Prepublished copy

Nature Environment & Pollution Technology

This is a peer-reviewed prepublished version of the paper to be published in Vol. 25, No. 3, September 2026 issue

Original Research

Evaluation of the Adsorption Performance of Geological Materials Based on Limestone and Green Shale from the Taza Region, Morocco: Application for Leachate Treatment

Imane El Machrafi[1], Abdennasser Baali[1], Ibrahim Touzani[2,3], Jamal Naoura[4], Mohamed Ben Abbou[3] and Kawtar Fikri-Benbrahim[2]†

[1] Laboratory of Engineering, Electrochemistry, Modelling and Environment, Faculty of Sciences Dhar El Mahraz, Sidi Mohamed Ben Abdellah University, Fez, Morocco

[2] Laboratory of Microbial Biotechnology and Bioactive Molecules, Sciences and Technologies Faculty, Sidi Mohamed Ben Abdellah University, Fez 30050, Morocco

[3] Higher Institute of Nursing Professions and Health Techniques of Fez (Annex Taza), Taza 35000, Morocco

[4] Laboratory of Natural Resources and Environment, Polydisciplinary Faculty of Taza, University of Sidi Mohammed Ben Abdellah, Taza 35000, Morocco

† Corresponding author: Kawtar Fikri-Benbrahim; kawtar.fikribenbrahim@usmba.ac.ma

ORCID IDs of Authors

Imane El Machrafi; https://orcid.org/0000-0002-5779-3836

Abdennasser Baali; https://orcid.org/0009-0000-3665-9980

Ibrahim Touzani; https://orcid.org/0000-0003-4202-2681

Jamal Naoura; https://orcid.org/0000-0002-3281-2738

Mohamed Ben Abbou; https://orcid.org/0000-0001-5088-3356

Kawtar Fikri-Benbrahim; https://orcid.org/0000-0002-2923-9299

Key Words	Leachate; Leachate treatment; Limestone; Green shale; Adsorption, Kinetic studies
DOI	https://doi.org/10.46488/NEPT.2026.v25i03.D1866 (DOI will be active only after the final publication of the paper)
Citation for the Paper	El Asli, H., El Machrafi, I., Baali, A., Touzani, I., Naoura, J., Ben Abbou, M. and Fikri-Benbrahim, K., 2026. Evaluation of the adsorption performance of geological materials based on limestone and green shale from the Taza Region, Morocco: Application for leachate treatment. *Nature Environment and Pollution Technology*, 25(3), D1866. https://doi.org/10.46488/NEPT.2026.v25i03.D1866

Abstract: The present study aims, on the one hand, to examine and evaluate the potential of natural geological adsorbents elaborated from limestone and green shale for leachate treatment. On the other hand, it highlights an innovative approach based on the separate evaluation of these two natural materials, which has not yet been explored in depth in the literature, with a view to offering a sustainable and economically accessible alternative to commercial adsorbents. To this end, the studied materials were prepared from rocks collected around the city of Taza -Morocco-. Then, absorbent properties of produced materials were evaluated for different types of pollutants contained in the leachate studied, through structural analyses carried out by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) before and after

the adsorption process. In addition, kinetic and isotherm models were analyzed to evaluate adsorption efficiency. The characterization before the adsorption process revealed that the prepared materials present a partially homogeneous surface with particles of irregular sizes and varied atomic compositions. The material prepared from limestone shows the highest performance, as reduction rates of 39 %, 43 % and over than 80 % were obtained respectively for COD, BOD and heavy metals (Cr, Fe, Ni, Pb, and Zn).The results of kinetic and isothermal models showed that the removal efficiency of COD is significantly related to the initial concentration and time of contact, with reduction rates of 40 % and 32 % for the materials prepared from limestone and green schist respectively. Furthermore, the kinetic and isothermal models are well adjusted by the pseudo-second order and Freundlich models. These results confirm the potential of these low-cost adsorbents for sustainable environmental applications, with a higher performance observed for limestone.

