Elimination of orthophosphate from synthetic leachate using adsorption on bentonite clay

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Abstract. The composition of leachates is very variable and rich in toxic compounds, which requires treatment before discharge into the natural environment in order to avoid their impact on the environment and/or human health and to comply with the requirements of regulatory discharge standards in the natural environment. Among the parameters indicating pollution by leachates, we have COD, BOD5, conductivity, pH, the presence of ammonium ions, nitrite, nitrate, chloride, orthophosphate, etc. This study presents the results of synthetic leachate orthophosphate adsorption tests on bentonite clays. For the determination of the orthophosphate concentration in the synthetic leachate, before and after adsorption, we applied the method of Ultra-Violet adsorption spectroscopy. The adsorption capacity of bentonite, the amount needed and the removal efficiency were determined. The orthophosphate adsorption yield on bentonite reaches up to 32.6 % for 5 g/L of bentonite stirred for 4 hours and exceeds 39,19 % after 24 hours of stirring. ***Keywords***: Leachate, Synthetic Leachate, Bentonite, Adsorption, Orthophosphate

1 Introduction

The production of leachate, which is a liquid effluent percolating through the solid waste placed in a landfill or contained in it by becoming chemically and bacteriologically loaded with suspended or dissolved organic and/or inorganic substances, can have a harmful impact on environment and human health [5, 13, 12] This implies treatment, before discharge into the environment or reuse, to avoid environmental and/or sanitary impacts and to respect the requirements of discharge standards [8, 6], on the other hand, the continuous production of leachate poses a serious warning to local waters, both at the surface and at depth. The composition of the leachate varies according to regions and seasons. Climatic factors and the age of the leachate also affect their quality and quantity [1]. So it is necessary to choose a treatment technique that is adaptable to the changes of the leachate characteristics.
Phosphorus pollution is generally represented by total phosphorus (TP) composed of organic phosphorus and orthophosphate (P and PO_4^{3-}) [9]. The level of phosphorus discharge into natural waters is set according to the sensitivity of the receiving environment. Eutrophication is one of the most well-known harmful effects linked to an excessive supply of phosphate in the environment, however, other effects, less reported, act in the long term and can also be detrimental to the health of living beings. . These are the influence of phosphates on soil acidity and the increase in the mobility of trace elements [19]. Indeed, several authors agree on the similarity of the adsorption mechanisms of orthophosphate and arsenate anions on soil minerals [20, 21], a high phosphate content leads to a competition between these two ions in the soil [22]. In general, the recommended values vary around 1 mg/L for total phosphorus and 0.5 mg/L for orthophosphates, for a pH between 6 and 9 [11]. The objective of this study is to perform orthophosphate adsorption tests of synthetic leachate on bentonite clays by studying the parameters affecting the yield.

2 Material and methods

2.1. Characteristics of controlled landfill leachate

The characteristics of leachates are different from landfill to landfill and from region to others, they depend on the composition of wastes, the exploitation method, the age of wastes, and they are also related to changes of seasons. The characterization of leachate is done by analysis of previous physicochemical and biological parameters, such as: COD, BOD, ammonium, chloride, nitrites, nitrates, orthophosphate. The following table

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shows the leachate from the controlled landfill of Al Hoceima characteristics (Table 1).

Table 1: Methods and techniques of characterization of synthetic leachate

Parameter	Units	Method and technique
pH		Hach HQ40d Dual-Input Multiparameter (Electrometric measurement)
COD	mg/L	COD Reactor (HANNA HI 839800) AFNOR NFT 90-101 norm
BOD_5		BOD Measuring System (OxiTop)
Conductivity	$\mu s.cm^{-1}$	Hach HQ40d Dual-Input Multiparameter (Electrical Conductivity)
NO_2^-; PO_4^{3-}; NO_3^-; NH_4^+	mg/L	Molecular Absorption Spectrometry
Cl^-	mg/L	Mohr method (Determination by mercuric nitrate)

