

Original Research

Amino Acid Modified Bentonite Clay as an Eco-Friendly Adsorbent for Landfill Leachate Treatment

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Abstract

Bentonite was modified by intercalation of amino acids into its interlayer space. Different amounts of L-glutamic acid were added to bentonite and its effect was investigated on the reduction of landfill leachate contamination. In the best result, the effect of pH adjustment on the structure and performance of the modified clay was studied. The composite was characterized by various techniques such as FTIR, SEM, XRD, TGA, and BET. Batch experiments were performed to evaluate the factors influencing leachate chemical oxygen demand (COD) and turbidity removal efficiency. The effect of surfactant loading amount, contact time, pH, and adsorbent dosage was evaluated. Under optimum conditions, the maximum COD and turbidity removal rates for row clay were 40.1% and 63.8%, respectively, but they were 65.7% and 92.1% for amino acid-modified clay under pH adjustment conditions, respectively. Also, the results showed that the adsorbent produced in pH adjustment conditions had higher efficiency for leachate treatment than the synthesized adsorbent under non-pH adjustment conditions. Under optimum conditions, the percentage of COD and turbidity removal for modified clay under pH adjustment was 65.7% and 92.1%, respectively, while they were 61.3% and 89.9% for non-pH adjustment, respectively.

Keywords: leachate treatment, adsorption, amino acid, modified clay, bentonite

Introduction

Historically, landfilling has been the oldest form of solid waste management around the world [1] and in many regions due to the simplicity of design and the

low cost of operations, It is still the most common and popular solid waste management strategy [2]. Although this strategy of solid waste management has some advantages, it leads to the production of leachate [3] so that the production of highly contaminated leachate is known as one of the main weaknesses of this type of waste management [4]. Leachate is a liquid that is generated through the percolation of water across the waste layers. This liquid absorbs nutrients and

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pollutants from the waste and accumulates as leachate [5].

Leachate production has become a long-term concern because it releases a wide range of toxic substances, such as heavy metals, inorganic compounds, organic pollutants, and xenobiotic materials [6]. The number of pollutants identified in landfill leachate is much more than those in other parts of the environment including soil, surface water, wastewater, air, and biosolid, which is likely to be associated with the concentration of pollutants in a central location [7]. This dangerous and poisonous leachate affects adjacent areas in the long run [5]. The adverse effects of overloading in susceptible ecosystems have significantly increased the potential of carcinogens were detected in landfill leachates, while these compounds are expected to be sustainable and bioaccumulate [8].

So, leachate treatment and removal of its contaminants have become a major concern in recent decades [5]. Landfill leachate, like wastewater, should be managed during the lifetime of the landfill and also 30 years after its closure [1]. Various methods have been used to remove various contaminations from leachates, such as chemical oxidation, adsorption, chemical precipitation, flocculation and coagulation, aeration/flotation, air stripping, membrane filtration, microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Each of these processes and other methods has its own advantages and disadvantages [5]. At present, the development of conventional techniques is limited due to their high costs, inefficiency, and undesirable rate of removal of contaminants [6].

Adsorption is one of the most effective methods for treating a wide range of wastewater [5]. It is one of the most suitable methods to remove contaminants due to its simplicity of operation, cost-effectiveness, high efficiency, easy adsorbent design, and most importantly, the absence of secondary pollutants during the adsorption process [9].

Commercial adsorbents, such as activated carbon, are very efficient and effective, but they are expensive because of the high costs of production and recovery [10]. Nowadays clay minerals and their modified products are a large family of adsorbents that has now drawn attention because they have relatively low cost and are environmentally friendly [11]. High specific surface area, chemical and mechanical stability, laminar structure, and high ionic exchange capacity have turned clay into super sorbents [12]. These compounds can significantly adsorb different types of contaminants [11]. By removing cations and anions through ion exchange or adsorption, or both, clays play an important role in the environment as a pollutant purifier [12]. Among different types of clay, bentonite is considered as one of the most commonly used adsorbents [10]. We chose bentonite for this study because the bentonite mine was located near the landfill site.

Contaminated water, such as municipal wastewater and landfill leachate, always contains hydrophobic

organic compounds and oxyanions. Therefore, it is essential to develop new adsorbents that can simultaneously remove both of these pollutants from wastewaters [13]. Different studies have focused on improving the properties of clay in order to use it as an adsorbent according to its adsorption capacity [14]. Some studies have suggested that the replacement of inorganic interchangeable cations of clay with organic cations can improve the capacity of these materials to remove organic compounds [15].

So far, various chemical agents have been used to modify clay in order to remove contaminants from water and wastewater. The risk of these chemical modifiers is that they may create a serious environmental pollution problem and they usually need an expensive treatment system for unused or additional chemicals [10]. Therefore, it is essential to functionalize clay in a simple method with non-toxic and biodegradable surfactants. Among many functional organic molecules, amino acids are an attractive species for modifying clay compounds [17]. Amino acids are the building blocks of proteins, and some of them are commercially available at affordable prices [17].