1. INTRODUCTION

Household waste is non-hazardous waste, including all waste coming from economic activities or households and guaranteed to be harmless. The production and management of waste have been part of daily life since the dawn of mankind (El-Saadony et al. 2023; Sun et al. 2022). In recent years, massive production of solid waste has been noted, due to annual demographic increase, booming industrialization, accelerated urbanization and large-scale consumption habits (Chen et al. 2020). Like a number of developing countries, Morocco has experienced rapid development over the last five decades, particularly in terms of population growth. At the same time, the quantities of household waste have undergone a similar evolution, mainly due to new production and consumption patterns as well as a progressive rate of rural exodus and urbanization. Indeed, household waste production is estimated at over 7 million tons per year.

To optimize the management of solid waste, local authorities set up strategies for collecting and handling it, particularly in controlled or uncontrolled open dumps. When precipitation or other sources of moisture come into contact with waste accumulated in landfills, they generate soluble compounds through biological and physicochemical reactions. These degradation processes subsequently produce a heavily polluted effluent known as leachate (Wang and Qiao 2024; Mor and Ravindra 2023). The compositional variability of this discharge compounds is explained by the influence of multiple physicochemical and environmental factors, such as the landfill's age, the accumulated waste typology, and the rainfall regime (Renou et al. 2008).

Landfill leachates represent the major direct cause of atmospheric pollution and are a concentrated source of pollutants that can contaminate soils and groundwater (Abdel-Shafy et al. 2024; Ahouach et al. 2023). They have a complex composition, variable over time and influenced by many factors (El-Saadony et al. 2023; Gutiérrez-Mosquera

et al. 2022), and are generally characterized by a high pollution load, both organic and inorganic. Organic load encompasses the quantified compounds in terms of biological oxygen demands (BOD), chemical oxygen demand (COD), volatile fatty acids, and also includes various hydrocarbons and volatile organic compounds (VOCs) (Kjeldsen et al. 2002). Whereas, the inorganic fraction is characterized by the presence of ammoniacl nitrogen, anions (chlorides, sulfates, bicarbonates) and a wide range of heavy metals including iron, cadmium, lead, zinc and copper (El-Saadony et al. 2023; Al-Yaqout and Hamoda 2020).

The structural diversity of this pollutant matrix constitutes a fundamental determinant of ecosystem pollution and has significant health implications at the community level. Indeed, these liquids, which are highly charged with pollutants, can infiltrate soils and contaminate groundwater (Ahouach et al. 2023). Moreover, pathogens can lead to adverse effects on water-based and ground-based ecosystems (Sharma et al. 2023). In terms of health, direct or indirect exposure to leachates can cause respiratory and dermatological problems, poisoning and even chronic illnesses in people dwelling near discharges (Daniel et al. 2021; Njoku et al. 2019).

Different leachate treatment approaches were considered, underlining benefits in terms of economic, ecological and sustainable viability. The complex and heterogeneous nature of these liquid matrices has required the development and implementation of diversified technologies. The technological arsenal available includes biological (Miao et al. 2019) and physicochemical methods (Abdel-Shafy et al. 2024; Renou et al. 2008). Adsorption remains the most used method to treat several micro-pollutants namely dyes, heavy metals and pesticides, thanks to its technical advantages and high efficiency to remove soluble, insoluble and biological contaminants. Subsequently to this process introduction, the choice of an efficient adsorbent material remains a crucial issue for many scientists. The choice of a treatment strategy must therefore be adapted to the characteristics of the leachate, local regulatory requirements and available technical resources, favoring an integrated and sustainable approach.