The Al Hoceima city controlled landfill is located 6 km southeast of the city and approximately 3.5 km northeast of Izafzafene, it covers an area of 34 Ha. It worked for the first time in 2008 and it receives more than 80t.day-1 of solid wastes from several urban and rural communities: Al Hoceima, Imzouren, Beni Bouayach, Ait Youssef Ouali, Izmouren, and Ait Kamra. Its leachate is young leachate, because of its values of COD that varies from 12365 to 33600 mg/L [10], it is also characterized by the presence of various other important parameters such as chloride which reaches a value up to 7196 mg/L, ammonium which varies between 1921 and 4060 mg/L and an average of 1298.5 mg/L, 383mg/L and 143mg/L of nitrates, nitrites and orthophosphate respectively.

Table 2: Al Hoceima city controlled landfill leachate Characteristics*

Parameters	Min.	Max.	Average	Unit
Temperature	11.5	30.5	21.1	°C
pH	7.2	8.6	7.9	pH
Conductivity	20000	37700	32933.3	µs/cm
COD	12365	33600	19435.5	$mg(O_2)/L$
BOD_5	2881	22501	9802.2	$mg(O_2)/L$
Ammonium	1921	4060	3184.5	mg/L
Nitrite	-	-	383	mg/L
Chloride	4660	7196	5691.5	mg/L
Nitrate	-	-	1298.5	mg/L
Orthophosphate	-	-	143	mg/L

*Data from the controlled landfill of Al Hoceima city 2013-2018

2.2. Physicochemical analysis

The characterization of leachate is done throw several physic-chemical analysis ; Leachate solution samples were taken then diluted respecting the analysis to be performed range. Several physicochemical and biological parameters were analysed to get an idea about the physicochemical and biological characteristics of this leachate. The following table shows the physicochemical and biological parameters analysed, materials, and methods used in this study (Table 2).

2.3. Adsorption treatment

2.3.1. Bentonite clay

Adsorption is a purification technique used to remove a wide range of toxic compounds from our environment. It is mainly intended for the treatment of liquid effluents (leachate, waste water, groundwater, and treatment of drinking water, etc.) and gaseous (air treatment). During this process, molecules, atoms or ions (all considered adsorbates) are retained on the surface of a solid material (considered an adsorbent).

This method is based on the phenomenon of mass transfer due to the different interactions between the molecules (of the aqueous or gaseous phase) and the surface of the adsorbent [14, 15].

Adsorption is considered as a technique of choice, in water treatment, for the elimination of dissolved elements [16]. It depends essentially on the nature of the solid and the solute. Some solids have adsorbent properties on several bodies [17, 18].

Others, on the contrary, have quite marked specificities. Among the adsorbents used, we can mention: activated charcoal, cabbage, sawdust, bentonite, etc. This study is interested in the adsorption on bentonite clay, which is a clay endowed with surface properties.

The bentonite used during our work was extracted from the Nador deposit (East region). It is characterized by high absorption, ion exchange and swelling capacity, as well as special rheological properties.

2.3.2. Orthophosphate reduction test by adsorption in leachate

This study evaluates the adsorption efficiency of orthophosphate (PO_4^{3-}) ions in synthetic leachate on bentonite clays. After preparing a synthetic leachate basing on leachate characteristics from the controlled landfill of the city of Al Hoceima, the COD adsorption efficiency reached 60.6% [7].

The characteristics of the synthetic leachate are variables; we can change them as we need. In this study, we increase the value of orthophosphate to allow evaluation of the effectiveness of the treatment of orthophosphate adsorption on bentonite clay.

Due to variation of the composition of leachate during time, it was necessary to carry out a check of the orthophosphate (PO_4^{3-}) initial concentration in the synthetic leachate before every experimental test.

The initial orthophosphate used in these tests is equal to 425 mg/L. All tests of adsorption were done at room temperature (25 ° C) with synthetic leachate at pH 8.5. For each orthophosphate measurement, a blank test serving as a control (bentonite + distilled water) was carried out in parallel, to be able to calculate the orthophosphate at equilibrium. The absorption percentage (or removal rate) of orthophosphate is calculated using the following relationship [16].