Amino acids have amine and carboxyl functional groups while they have side chains in their molecular structure (except for glycine) [18]. On the other hand, amino acid molecules in the solid-state or solution are zwitterionic compounds that contain chemical groups with both positive and negative charges [16,19]. In both cases, they allow the formation of hydrogen bonds and create a stable ionic form ($R-CH(COO^-)NH_3^+$) [16]. The use of amino acids to modify inorganic compounds has extensively been studied in recent years. Amino acid-modified compounds have been explored in many fields such as the production of pharmaceuticals and agrochemicals, biomedical sensors, and the synthesis of solid-phase peptides [20]. The use of amino acid-modified clay to reduce environmental pollution is another issue that has recently drawn the attention of researchers.

Singh et al. (1996) investigated the effect of citric acid and glycine on the adsorption of Hg^{2+} by kaolinite under different pH conditions. The results of this study showed that glycine, as a chelating agent in kaolinite, is capable of complexing with Hg^{2+} . Two important functional groups, one of the carboxylic group (O-ligand) and the other of the amine group (N-ligand), are responsible for the bonding between Hg^{2+} and modified kaolinite [21]. Shokri et al. (2017) used arginine to modify montmorillonite and remove anionic contaminants. This study showed that the adsorption capacity of the modified clay for anionic contaminants was five times higher than that of the unmodified clay [22]. Shokri and Yegani (2017) used lysine-modified montmorillonite to remove arsenic from water. The results showed that the removal efficiency was 96% in optimum conditions and the composite could be recovered and used up to five times [19]. Khaled El Adraa et al. (2017) used cysteine to modify

montmorillonite and used it to remove heavy metals. The results showed that the modified clay had higher adsorption capacity for the removal of cationic metals such as Cd^{2+} , Hg^{2+} , Pb^{2+} , Co^{2+} and Zn^{2+} than the row clay [23]. Pires et al. (2018) used glycine, arginine, and histidine-modified montmorillonite to adsorb CO_2 to produce biogas fuel. The results showed that histidine and arginine were more potent adsorbents for CO_2/CH_4 removal, and glycine had the lowest CO_2 and CH_4 adsorbent [17].

Since the length of the organic modifier chain has a significant effect on the structure, crystallinity, and nanomechanical properties of the clay polymer composites (PCN) [24], we, therefore, chose a long-chain amino acid as the modifier. For this reason, in this study, among different surfactants with the amine group, L-glutamic acid was used as a promising modifier for bentonite. L-glutamic acid has five carbon chains ($\text{C}_5\text{H}_9\text{O}_4\text{N}$) and is one of the most widely used biological amino acids. Due to its fundamental properties, its application has extensively been studied in various fields of biochemistry, medicine, food, and pharmaceutical industries [25]. But, no study has yet been done on its effects on the removal of contaminants.

The main purpose of the present study was to investigate the effect of L-glutamic acid-modified bentonite on reducing the amount of organic contamination and turbidity of leachate and to explore the structural changes caused by clay modification with L-glutamic acid. The concentration of this surfactant was variable from 0.25 CEC to 3 CEC, and XRD, FTIR, TGA, and BET analyses were used to identify the modified clay. As well, the effect of various parameters such as pH, contact time, and adsorbent

dosage was investigated on reducing the amount of leachate contamination. We modified bentonite with amino acids for the first time to improve the efficiency of the removal of leachate contamination.

Materials and Methods

Landfill Leachate

The leachate samples used in this study were obtained from the evaporation lagoons in the sanitary landfill of Mohammad Abad located 25 km south of Qazvin, Iran. The site covers an area of 110 ha and receives approximately 750 tons of municipal solid waste per day. This landfill has been operating since May 2013 and was expected to have 20 years of life span. The leachate was collected in clean glass bottles and was immediately transported to a laboratory in ice (4°C) and in a dark environment to prevent chemical degradation. The sampling of the leachate was repeated weekly and the average was taken. The characteristics of the landfill leachate samples are presented in Table 1.

Materials

Bentonite was obtained from the Avaj mine in Qazvin province. To remove contaminations and dust, it was washed with deionized water and dried in an oven. The cation exchange capacity (CEC) of the clay was 40 meq/100 g, which was calculated using the copper bisethylenediamine complex method. The composition of the bentonite used in this study is presented in Table 2.

Table 1. Characteristics of the leachate samples.

Parameter	Unit	Average Value	Parameter	Unit	Average Value
COD	mg /L	185907	Lead	ppm	0.5
BOD ₅	mg /L	40500	Zinc	ppm	<1.5
Turbidity		1673	Arsenic	ppm	1.1
pH	-----	7.4	Cadmium	ppm	<0.03
Aluminum	ppm	2.5	Mercury	ppm	<0.6
Cobalt	ppm	<0.5	Total Iron	ppm	12.5
Chromium	ppm	<0.5	Calcium	ppm	10047.6
Copper	ppm	<0.2	Potassium	ppm	3988.97
Manganese	ppm	1.9	Sodium	ppm	9918.4

Table 2. Composition of Bentonite.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	MgO	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
Percentage	67.046	11.72	1.737	3.253	0.95	3.391	3.028	0.138	0.047	0.031	8.6

The amino acid that was used to prepare this organoclay was L-glutamic acid ($C_5H_9NO_4$) with a purity of 99%, which was purchased from Merck Company.