Conventional adsorbents, although effective, have high costs limiting their large-scale application. In this context, the exploration of natural geological materials such as shales, limestone, dolomite, clays and zeolites appears to be a promising solution (Ahamad and Nasar 2024; Aljabarin 2023; Hussain and Ali 2021). These materials are abundant, inexpensive, sometimes derived from quarry waste, and have physico-chemical properties favorable to adsorption. Although these geological adsorbents have several advantages, they are still facing limitations that restrict their use on a large scale. Their adsorption power is always less important than that of commercial materials such as activated carbon

or synthetic zeolites (Foo and Hameed 2010). Moreover, their efficiency decreases in the presence of several competing ions, which reflects a limited selectivity. Performance is also strongly conditioned by parameters such as pH, temperature or initial concentration, which restricts their use in variable environments (Kordala and Wyszkowski 2024). Finally, the material's regeneration is problematic, leading to a decrease in efficiency after several cycles of use (Gupta et al. 2009).

In this context, the present study aims to examine and evaluate the potential of natural geological adsorbents prepared from limestone and green shale in the treatment of leachates from the controlled landfill of the city of Fez. With a view to offering a sustainable and inexpensive alternative to commercial adsorbents. The novelty of this study lies in the use of these two materials, which has yet to be explored extensively in the literature. Limestone and green shale were selected for their local abundance, ensuring economic and sustainable availability, as well as for their mineralogical properties rich in carbonates and silicates, which facilitate the adsorption of organic and metallic pollutants. Compared to conventional adsorbents, these materials stand out for their natural nature, low cost, and potential for regional recovery. The two materials obtained were characterized before and after the leachate treatment process by SEM, XRD and FTIR, in order to confirm and evaluate the reduction potentials of certain types of pollutants present in the leachates. Another part of this study was conducted to evaluate the effect of temperature, contact time and COD content of leachate on the COD reduction efficiency by both materials. In which, kinetic models the pseudo-first and pseudo-second order as well as the Langmuir and Freundlich isotherms have been examined. The underlying assumptions suggest that these materials have significant adsorption capacity, can be effectively regenerated, and constitute a sustainable solution for the treatment of contaminated water, with performance that can be optimized through in-depth analysis of operating parameters.

2. MATERIALS AND METHODS

2.1. Preparation of Materials

The limestone and green shale rocks used in this study were collected around of the city of Taza -Morocco- (figure 1). The preparation of materials based on those rocks by physical processes follows several steps. The collected limestone and raw green schist were first cleaned and dried, then crushed using a jaw crusher of the type FRITSCH PLUVERISETTE 1. After being ground in a ball mill, the obtained material was sieved using a sieve with a mesh diameter of less than 100 µm. Thus, the particle size of the material used corresponds to a fraction strictly smaller than 100 µm. The material was then dried at 60°C for several hours. The materials produced from limestone and green shale are named

T1 and T2 respectively. The two materials used in this work have not undergone any additional chemical modification or treatment. The characterization of T1 and T2 was carried out using: SEM identified by the SEM Quanta 200 equipped with a tungsten filament electron gun; the XRD method realized by the XPERT-type XRD-PRO in a scanning area ranging from 5 to 120° 2θ and the FTIR spectroscopy achieved in the mid-infrared domain using a Vertex 70 spectrometer, at the "Cité d'Innovation" of the University of Sidi Mohamed Ben Abdellah (USMBA) - Fez.

Fig. 1: Location map of the Limestone and the green schist rocks of the Taza Region -Morocco-

2.2. Leachate Sampling and Characterization

Leachate collection was carried out at the landfill site of Fez city (Morocco), extending over 120 hectares and accommodating more than 800 tons of mixed municipal solid waste streams daily. The leachate samples intended for physicochemical and heavy metal analyses were collected in polyethylene bottles of 500 ml, then labeled and transported in a temperature cooler, at 4°C, to the laboratory. The multiparametric instrument Consort was used to perform local measurements of electrical conductivity (EC) and pH. All physicochemical analyses were conducted following the techniques suggested by Rodier et al (2009), and these parameters are indicated in table 1.

Table 1: Physicochemical parameters analysis methods.