% adsorption = $[((PO_4^{3-})i - (PO_4^{3-})e) / (PO_4^{3-})i]$ 100 (1)

(PO_4^{3-})i: the initial orthophosphate (mg / L)

(PO_4^{3-})e: the residual orthophosphate (mg / L)

2.3.3. Batch Test: Sample Preparation

The bentonite used in the adsorption tests was grinded into powder, washed with distilled water, filtered using a Buchner funnel, and dried in an oven at 100 °C until we obtained a clean powder [16]. We prepared 4 pairs of 100 ml of synthetic leachate, and 0.5 g of bentonite clay was added in every sample. We stirred the first pair for 1 hour, the second pair was stirred for 2 hours, the third pair for 3 hours, and the last pair was stirred for 4 hours.

We used a blank test (distilled water + 0.5 g of bentonite), in parallel with each pair of samples. All samples were filtered to eliminate the adsorbent. And to study the effect of temperature we have decided to take 3 different degrees more by increasing by 10°C. We prepared 4 samples of 100 ml of synthetic leachate, we added 0.5g of bentonite to each sample, and we set the stirrers fitted with heating plates to 35°C.

The first sample was stirred for 1 hour, the second for 2 hours the 3rd for 3 hours and the 4th sample for 4 hours. As in the case of the tests of adsorption in 35°C, 8 samples of 100 ml of synthetic leachate were prepared by adding 0.5g of bentonite to each sample, experiments were carried out in two parallel samples, we set 4 stirrers fitted with heating plates to 45°C and 4 other to 55°C.

The first 2 samples (one placed on the stirrer set to 45°C and the other on the stirrer of 55°C) were stirred for 1 hour, the second couple of samples (45°C and 55°C) were stirred for 2 hours, the 3rd couple for 3 hours and the 4th couple of samples for 4 hours.

3. Results and discussion

3.1. Synthesis of leachate

The synthetic leachate we used for the experiments in this work is a fluid synthesized in the laboratory to represent the same physicochemical characteristics of the real leachate from the Al Hoceima controlled landfill. The synthetic leachate used in this study is prepared in the laboratory basing on the concentrations of the compounds used in the study by D. Guyonnet [7], according to the difference between Moroccan and European leachate, a synthetic leachate concentrated twice more than the Guyonnet's study was prepared.

After preparing the synthetic leachate, and because the COD is a significant parameter for the treatment of leachate, COD analyzes were carried out to check the solution prepared. The following table shows the concentrations of the compounds used for the preparation of synthetic leachate (Table 3).

Table 3: The components of the first composition of the synthetic leachate.

Components		Concentration
Magnesium chloride	$MgCl_2$	1.92 g/L
Potassium hydroxide	KOH	1.92 g/L
Ammonium chloride	NH_4Cl	5.2 g/L
Acetic acid	CH_3CO_2H	3.5 ml/L
Sodium acetate	CH_3CO_2Na	4.93 g/L
Calcium hydroxide	$Ca(OH)_2$	1.04 g/L
Calcium chloride	$CaCl_2$	4.22 g/L
Magnesium sulfate	$MgSO_4$	1.2 g/L

The real leachate from the controlled landfill of Al Hoceima city is characterized by 143 mg/L of orthophosphate, we choose to increase the amount of the orthophosphate in the synthetic leachate to 425 mg/L to allow the evaluation of the treatment. The table below shows the composition of the synthetic leachate which was adjusted to the characteristic of the Al Hoceima city controlled landfill real leachate (Table 4).