The pH of the leachate was adjusted by adding 1M HCl and NaOH using the WTW pH meter. All other chemicals used were analytical grades and were used without further purification. All solutions were prepared with distilled water.

Purification of Bentonite

To purify the clay, a certain amount of bentonite was dispersed into distilled water and the mixture was agitated by a stirrer at 250 rpm for 24 hours at room temperature. It was then centrifuged for at 4000 rpm 20 minutes. The purified bentonite was then oven-dried at 45°C for 48 hours.

Synthesis of Adsorbent

The ion exchange method was used to modify the clay by replacing the interchangeable cations of bentonite with protonated amino acids. So, 30 g of bentonite was dispersed in 300 ml of deionized water, and the mixture was agitated by a magnetic stirrer for about 30 minutes to swell the clay. In another container, a stoichiometric amount of amino acid was poured in distilled water and the pH of the solution was adjusted to 2 by adding 0.1 molar HCl. To dissolve the amino acid, the solution was stirred at 60°C for about 30 minutes.

To study the effect of pH on the modification of bentonite, the above steps were repeated without pH adjustment. In the absence of pH adjustment, at 3 CEC, the pH of the L-glutamic acid solution was 3.5. Then, the dissolved amino acid was slowly added into the bentonite suspension at 60°C. The mixture was stirred at 60°C for about 4 hours using a magnetic stirrer. Then, the modified bentonite was centrifuged and washed several times with DI water. Washing was repeated several times to remove excess ammonium salts. The final composite was oven-dried at 60°C for 48 hours. The dried organoclay was converted into nanoparticles using a planetary ball mill (120 rpm for 15 hours). The particle size was calculated to be about 27.8 nm by using the Scherrer equation. The final product was stored in a plastic container for later use.

Characterization and Analysis

To characterize the prepared composites, different characterization techniques were used. The surface morphology of the raw and modified bentonite was examined by a scanning electron microscope (FESEM-MIRA3). The functional groups and chemical structure of the nanoclay, was characterized before and after modification by FTIR spectrum in the range 400-4000 cm^{-1} . The IR technique is a basic method for

detecting the position of surfactant molecules loaded in an interlayer space of clay. Structural geometry, crystallinity, and basal spacing (d_{001}) of raw and modified bentonite were determined by using X-ray diffraction. The XRD patterns were recorded at room temperature on a Philips, PW1730 model with Cuka radiation ($\lambda = 1.541874 \text{ \AA}$) at 40 kV and 150 mA in the range of 1-80° and a scan speed of 2°/min. The thermogravimetric analysis of the clay and organoclay was carried out using a TA Instrument Inc. Q600 at a ramp of 10°C/min from room temperature to 1000°C under a high-purity flowing nitrogen atmosphere. Specific

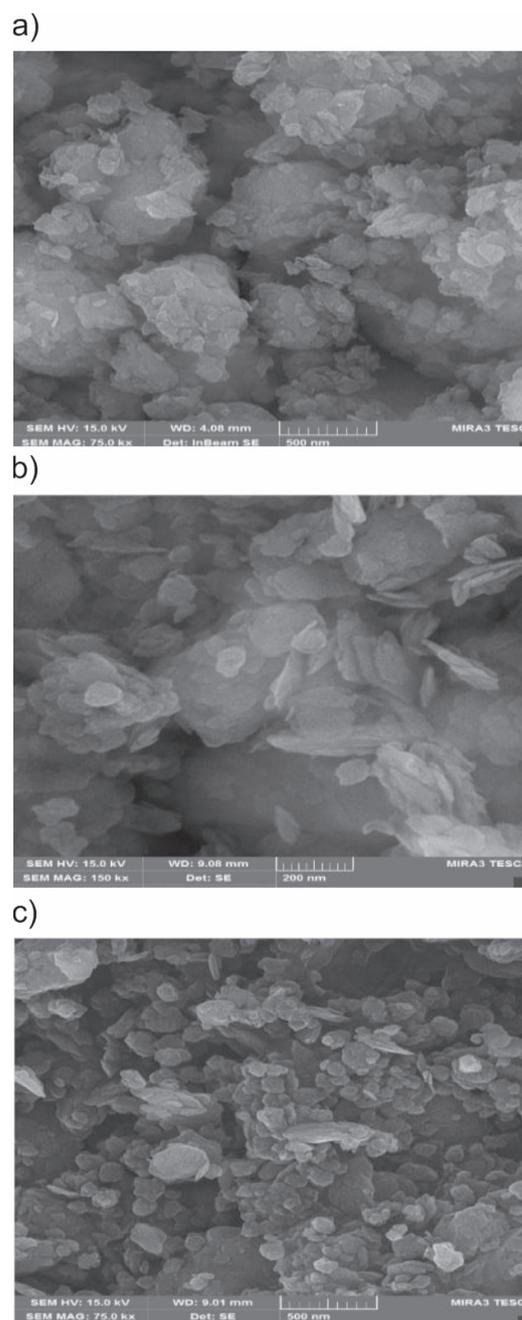


Fig. 1. a) Scanning electron microscopy of bentonite, b) SEM of Glu-bentonite in non-pH conditions, and c) SEM of Glu-bentonite in pH conditions.

surface area, porosity, and average pore diameter were obtained using the Brunauer-Emmett-Teller (BET) method in the presence of N_2 (BEISORP MINI II, Japan). The samples were previously degassed for 12 hours.