Parameters	Unit	Analysis methods
pH	--	Multi-parametre Consort C561
EC	mS/cm	
SS	mg/L	Filtration method

COD	mg/L	Colorimetric
BOD_5	mg/L	OXITOP
NTK	mg/L	Mineralization
Al	mg/L	ICP-AES
Cr		
Fe		
Ni		
Pb		
Zn		

2.3. Experimental Study of Leachate Treatment

In order to assess T1 and T2 materials efficacy and performance for leachate treatment, a volume of 75 ml of leachate was brought into contact with 5 g/L of T1 or T2 in a closed reactor, then each solution was stirred at 300 rpm. Following a 24 hour's contact, the suspension was subjected to centrifugation at 5000 rpm for 10 minutes. The final concentration of physicochemical parameters and heavy metals was determined in the supernatant by the methods described above. The adsorption experiments were conducted at room temperature without a temperature control device, and no pH adjustments were made in order to evaluate the natural behavior of the materials under actual leachate conditions. The reduction rate R (%) and the adsorption capacity q_e (mg/g) of the various physicochemical parameters (pH, COD, BOD_5, NTK, Ni, Fe, Cr, Zn, Pb and Al) were determined according to equations (1) and (2):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e).V}{m} \qquad (2)$$

Where C_i and C_e are the initial and equilibrium concentrations parameters in solution, respectively (mg/L); V is the volume of solution (l) and m is the mass of adsorbent (g).

2.3.1. Contact Time's Effect and Kinetic Models

In a batch system, 75 ml of crude leachate solutions (EC1, EC2 and EC3) were acidified using sulfuric acid (H_2SO_4) to inhibit microbial activity then mixed with 5 g/L of T1 or T2. Sample mixtures with varying concentrations were stirred for 24 hours at 300 rpm at room temperature. Every two hours of contact, the suspension was centrifuged for five minutes

at 5000 rpm and filtered, then the filtrate was analyzed colorimetrically to determine the COD. The monitoring of this indicator was carried out due to its relevance for assessing the effectiveness of treatment procedures and compliance with required standards.

To learn more about the mechanism of COD elimination on both generated materials T1 and T2, two classical kinetic models were investigated: the pseudo-first order kinetic model (Achak et al. 2014) defined by equation (3), and a pseudo-second order kinetic model (Fayoud et al. 2015) indicated by the equation (4):

$$\log\ (q_e - q_t) = \log q_e - K_1\ t \quad (3)$$

Where: q_e and q_t are the adsorbed quantities (mg/g) and k_1 is the pseudo-first order equilibrium rate constant (min^{-1}).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where: k_2 is the pseudo-second order adsorption rate constant (g/mg.min).

Kinetic model is mainly used in linear form because fewer calculations are required to determine the model parameters. Error analysis for a kinetic model using a non-linear model consists of evaluating the accuracy and reliability of the model used to estimate the parameters of adsorption models. The application of the model used can also be verified using error analysis techniques such as the sum of squares error (SSE) which is a measure of the difference between experimental values and values predicted by a model. The lower the SSE value, the better the model fits the experimental data. SEE is calculated using the following mathematical method (Zand and Abyaneh 2020).

$$\text{SEE}\ (\%) = \frac{\sqrt{\sum(qe_{(exp)} - qe_{(cal)})^2}}{N}$$

Where $q_{e(exp)}$ is the equilibrium adsorption capacity obtained from adsorption experiments, $q_{e(cal)}$ is the calculated value of the equilibrium adsorption capacity, and N is the number of data points.

2.3.2. Temperature's Effect and Isotherm Models

To assess the impact of temperature on the adsorptive ability, 5 g/L of T1 or T2 together with a crude leachate sample (75 ml) were added to the system in batches for 6 hours, and maintained at various temperatures (25, 30 and 40 °C). For each adsorbate, the residual concentrations ($C_{e)}$ have been determined.

In this work, the Langmuir and Freundlich isotherms were used according to their mathematical model, respectively equations (5) and (6) (El Khomri et al. 2020) and (Nourmoradi et al. 2016):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (5)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (6)$$

Where: C_e (mg/L) the adsorbate concentration in the liquid phase at equilibrium; q_e (mg/g) the adsorption capacity at equilibrium; q_{max} (mg/g) maximum adsorption capacity; K_L, K_f and n are constants of Langmuir and Freundlich model.