Table 4: The composition of Al Hoceima controlled landfill synthetic leachate

Components		Concentration
Magnesium chloride	$MgCl_2$	1.92 $g.L^{-1}$
Potassium hydroxide	KOH	1.92 $g.L^{-1}$
Ammonium chloride	NH_4Cl	5.20 $g.L^{-1}$
Acetic acid	CH_3CO_2H	3.50 $mL.L^{-1}$
Sodium acetate	CH_3CO_2Na	4.93 $g.L^{-1}$
Calcium hydroxide	$Ca(OH)_2$	1.04 $g.L^{-1}$
Calcium chloride	$CaCl_2$	4.22 $g.L^{-1}$
Magnesium sulfate	$MgSO_4$	1.20 $g.L^{-1}$
Potassium dihydrogen phosphate	KH_2PO_4	0.10 $g.L^{-1}$
Potassium nitrate	KNO_3	2.12 $g.L^{-1}$
Sodium nitrate	$NaNO_2$	0.58 $g.L^{-1}$
Glucose	$C_6H_{12}O_6$	3.0 $g.L^{-1}$

After preparing the last composition of the synthetic leachate, physicochemical analyzes were carried out to characterize it and make a comparison with the real leachate from the controlled landfill of Al Hoceima city. Analyzes of COD, chloride, ammonium, nitrites, nitrates, and orthophosphate were carried out, the results of the analyzes were close to those of the real leachate from the controlled landfill of Al Hoceima,

The table below presents the characteristics of the synthetic leachate (Table 5).

Table 5: Characteristics of the synthetic leachate of the Al Hoceima controlled landfill

Parameters	Average	Unit
Temperature	27	°C
pH	8.5	pH
Conductivity	13000	µs/cm
COD	32880	mg (O_2)/L
BOD_5	4000	mg (O_2)/L
Ammonium	2159	mg/L
Nitrite	535.7	mg/L
Chloride	7400	mg/L
Nitrate	1330	mg/L
Orthophosphate	425	mg/L

3.2.Treatability test of synthetic leachate using adsorption process

For the first bentonite adsorption treatment tests, we studied the COD adsorption yield as a function of stirring time and the mass of bentonite needed. After performing several treatability tests, we found that the yield increases by increasing the stirring time up to 24 hours. The adsorption yield of COD on bentonite reaches up to 60.6 % and 50.4 % using 20 g/L and 5 g/L of bentonite respectively [2]. To study the orthophosphate adsorption yield we used 5 g/L of bentonite and evaluate other parameters.

3.2.1. The effect of stirring time on orthophosphate adsorption yield

Table 6: The effect of stirring time on the orthophosphate adsorption yield using 5g/L of bentonite.

Stirring time (h)	Initial PO_4^{3-} (mg/L)	Residual PO_4^{3-} (mg/L)
1	425	421,11
2	425	415,47
3	425	402,57
4	425	398,93

From Table 6 above, it is conspicuous that stirring time does not make this large difference in orthophosphate adsorption yield. The adsorption percentage varies from 0.91% for 1 hour of stirring to 6.13% for 4 hours of stirring. Following these results, we decided to study the effect of temperature on the adsorption efficiency.

3.2.2. The effect of temperature on orthophosphate adsorption yield using bentonite clay

For the removal of orthophosphate from synthetic leachate by adsorption on bentonite clay, temperature is considered an important parameter. For the first test, to study the effect of stirring time on the orthophosphate adsorption yield, we chose to work at room temperature (25°C). The effect of temperature on the adsorption efficiency of orthophosphate is shown in Figures 1. The concentration of orthophosphate in synthetic leachate decreases from 425 mg/L to 286,44 mg/L after 4 hours of stirring in a temperature of 35°C. This result shows us that temperature affects the efficiency of orthophosphate adsorption since the concentration of orthophosphate after adsorption on bentonite clay did not decrease from 398.93 mg/L when we started stirring at room temperature (25°C).

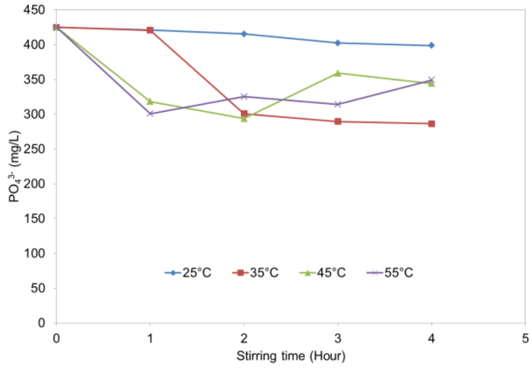

Figure 1: Orthophosphate adsorption yield on bentonite as a function of temperature,. Initial PO_4^{3-} concentration: 425 mg/L, bentonite dosage: 5 g/L.