Results and Discussion

SEM

The SEM technique was used to illustrate the morphology of the raw and modified clay. Fig. 1 shows the SEM images of the unmodified and modified bentonite. The raw bentonite has bulky and massive morphology. Compared to the raw bentonite, the bentonite modified with L-glutamic acid (in both pH and non-pH conditions) shows more pieces with smaller plates.

On the other hand, Glu-BEN in both pH and non-pH adjustment conditions shows a rougher morphology. This change is influenced by the molecular interactions of the compounds present in the organoclay, so it can be said that after modification, the dense stacking sheets are broken and the sample surface becomes rough [9]. that this confirms our assumption.

Due to the hydrophilic properties of the clay sheets and the hydrophobic properties of the surfactant, it is predicted that severe repulsion will occur between the groups [26]. The presence of amino acids increases the interlayer spacing and creates a more open morphology.

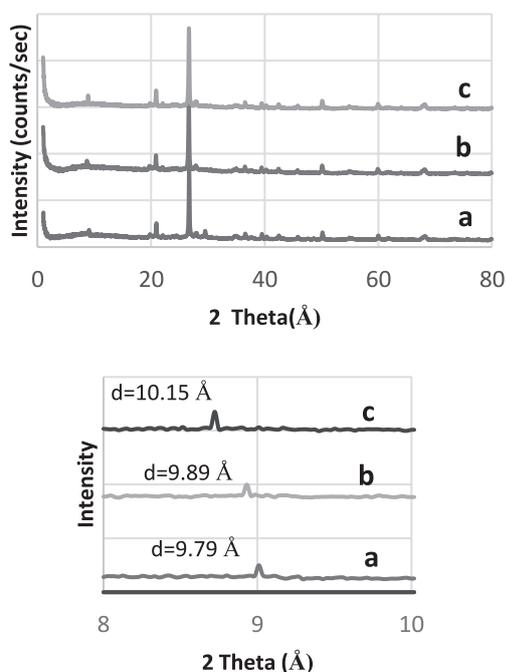


Fig. 2. XRD pattern of a) bentonite, b) bentonite intercalated with L-glutamic acid in non-pH adjustment conditions, and c) bentonite intercalated with L-glutamic acid in pH adjustment conditions.

Therefore, the results of SEM analysis are corroborated by the results of the XRD analysis, which shows an increase in the basal spacing in the modified clay compared to the raw clay. However, determining the exact impact of pH on clay properties requires the use of other techniques such as XRD, FTIR, and BET, and SEM alone cannot reflect this change.

XRD

The XRD pattern of the original and modified bentonite are compared in Fig. 2. Clays are always mixed with non-clay minerals, which can cause intense peaks even in small amount [27]. As shown in Fig. 2, the clay is not pure bentonite. The most intense peak is seen at $2\theta = 26.69$, which is due to the presence of quartz. The results of the XRD diffractogram show that bentonite of the Avaj region is rich in non-clay phases and it consists of four minerals including quartz, calcite, illite, and albite. Bentonite has a basal spacing of about 9.79 \AA which, after functionalization with L-glutamic acid, changes to 10.15 \AA in the pH adjustment conditions and to 9.89 \AA in the non-pH adjusted state. These results indicate that the basal space of bentonite is increased as the pH of synthesis is decreased.

Increasing the basal space is often attributed to the successful loading of amino acid molecules in the interlayer space of clay [22]. However, more evidence is needed to confirm the absorption of amino acid molecules. Because the assumption resulting from the change in the basal spacing obtained from the XRD results does not provide complete information on local conformation and phase state of the loaded amino acid [2]. Therefore, it is necessary to perform TGA and FTIR analyses.

On the other hand, theoretically, the loading mechanism changes the reflection of pages d_{001} to lower angles [28]. This is consistent with the results of the experiments. The results indicate that the peak of pages d_{001} in the raw bentonite is observed at $2\theta = 9.01$, which shifted to $2\theta = 8.70$ after modification by L-glutamic acid under pH adjustment conditions and shifted to $2\theta = 8.93$ under non-pH adjustment conditions. The reason for creating the peaks at lower angles after functionalization is not completely clear, but more than loading can be attributed to the relative purity of clay.

