **Table 4** it was found COD removal is of 63.9% was obtained at 60 min.

Table 4: Results of experiments with Chemical coagulation +modify bentonite adsorption

Treatment Alternative	Pretreatment		Chemical coagulation followed by bentonite adsorption						
Parameter	pH	PAC Dose (mg /L)	Effluent COD (mg/ L)	pH	bentonited ose	time	Effluent COD (mg/ L)	Langmuir izoterm	
	6	250	810	2	0.5	60	555	Q^0	R^2
								344.83	0.9605

The solution pH is an important parameter in adsorption processes. Fig. 1 shows the effect of initial pH of solution on the adsorption of leachate by modify bentonite. An investigation of the effect of pH on adsorption of the leachate was carried out at pH range of 2–10. Removal of COD in pH = 2 has been carried out by adsorption process using modified bentonite. The point of zero charge of modified bentonite used in the present study is 6.8 [23]. At pH less than 6.8, the surface of modified bentonite is predominated by positive charges. While at pH greater than 6.8 the surface is predominated by negative charges. The COD removal efficiency is Maximum below the point of zero charge and decreases after the point of zero charge. This is due to repulsion between colloidal organic matter and negatively charged modified bentonite surface. From the Figure 2, it has been observed that the COD removal is 68.8% for 0.5 g/L. the COD removal efficiency decreases by increasing the modified bentonite dose beyond the 1.5 g/L, which is due to the decrease in adsorbent surface area of the adsorbent [24].

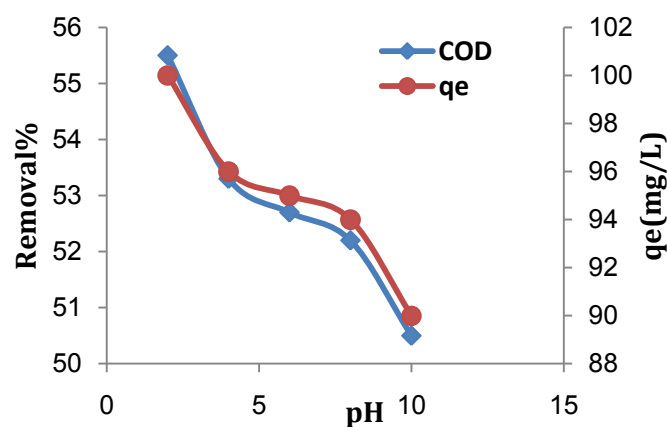


Figure 1: Effect pH on removal efficiency of COD (time = 90 min, dosage 1g/L)



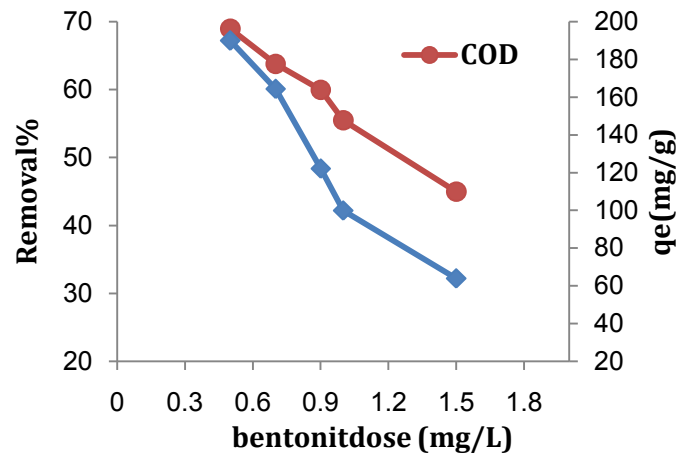


Figure 2: Effect of bentonite concentration on removal efficiency of COD
(time = 90 min, dosage: 0.7g/L, pH = 2)

Adsorption Equilibrium

Langmuir sorption isotherms, which is one of the most widely used models to describe the equilibrium behavior of adsorption was used to correlate the isotherm data in this study. The Langmuir equation is expressed as in Equation 1:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q^0 b} + \frac{C_{eq}}{Q^0}$$

Q_0 and b (Langmuir constant in L/mg) can be determined from the linear plot of C_{eq}/q_{eq} and C_{eq} [25]. The plots of C_{eq}/q_{eq} versus C_{eq} , respectively were found to be linear with a significantly high regression correlation coefficient ($R^2 = 0.9605$) and this coefficient indicates the applicability of the classical maximum adsorption capacity (Q_0) under the experimental conditions was found to be 89.85 mg COD g⁻¹ bentonite in this study (Figure 3). Initial COD: $C_0 = 1800$ mg COD L⁻¹; Effluent COD: $C_e = 650$ mg COD L⁻¹; maximum adsorption capacity after 60 min of contact: $Q_0 = 344.83$ mg COD g⁻¹ bentonite.

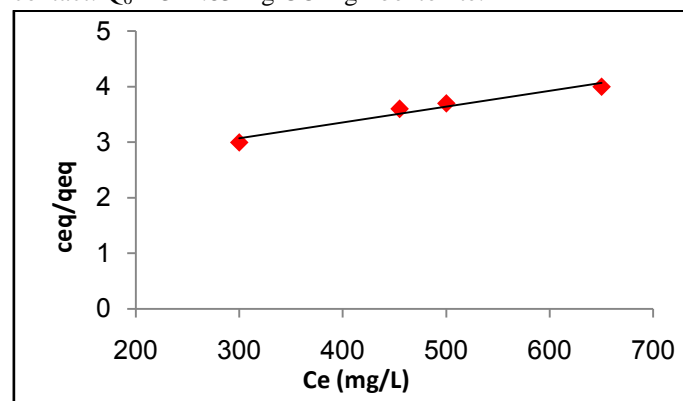


Figure 3: Graphics of Langmuir isotherm

Thereby, the overall COD removal efficiency of 69% has been obtained for leachate by combined coagulation and adsorption process. This indicates that this combination can be used as pretreatment or full treatment of landfill leachate. The adsorption isotherm data were well fitted with the linearized Langmuir model.

Conclusions

The experimental study shows that Combination of coagulation and adsorption process can have high efficiency in treatment of the zahedan landfill leachate.

The optimum of conditions in this study for parameters the COD removal is (as 55% at pH = 6, the PAC concentration of 250 mg/L). Adsorption process is influenced by different parameters. The results of this study indicate that the Adsorption process to Optimum conditions for the operation with pH=2, bentonite



dose=0.5g/Lat time of 60 min can treatment a large impact on the concentration of leachate. Leachate requires efficient treatment techniques prior dispose to the natural environment. Selection of an appropriate efficient treatment technique depends on the quality and age of the landfill leachate.

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