3. RESULTS AND DISCUSSION

3.1. Characterization of Materials

SEM and EDX analysis: SEM is used to determine the morphological features and surface porosity of the investigated material. A developed porosity makes it possible to enhance the number of active sites on which the different types of pollutants can be fixed (Davarnejad et al. 2020). The results of the SEM analysis for T1 and T2 before treatment are shown in Figures 2.A and 2.B, respectively, while Figures 2.C and 2.D show the results for T1 and T2 after treatment. Table 2 also shows the chemical composition of T1 and T2 before and after treatment. These results show that the surface of T1 and T2 are partially homogeneous with a fragmented and rough structure, which may indicate natural weathering and significant porosity, likewise these results show the presence of carbonate crystals at the limestone level. The results of the atomic element composition of T1 revealed the presence of calcium (Ca) (34.82 %), oxygen (O) (26.16 %) and carbon (C) (20.79 %) with a very dense atomic mass, highlighting the presence of calcium carbonate ($CaCO_3$) in large quantities. Furthermore, the sample T2 mainly contains silicate minerals, with a strong presence of silicon (Si) and oxygen (O), at respective percentages of: 21.13 and 45.4 %; which is specific to green shale rich in chlorite. These results also reveal the presence of potassium and aluminum, suggesting the presence of certain feldspars or minerals such as muscovite, which are frequently observed in these types of rocks.

Regarding the morphological characteristics and chemical composition of the two samples following leachate treatment, the images obtained by SEM indicate a change in their morphologies and an obstruction of the pores caused by various pollutants or by chemical reactions or interactions with the effluent elements (figure 2.C and 2.D). These results are consistent with the EDX analysis (Table 2), which indicates an increase in carbon and the presence of chlorine as well as certain heavy metals such as aluminum and iron. Overall, these results corroborate the decrease in organic load and heavy metals from leachate samples treated by both T1 and T2.