FTIR

FTIR is an essential technique for determining the qualitative characteristics of adsorbent's functional groups [29]. The intercalation of amino acid was investigated by the FTIR spectroscopy. The infrared spectrum of the raw and modified bentonite at $4000\text{-}400 \text{ cm}^{-1}$ wavenumbers is shown in Fig 3. The raw bentonite has bands at $3626, 3401, 2372, 1643, 1439, 1028, 793, 690, 520,$ and 470 cm^{-1} , as depicted in Fig. 3. The internal hydroxyl groups, between the octahedral and tetrahedral layers, are clearly visible at 3626 cm^{-1}

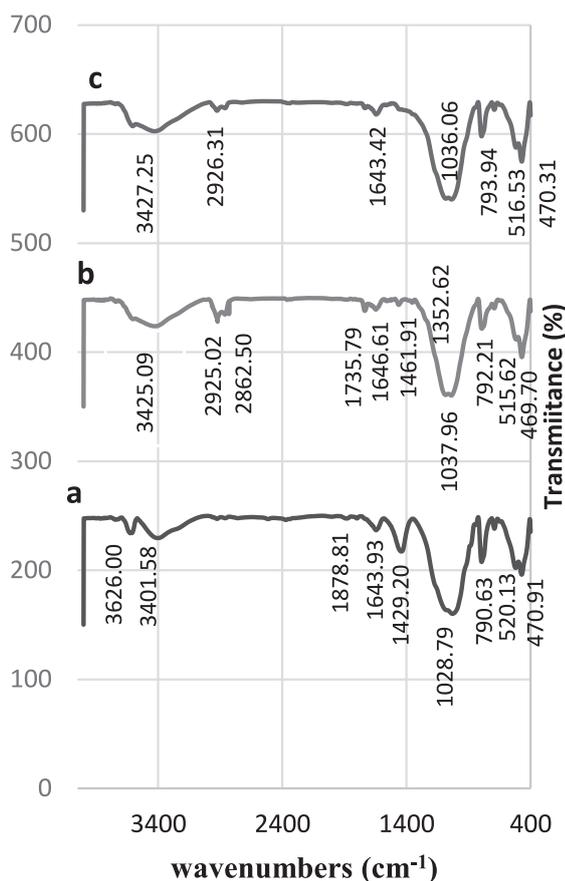


Fig. 3. FTIR pattern of a) bentonite, b) Glu-bentonite in non-pH conditions, and c) Glu-bentonite in pH conditions.

[30]. This band is eliminated after modification with L-glutamic acid in both conditions of pH adjustment and non-pH adjustment. This change is probably due to the fact that water molecules are replaced by loaded amino acids in the interlayer space of clay [14,31]. Removing hydrogen bands in the modified clay indicates the change in surface properties of clay from hydrophilic to hydrophobic [31, 32]. Changing the surface properties of clay from hydrophilic to hydrophobic in the preparation of modified clay may lead to an increase in adsorption capacity to hydrophobic non-ionic contaminations [32].

On the other hand, adsorption bands at 3401 and 1643 cm^{-1} are probably attributed to the -OH stretching and bending vibration, which is related to water molecules adsorbed on the surface of the clay [9,30]. After modification of the clay by amino acid, the intensity of these bands was increased to 3425 and 1646 cm^{-1} for the modified clay in the pH adjustment conditions and to 3427 and 1643 cm^{-1} for the modified clay in the non-pH adjustment conditions.

The presence of carbonate was detected by the band at 1450-1410 cm^{-1} , which confirms the presence of calcite in the sample [30]. In the raw bentonite, this peak was seen at 1439 cm^{-1} but in the clay modified with the amino acid in the pH adjustment conditions, it was shifted to 1461 cm^{-1} and in the non-pH adjustment conditions, it was disappeared.

The bentonite infrared spectrum also has a band at 1028 cm^{-1} , which is attributed to the Si-O-Si bending vibrations [14,23,30]. Quartz bands (Si-O) are close to 790 cm^{-1} [9,14,24,33], and the bands at 520 and 470 cm^{-1} are assigned to the O-Si-O bending vibrations [33].

The modification of clay with L-glutamic acid under the pH adjustment conditions leads to the formation of bands at 2862, 2925, 1735, and 1352 cm^{-1} . However, the clay modification under the non-pH adjustment conditions leads to the appearance of only a new peak at 2926 cm^{-1} .

Bonds at 2862 and 2925 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of CH_2 , respectively [33]. The band at 1735 cm^{-1} refers to the presence of amino acids in the modified clay. This band is attributed to the stretching vibrations of the C=O carboxylic groups in amino acids [17, 34]. The presence of the carboxylic acid group in the clay-amino acid composite is probably due to the hydrogen bond formed between the carboxylic acid and the amine group in the side chain. This finding confirms the stability of the amino acid-modified compounds by hiding the negative charge of carboxylic acid through intermolecular hydrogen bonding [17]. The band at 1352 cm^{-1} is likely to be devoted to the symmetric stretching of CH_3 in the NHCOCH_3 group.

