



Multi-response modeling and optimisation of wastewater pretreatment by bentonite

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ABSTRACT

The disposal of municipal waste by landfill is widely used around the world. Treatment of landfill leachate generated from these sites has become essential because of its several environmental threats. The main objective of this study is the treatment of leachate of Ouled Fayet (Algeria). Bentonite collected from the region of Maghnia (Algeria) was employed to optimize the removal efficiency of chemical organic demand (COD) and Nitrite (NO₂⁻). The effect of stirring speed and contacting time was studied. Algerian bentonite showed significant removing potential for COD, NO₂⁻ and PO₄⁻³ successively 75%, 67% and 72%. The experimental data and model predictions agreed well. COD, NO₂⁻ and PO₄⁻³ removal efficiencies of 75%, 69% and 72% were demonstrated. The results found have provided a cost-effective method for treatment of landfill leachate.

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Introduction

Nowadays the problem of dealing with solid domestic waste (SDW) is of great concern in the entire world. A widely used method for treating municipal solid waste (MSW) is disposal landfill. Fadel, et al., [1997] have shown that up to 95% of the MSW collected worldwide is disposed of in landfills.

Produced in the landfill body as a result of percolation of rainwater through the waste deposited or originated from the waste itself [Svojitka, et al., 2009], landfill leachate is a complex wastewater highly loaded with organic matter, nitrogen, suspended solids and heavy metals [Zainol, et al., 2011]. The physico-chemical composition of leachates is strongly influenced by the nature of the landfilled waste, the water balance (which depends on the amount of precipitation), pH, BOD₅/COD ratio, the mode of operation, and the age of the site [Papastavrou, et al., 2009]. Leachate may be classified as young (or raw), and stabilized (mature) [Amir, et al., 2009]. The organic load (mainly humic substances and fatty acids) is usually between 500–20000 mg/L COD [Aziz, et al., 2007]. Young leachates are generally low in pH (<6.5) and high in

COD (>15,000 mg/L), biodegradable matters, BOD₅/COD ratio (0.5–1), and heavy metals (>2 mg/L); whereas old or stabilized leachates are usually high in pH (>7.5) and NH₄-N (>400 mg/L) and low in COD (<3000 mg/L), BOD₅/COD ratio (<0.1) and heavy metals (<2 mg/L) [Rajan, et al., 2013]. The discharge of landfill leachate can lead to serious environmental problems as they may percolate through soils and sub soils, causing extensive pollution of ground and surface waters if they are not properly treated and safely disposed. Biological processes are considerably effective for young leachate but less efficient for older or stabilized leachate [Tatsi et al., 1932; Renou et al., 1954].

According to Inanç et al., [2000] there are many methods of leachate treatment such as:

- Aerobic and anaerobic biological treatments
- Physiochemical treatments such as air stripping, chemical precipitation and oxidation.
- Coagulation using lime, alum and ferric chloride
- Advanced techniques such as carbon adsorption, ion exchange (clays).

Loretta et al., [2015], have indicated that sodium bentonite often serves as a containment barrier in landfill liners, essentially composed of montmorillonite (80%) and related clay minerals of the smectite group, which have a large surface area per unit weight and a high cation exchange

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capacity (CEC) [Hocine et al., 2004; Chegrouche et al., 2014]. Arbaoui et Boucherit [2014] have shown in their results that the Bentonite of Maghnia contains more montmorillonite and fewer impurities and it is known as a good adsorbent for heavy metal ions and organophilic. Bentonite has been used as an appropriate adsorbent for organic compounds [Mostafa et al., 2016].

This work first characterizes the landfill leachate by measuring the physico-chemical parameters. Then, it investigates the potential use of Algerian natural bentonite coming from the deposit of Hamam Boughrara (Western Algeria), as a competitive adsorbent material for the removal of chemical oxygen demand (COD) NO_2^- and PO_4^{3-} . The choice of this material is based on its low cost and its abundance in Algeria. In the final part of this work a linear regression was used to build models and determine the optimum conditions. In addition, removal of COD, NO_2^- and PO_4^{3-} were monitored throughout the experiments. Thus, the statistical analysis was based on one factors (bentonite dose) and three responses (COD, NO_2^- and PO_4^{3-}).