As seen in the figure 1, the maximum adsorption yield of orthophosphate was reached in 2 hours when we stirred the samples in a temperature of 45°C and it start to decrease after 3hours and 4 hours. After 2 hours of stirring the orthophosphate adsorption yield attend 30.82 % and it decrease after 4 hours to 18.97%. The same thing in 55°C, the maximum adsorption yield was reached after 1 hour of stirring with 30.82%, and it start to decrease in 2 hours to attend 17.78% after 4 hours. According to these results we realize that the orthophosphate adsorption yield is better when we stirred the samples in 35°C for 4 hours.

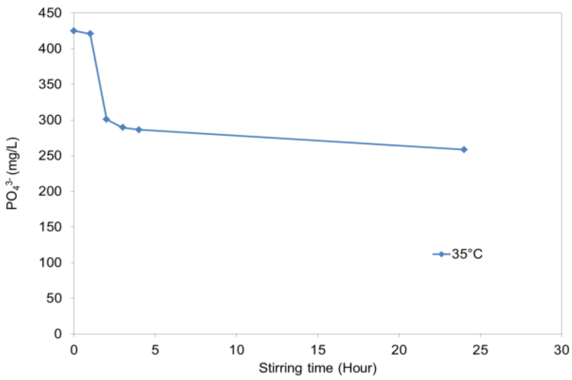

Figure 2: The adsorption of orthophosphate on bentonite clay. Initial PO_4^{3-} concentration: 425 mg/L, contact time: 24 h, bentonite dosage: 5 g/L, temperature: 35°C

As it is shown in the figure 1 the best orthophosphate adsorption yield was achieved after 4 hours of stirring in 35°C, so we decided to increase the stirring time to 24 hours as it was done for the elimination of COD [3]. A sample of synthetic leachate was prepared by adding 0.5 g of bentonite to 100 mL of synthetic leachate and placed on the stirrers fitted with heating plates to 35°C. After 24 hours, the leachate sample was removed and filtered; the following figure shows the result of orthophosphate adsorption yield using bentonite clay in 35°C for 24h (Figure 2). The orthophosphate adsorption yield starts to increase after 2 hour of stirring and attend 39.19 % after 24 hours of stirring. This test was realized to show the relationship between time and the adsorption performance of PO_4^{3-} on the bentonite clay.

4. Conclusion

The objective of our work is the choice of an appropriate treatment of the leachate taking into consideration the variation of its characteristics, the choice to work with the synthetic leachate was made to control the monitoring parameters in order to study the performance of the treatment processes studied for each parameter, this study aimed to evaluate the adsorption yield of synthetic leachate orthophosphates on bentonite clays. The bentonite clay was used to remove orthophosphate from synthetic leachate. The mass of bentonite used was fixed to 5 g/L when we studied the COD removal of synthetic leachate [2]. We started by studying the effect of stirring time on orthophosphate adsorption yield in ambient temperature (25°C), the adsorption yield reaches 6.13% after 4 hours of stirring. The second stage was devoted to the study the effect of temperature, we studied 3 different temperatures (35°C, 45°C, and 55°C), after 4 hours of stirring the adsorption yield attend 32.60%, 18.97%, and 17.78% respectively for 35°C, 45°C, and 55°C. When it was found that the best yield was reached after 4 hours of agitation at 35°C, it was decided to increase the agitation time to 24 hours because in the case of the elimination of the COD we attended the best performance only after 24 hours of stirring [3]. The orthophosphate removal result using bentonite clay after 24 hours of stirring at 35°C reached 39.19%. This result can be added to the results of the elimination of other monitoring parameters in order to study the characteristics of the synthetic leachate after treatment by adsorption on bentonite and combine it with another treatment process in order to have sufficient results for discharge standards.

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