In other words, the FTIR spectrum in Glu-BEN under the pH adjustment conditions shows peaks, which are attributed to both BEN and Glu functional groups in their pristine state. While, under the non-pH adjustment conditions, some Glu peaks are not observed. Notable IR peaks attributed to Glu include the C=O stretching bands, the CH_2 symmetric and asymmetric stretching bands, and the N-H stretching bands. On the other hand, the significant IR peaks attributed to bentonite include the -OH and Si-O and Al-O stretching/bending bands.

TGA

Fig. 4 shows the thermogravimetric (TGA) curve of the raw and modified clay from room temperature to 1000°C under inert conditions. As is evident in the figure, the thermal stability of the unmodified clay is higher than that of the modified clay.

Two stages of mass loss were observed for the raw bentonite. The first stage is from room temperature to about 200°C, which results in a slight decrease in the weight of the clay. This weight loss is attributed to the loss of moisture. After the temperature rises to about 400°C, the weight is almost constant. From 400°C to about 800°C, the weight again decreases due to the dehydroxylation of the clay or the release of interchangeable water coordinated to cations [11, 14, 17, 35].

In the thermogram (Fig. 4), as seen in organoclay, weight loss occurs in three stages in both the pH and non-pH conditions [11, 36]. The first stage is similar to the bentonite and occurs at room temperature up to about 240°C, which is attributed to the loss of absorbed

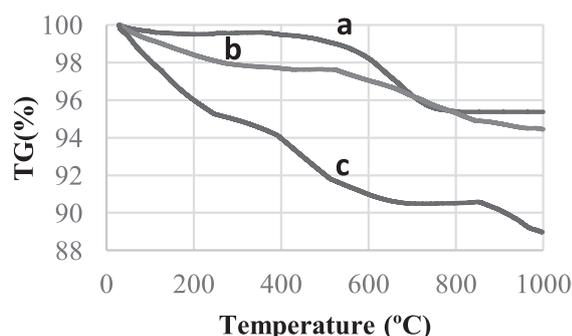


Fig. 4. The TG pattern of a) bentonite, b) Glu-bentonite in non-pH conditions, and c) Glu-bentonite in pH conditions.

Table 3. Contents of the amino acids.

Glu-BEN	pH	Conditions	(wt%) Amino acid content
	2	pH adjusting	5.33
3.5	non-pH adjust	3.7	

surface water [17]. The second stage is from 240°C to 825°C, which can be attributed to the oxidative decomposition of the amino acid [17]. The contents of the amino acid determined from this stage of weight loss are summarized in Table 3. The third stage (above 825°C) is assigned to the loss of structural hydroxyl groups of clay [11, 36].

BET

Specific surface area and porosity of an adsorbent are significant parameters in determining adsorption capacity and the efficiency of an adsorbent [37].

In this study, the Brunauer-Emmet-Teller (BET) analyzer was used to determine the pore size and surface area. Table 4 shows the list of surface area, pore volume (porosity), and the average pore diameter of the raw and modified bentonite in the pH adjustment and non-pH adjustment conditions.

Under the pH adjustment conditions, the modified bentonite has a higher surface area than the raw bentonite. However, in the non-pH adjustment conditions, the specific surface area decreases after modification. This is probably due to the fact that in the non-pH adjustment conditions, the interlayer space of

the clay is blocked by surfactant molecules, which leads to a reduction in the number of active sites available for absorbing N_2 gas [14, 32, 33]. But, in the pH adjustment conditions, new pores are likely to be created which leads to an increase in the specific surface area.

By adding amino acids, pore volume and average pore diameter increase in both the pH and non-pH adjustment conditions. This is the result of the expansion of the interlayer space of the clay by organic compounds and the formation of interlamellar small-diameter pores [32].

For the raw and modified clay, the pore diameter distribution of mesopores can be computed using the BJH (Barret-Joyner-Halenda) method of adsorption branches [9]. The raw and modified clay pores both appear at 1.29 nm.

Adsorption Experiment

Batch adsorption studies were performed to determine the adsorption capacity of the raw and modified clay. In this study, the effect of parameters including the amount of intercalated surfactant (0.25 -3 CEC), contact time (20-100 min), pH (11-2) and adsorbent dosage (10-40gr/L) was investigated on the COD and turbidity removal of the landfill leachate.

All the adsorption studies were carried out in a 100ml beaker, containing 50 ml of landfill leachate and the desired dosage of adsorbent at different pH's and contact times at room temperature and the rotating speed of 150 rpm. At the end of a predetermined time, the suspension was centrifuged at 3500 rpm for 15 minutes and the supernatant was analyzed. To measure the turbidity, a WTW turbidity meter (Turb550) was used. The chemical oxygen demand (COD) was determined a standard method.

All experiments were repeated three times and the average values were considered. The standard deviation for triple tests in all experiments was less than 0.7%. The removal percentage of contaminants (R%) was calculated from the following equation:

$$R(\%) = \frac{C_0 - C_e}{C_0} * 100$$

...where C_0 and C_e are the initial and final concentration, respectively and R is the removal efficiency (COD and turbidity).

Table 4. Textural characteristics of clay and modified clays.