Material and methods

Sample composition

Leachate samples from landfill site of Ouled Fayet were collected in plastic container, transported to the laboratory and stored at 4°C. They were removed from the refrigerator and left under ambient temperature for about 2 hours before the jar test was performed. Then, samples were thoroughly agitated for re-suspension of settled solids before conducting any tests. Techniques used for sampling analyses were in accordance with the Standard Method for the Examination of Water and Wastewater [APHA, 2005]. The experiments were repeated seven times to obtain a consistent average. All analyses were undertaken at room temperature of $28 \pm 2^\circ\text{C}$. Characteristics of leachate are presented in Table 1. Removal efficiency for parameters was obtained using the following formula:

$$R(\%) = \frac{C_i - C_f}{C_i} * 100 \quad (1)$$

Where, C_i , C_f are respectively the initial and final concentration expressed in mg/L.

Table 1. Raw leachate average composition.

Parameter	Sampling point P2	
	Average	Value range
pH	6.19	5.84 - 6.6
Conductivity (ms/cm)	28.4	10.25 - 42.6
T (°C)	26.8	24 - 31.5
COD (mg/L)	84942.2	78000 - 94080
BOD ₅ (mg/L)	27500	12000 - 48000
BOD ₅ /COD	0.31	0.15 - 0.62
NO_2^- (mg/L)	200.8	9.95 - 513.68
PO_4^{3-} (mg/L)	130.2	32.6 - 364.1
Fe (mg/L)	24.07	10.7 - 35.5

Material characteristics

Bentonite was characterized by X-ray powder diffraction (XRD). The grain size of used natural bentonite is 200 µm. Humidity was measured by an infrared dryer of type Sartorius MA 40 IR. Analyses of samples were performed in the laboratory of mineral engineering, Algiers. Physical properties of natural bentonite are reported in Table 2. Table 3 summarizes the chemical composition.

Experimental procedure and data analysis

The experiments have been performed in mixed suspension, in a reactor containing a concentration given of natural bentonite ranging between 0 and 90 g/l. Contact time and stirring speed were respectively chosen 30 min and 300 rpm. After settling time of 30 minute, the supernatant was withdrawn from the beaker and analyzed.

In order to obtain the optimum dose, three dependent parameters were analyzed as responses; COD, NO_2^- and PO_4^{3-} . The dose of bentonite expressed in m/v ratio was considered as the independent variable. The two process parameters, stirring speed and reaction time, were both kept constant. The relationship between the dose used and the responses was investigated. Collected data was analyzed statistically using regression analyses employing the software package of TableCurve 2D Version 5.01.01.

Table 2. Physical properties of bentonite.

Sample	pH	Humidity (%)	Specific surface (m ² /g)	CEC (Meq/100g)				T
				Na ⁺	Mg ⁺⁺	Ca ⁺⁺	K ⁺	
Bentonite	10.24	10,35	56.44	36.7	46	11	27	122.3

Where, T is the total exchange capacity that the clay can fix it.

Table 3. Chemical composition of bentonite expressed in weight (%).

Sample	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	Fe ₂ O ₃
Bentonite	65.1	17.1	0.52	2.82	0.21	2.53	2.56	0.06	0.36	2.68

The SiO₂/Al₂O₃ ratio of bentonite equal to 3.8 can be explained by the high content of SiO₂.

After testing increasingly different models, a cubic polynomial model was found to be suitable for studying the effects of the dose on the responses. The conformity between experimental data and the model-predicted values and optimization of the selected models were expressed by the correlation coefficients R^2 , R^2_{adjusted} and residual error. Model terms were evaluated by the P-value (probability) with 95% confidence bounds. An analysis of variance (ANOVA) was used to determine whether the developed models were statistically significant. Measured COD, NO_2^- and PO_4^{3-} data are simulated by a mathematical function: The responses can be expressed as cubic polynomial equations, according to Eq. (2).

$$Y = a_0 + a_1 * x^{0.5} + a_2 * x + a_3 * x^{1.5} + a_4 * x^2 + a_5 * x^{2.5} + a_6 * x^3 \quad (2)$$

Where Y is response; a_0 an intercept constant; a_i the regression coefficients.

Results and discussions

The choice of using natural untreated clay is justified by the fact that it is friendly environmental adsorbent material. This local bentonite is a montmorillonite clay type with a relatively high cationic exchange capacity of 122.3 meq/100 g, which agreed with the study by Mohellebi et al. [2015]. Magnesium is the main exchangeable cation.

Characterisation of leachate

According to the results presented in table 1, we note that leachate contains a high quantity of COD (84942 mg/L), pH ranging from 5.8 to 6.6 and NO_2^- (200.8 mg/L). It was found that leachate had a medium biodegradability as reflected in low value of BOD5/COD ratio 0.31. The mineral pollution is also present because of the important concentrations in orthophosphate (130.2 mg/L) and Fe (24.07 mg/L) in landfill percolates. According to its characteristics, the effluent was classified as a 'young leachate' [Bader, et al., 2014].