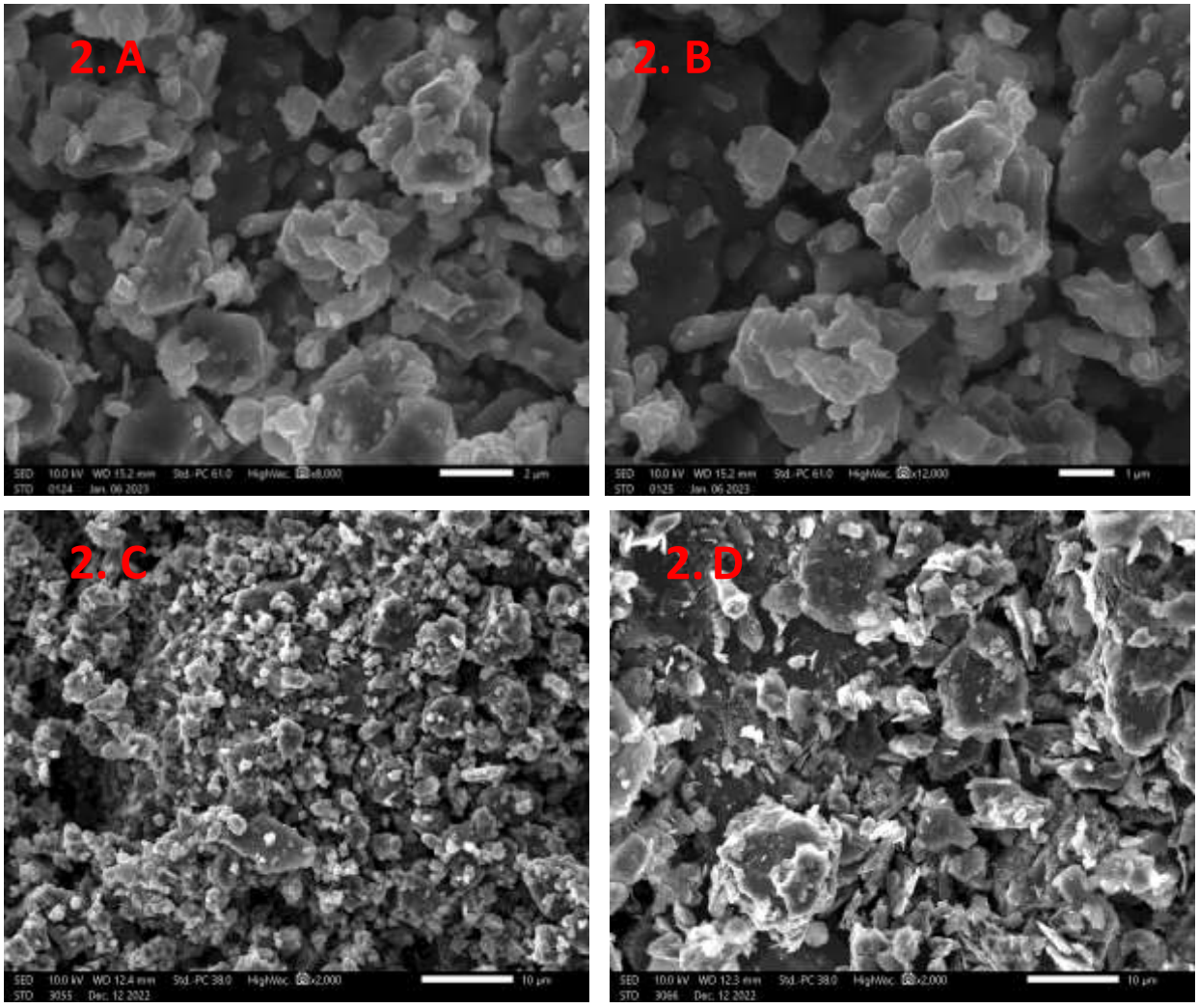

Fig. 2: Image of the T1 and T2 observed by Scanning Electron Microscopy (SEM) before (2.A, 2.B) and after (2.C, 2.D) treatment.

Table 2: Elemental analysis of the T1 and T2 by EDX before and after treatment.

T1		T2	
	Before treatment		
Element	Atom%	Element	Atom%
C	20.79	C	14.97
O	26.16	O	45.40
Si	18.23	Mg	0.60
Ca	34.82	Al	13.72
		Si	21.13
		K	4.19
	After treatment		
C	24.33	C	42.19
O	33.87	O	36.31
Mg	0.22	Na	0.78
Al	0.34	Mg	0.39
Si	5.88	Al	6.51
Cl	0.37	Si	10.24
Ca	33.68	Cl	0.26
Fe	1.31	K	1.43
		Ti	0.23
		Fe	1.65

X-ray diffraction: XRD is used to determine the mineralogical composition and crystalline arrangement of samples. Figures 3.A and 3.B show the X-ray diffraction of the two materials T1 and T2, with several marked diffraction peaks. The spectral analysis of T1 mainly reveals the presence of an intense peak at 29.43° corresponding to calcite ($CaCO_3$), while the peaks identified at 26.60° and 50.14° correspond to the presence of quartz (SiO_2), which reports that the T1 material is essentially calcite, with a negligible amount of quartz. The result of the T2 diffractogram reveals the presence of a dominant peak at 26.72° corresponding to quartz (SiO_2), which is a frequent compound of green shale, and also the presence of chlorite marked by the peak 25.30°. Figures 3.C and 3.D of the T1 and T2 X-ray diffraction after treatment show a slight variation in the peaks. The peaks 20.96°, 29.5° and 43.30° of limestone before and after treatment are subject to a slight variation in their intensities, thus the peaks at 36° and 39° also show the presence of other phases of calcite or secondary minerals. Similarly, the XRD of green shale after treatment revealed the presence of more chlorite and less quartz compared to the raw T2 material. The differences observed between the two samples are therefore probably due to leachate treatment. This treatment can introduce additional phases or disrupt the structure of minerals present in limestone and green shale.