	Surface area S_{BET} (m ² /g)	Total pore Volume (C ³ /g)	Mean diameter (nm)	BJH (nm)
Bentonite	28.981	0.1158	15.982	1.29
Glu-BEN By pH adjusting	30.512	0.1308	17.152	1.29
Glu-BEN Non-pH adjusts	20.678	0.1226	23.709	1.29

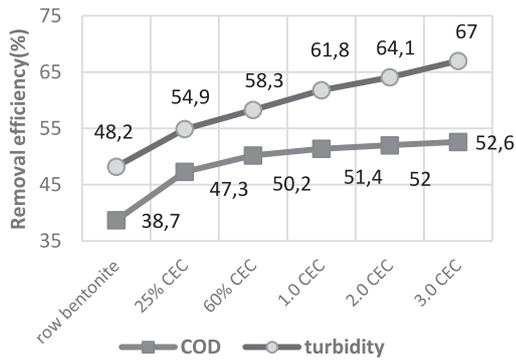


Fig. 5. Optimal amount of modifier.

In this research, the pH of the leachate was adjusted using a 1molar solution of HCl and NaOH.

Determining the Optimal Amount of Modifier

To evaluate the optimal amount of the modifier, the bentonite was intercalated with different values of L-glutamic acid from 0.25 CEC to 3 CEC, and the percentage of COD and turbidity removal of landfill leachate was examined. The results (Fig. 5) showed that the highest removal percentage for both parameters was obtained at 3.0 CEC. It is worth noting that this step was carried out under the non-pH adjusting conditions and after determining the optimal amount of surfactant loaded, the other steps were performed in both the pH adjustment and non-pH adjustment conditions.

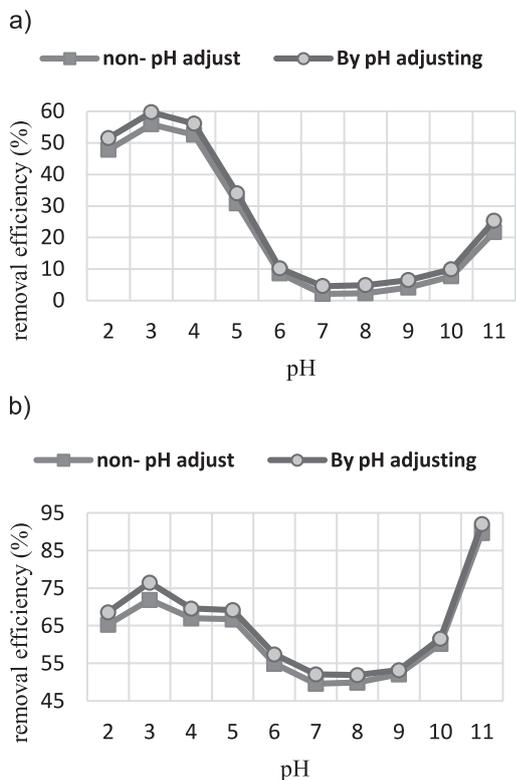


Fig. 6. Effect of pH on a) COD and b) turbidity removal.

Effect of pH

The pH of an aqueous solution is an important factor that can affect adsorption. The pH of an aqueous solution can affect the degree of ionization and the formation of various pollutants, which ultimately changes the reaction kinetics and equilibrium of the adsorbing process [38].

To study the adsorption mechanism, the pH range of 2-11 at 30 minutes and the adsorbent dosage of 40 g/l were used. The effect of pH on the reduction of COD and turbidity with the L-glutamic acid modified clay under the pH adjustment and non-pH adjustment conditions is shown in Fig. 6.

As is evident in Fig. 6, it is clear that the removal of COD and turbidity in both adsorbents depends on the pH value. In both adsorbents, the removal of COD is improved under acidic conditions and reaches its maximum at pH = 3. When the pH rises above 4, adsorption gradually decreases and reaches its minimum at pH = 7. These results can be explained by the surface charge of the clay. In the external surface of the bentonite, siloxane groups (Si-O) and tetrahedral sheets are weaker and converted to Si-O bands, which later become Si-OH with pH changes [29]. As the pH rises to alkalinity, again COD removal gradually increases as precipitation occurs.

In the case of turbidity, the highest removal occurs at pH = 11, which can be attributed to simultaneous adsorption and precipitation. Therefore, pH = 3 for