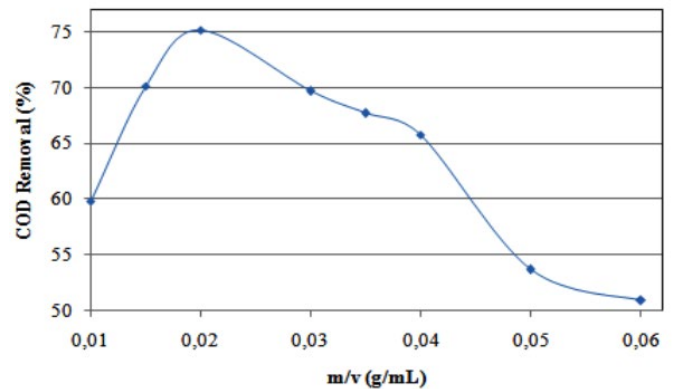


Fig. 1. Removal efficiency of COD using different dosages.

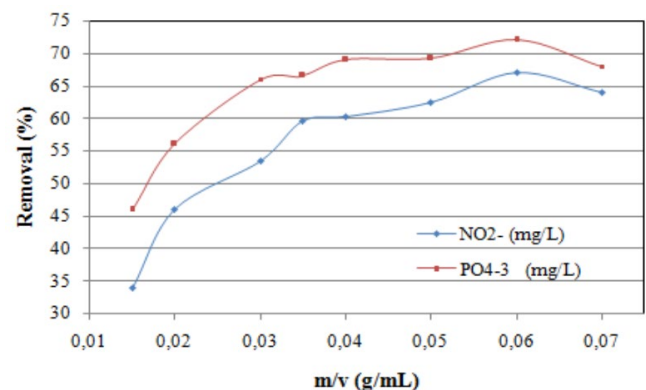


Fig. 2 Removal efficiencies of NO_2^- and PO_4^{3-} using different dosages.

Model results and analysis of variance (ANOVA)

Significant model terms are desired to obtain a good fit in a particular model. The results of the fitted models for COD, NO_2^- and PO_4^{3-} removals are given in Eqs. (3) – (5).

$$\text{COD} = 9200 - 35.8 * 10^4 * x^{0.5} + 5.7 * 10^6 * x - 4.7 * 10^6 * x^{1.5} + 2.2 * 10^8 * x^2 - 5.1 * 10^8 * x^{2.5} + 5.03 * 10^8 * x^3 \quad (3)$$

$$\text{NO}_2^- = -20333 - 67.3 * 10^4 * x^{0.5} - 9.2 * 10^6 * x + 6.6 * 10^7 * x^{1.5} - 2.6 * 10^8 * x^2 + 5.5 * 10^8 * x^{2.5} - 4.7 * 10^8 * x^3 \quad (4)$$

$$\text{PO}_4^{3-} = -3209 - 11.01 * 10^4 * x^{0.5} - 1.6 * 10^6 * x + 1.2 * 10^7 * x^{1.5} - 5 * 10^7 * x^2 + 1.1 * 10^8 * x^{2.5} - 10^8 * x^3 \quad (5)$$

Table 4. Summary of the analysis of variance result for the response models

	COD	NO_2^-	PO_4^{3-}
R^2	0.9999	0.9979	0.9966
R^2_{adjusted}	0.9993	0.9858	0.9767
Prob. > F	0.0003	0.0061	0.0099
Fit Std Err	0.220	1.309	1.327
Max Abs Err	0.166	0.944	0.957
coefficient of variance (%)	0.3354	2.35	2.07
SSE	0.07	1.65	1.71