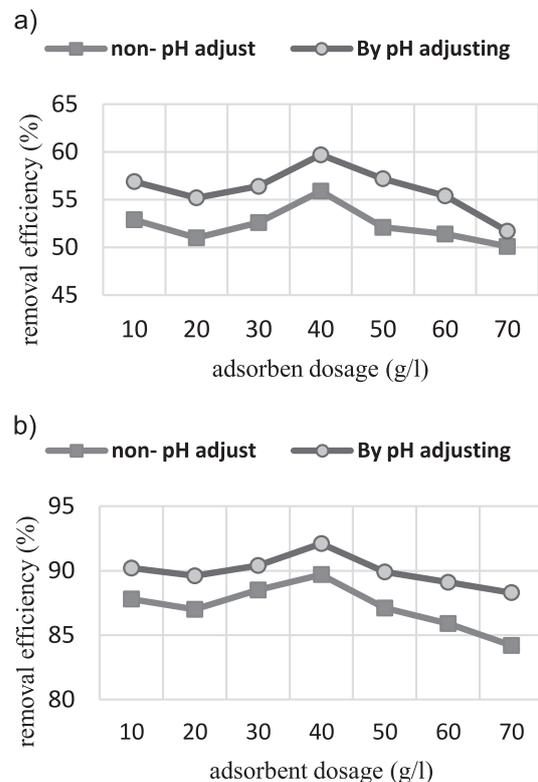


Fig. 7. Effect of adsorbent dosage on a) COD and b) turbidity removal.

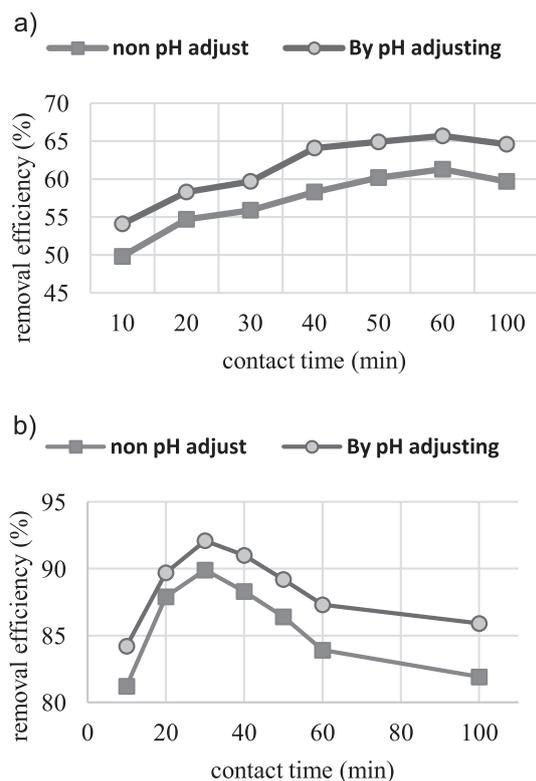


Fig. 8. Effect of contact time on a) COD and b) turbidity removal.

COD and pH = 11 for turbidity were selected for further study.

Effect of Adsorbent Dosage

Fig. 7 displays the effect of adsorbent dosage (in the range of 10-70 gr/L) to reduce COD and turbidity at the optimal pH. It is observed that by increasing the adsorbent dosage, the efficiency of COD and turbidity removal increases for both adsorbents. This can be simply attributed to an increase in the surface area of adsorbents and the availability of more adsorption sites [37].

The COD and turbidity reach its maximum at 40 g/L, and then it decreases with increasing the amount of adsorbent. This decrease may be due to the overlap of the adsorption sites because of the over-crowd of the adsorbent particles [38].

Effect of Contact Time

In any batch system, contact time plays a vital role in COD reduction [39]. As can be seen in Fig. 8, with the increase in contact time, the COD and turbidity removal efficiencies were gradually increased and then stopped after a certain time. The maximum COD reduction efficiency was achieved in 60 min and the maximum turbidity reduction rate was obtained in 30 min. Much more adsorption in the early stages can be attributed to the availability of accessible sites

during the early stage and the remaining empty sites were hard to occupy due to the repulsive forces between the dissolved molecules and solids phase when it comes to equilibrium [40].

Conclusions

In this research, a simple, efficient and environmentally friendly method was used to prepare a natural organoclay. Bentonite was modified by L-glutamic acid under pH adjustment and non-pH adjustment conditions and its effect was studied on reducing the contamination of landfill leachate. The FTIR, XRD, SEM, BET, and TGA analyses confirmed that amino acid was well intercalated on the bentonite. The results of the batch experiments showed that the pH of the solution, the amount of composite, and the contact time affect the COD and turbidity of landfill leachate. The results of the experiments also indicated that the composite prepared under the pH adjustment conditions was a more suitable adsorbent for COD and turbidity removal of landfill leachate compared to modified clay in the non-pH adjustment conditions. The results confirmed that the clay modified by L-glutamic acid could reduce COD and turbidity of landfill leachate. The maximum removal efficiency of COD for amino acid-modified clay under the pH adjusting and non-pH adjusting conditions was 65.7 and 61.3%, respectively, and the maximum removal rate for turbidity in the pH adjusting and non-pH adjusting conditions was 92.1% and 89.9%, respectively under optimum conditions. Due to the low ion exchange capacity of the clay used in this study (40 meq/100 gr), it can be concluded that the removal rate of leachate pollutants increases with the use of high ion exchange clay. These results show that the use of amino acids for organoclay preparation can limit the use of toxic and conventional organic compounds and provide a clean and environmentally friendly technology for the synthesis of nanocomposites. Briefly, L-glutamic acid-modified bentonite can be used as an efficient and economical adsorbent to remove COD and turbidity from landfill leachate.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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