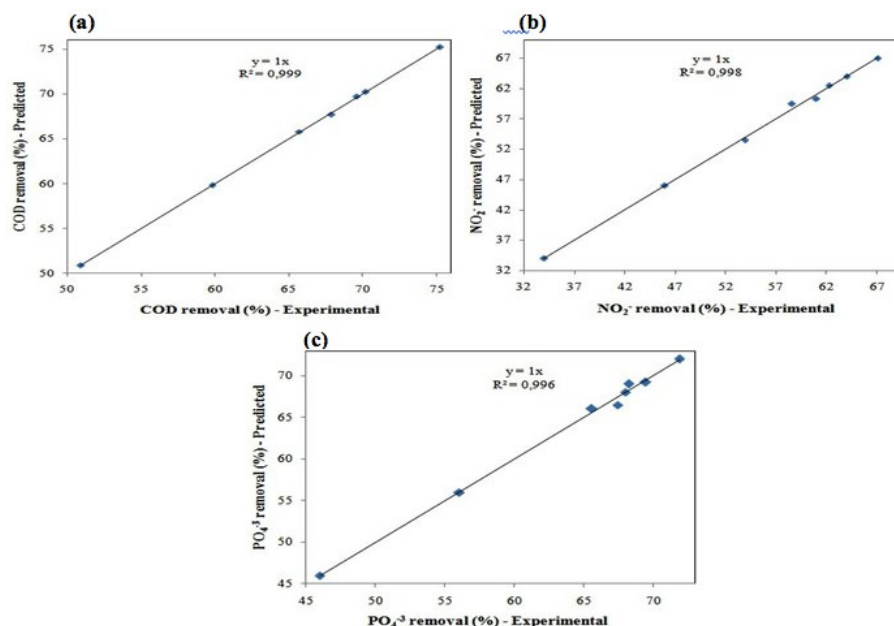


Fig. 3. Predicted vs. actual values plot for (a) COD removal, (b) NO_2^- removal, and (c) PO_4^{3-} removal.

The R-squared coefficient represents total variation of the predicted response which indicates ratio of sum of squares for regression (SSR) to total sum of the squares (SST) [Mahsa and Farshid, 2014]. A high R^2 value, close to 1, indicates that the model successfully describes the response and represents a real relationship among the parameters [Lee et al., 2010; Rasool et al., 2016; Nordin et al., 2004]. At the same time, adjusted R^2 allowing for the degrees of freedom associated with the sums of the squares is also considered in the lack-of-fit test, which should be an approximation value of R^2 . According to Thuy et al., [2011] when R^2 and adjusted R^2 differ dramatically, there is a good chance that non-significant terms have been included in the model. Here, the two R^2 values are very close as shown in Table 4. $R^2=0.9999, 0.9979, 0.9966$ for COD, NO_2^- and PO_4^{3-} , respectively, indicates that a linear least-squares fit of the responses explains 99% of its variance. So, cubic fit of data seems to be a better predictor.

The p-value is used as a tool to check the significance of each factor. A p value less than 0.05 indicates that the effect is significant and the smaller p-value expresses the more significant effect [Montgomery, 2001]. Table 4 illustrates the statistical parameters. Data given in this table demonstrates that all the models were significant and had no lack of fit at the 5% confidence level since p-values were less than 0.05. The model fits the data exactly and the minimum SSE was close to zero: 0.07, 1.6, 1.7 for COD, NO_2^- and PO_4^{3-} , respectively. The coefficient of variance (CV) as the ratio of the standard error of estimate to the mean value of the observed response defines reproducibility of the model [Hamidi et al., 2009]. A model normally can be usually considered reproducible if its CV is not greater than 10% [Beg, et al., 2003]. According to Table 4, All models measure up in terms of reproducibility.

Diagnostic plots like the predicted versus actual values allow us to assess the satisfactoriness of the model. The predicted parameter removal plots versus actual values are shown in Fig. 3. These plots show a satisfactory alignment between the actual data and the models collected. The correlation

coefficient of 0.99 indicates the high validity of the obtained models for COD, NO_2^- and PO_4^{3-} removals.

As shown in Table 5, the removal efficiencies for all response parameters obtained from the experiments and as estimated by models were in close agreement. The maximum COD, NO_2^- and PO_4^{3-} removals (75.23%, 68.9% and 72.1 %, respectively) were predicted under treatment conditions of m/v 20 g/L, mixing speed 300 tr/min and contact time of 30 min. The actual experimental values obtained were 75.2% with 0.03% deviation for COD reduction, 67% and 72% with 1.9% and 0.1% deviation for NO_2^- and PO_4^{3-} removals, respectively.

Table 5. Removal of leachate pollutants using model-predicted optimum values.

Condition m/v=20g/L, 300tr/mn	Responses removal (%)		
	COD	NO_2^-	PO_4^{3-}
Expérimental value	75,2	67%	72%
Model response	75.23	68.9	72.1
Error	0,03	1,9	0,1
Standard deviation	0.021	2,97	0.071

Conclusion

Natural bentonite from Mostaganem, northern west of Algeria, can be used as an effective adsorbent for the removal of COD, NO_2^- and PO_4^{3-} from wastewater. Data fitting of the to various models and their subsequent variance analysis showed that the responses reductions were well described with a cubic polynomial model : 75 % COD, 69% NO_2^- and 72 % PO_4^{3-} , respectively. This study showed that untreated clay served as an effective way to remove organic matter, nitrite and orthophosphate from landfill leachate. Therefore, bentonite is an environmentally friendly product and should be considered as a viable alternative in the field of wastewater treatment.

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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