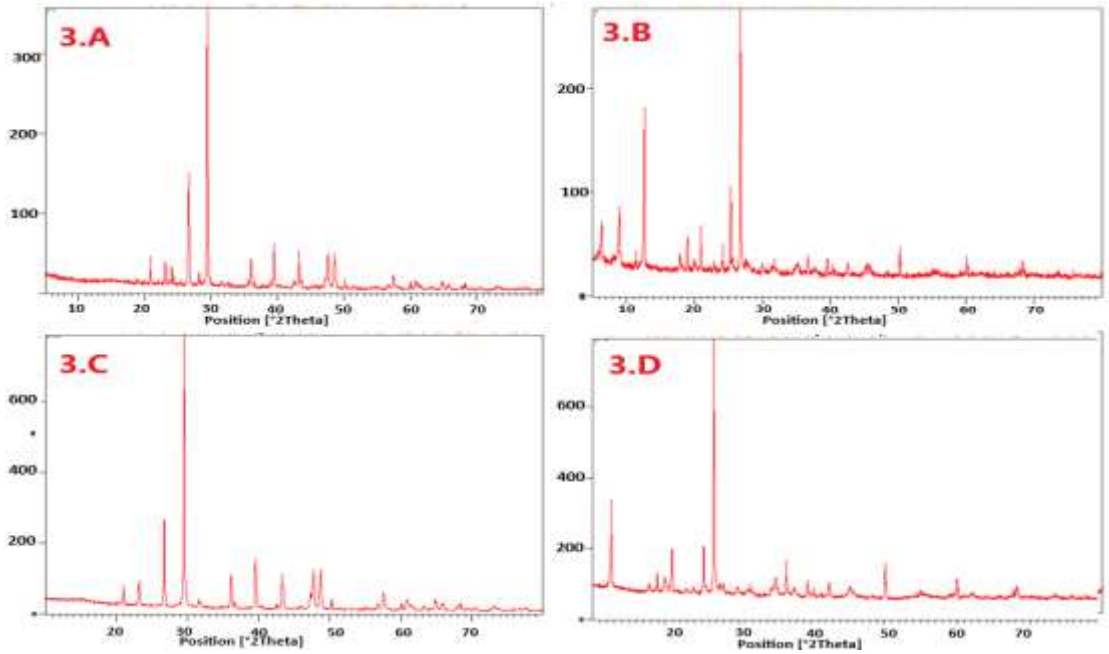

Fig. 3: X-ray diffraction of T1 and T2 before (3.A, 3.B) and after (3.C, 3.D) treatment.

Fourier transform infrared spectroscopy: The FTIR is an analysis technique based on the vibrational properties of inter-atomic bonds, which can be used to identify the functional groups present in molecules. This technique was used on a spectrum of 4000-400 cm^{-1}, to identify the main functions present on the surface of the raw product T1 and T2 before and after leachate treatment. Figures 4.A, B and 4.C, D show the infrared spectra of T1 and T2 before and after treatment respectively. Analysis of the T1 spectrum revealed the presence of several bands, particularly in the region around 1400-1500 cm^{-1} and 780-870 cm^{-1}. Concerning the band between 780 and 840 cm^{-1}, this range is generally related to out of plane deformation of the CO_3^{2-}, indicating the presence of calcite. The bands between 1200 and 1250 cm^{-1} are attributed to silicates. A broad band between 1300 and 1500 cm^{-1} is ordered by the asymmetric stretching of carbonate (CO_3^{2-}), confirming the presence of calcite ($CaCO_3$). Similarly, three bands were detected for the T2 spectrum (Figure 4.B). The bands between 600 and 700 cm^{-1} may be related to the bending vibration of Si-O bonds, which are present in minerals such as chlorite. The bands between 700-800 cm^{-1} can also be linked to bending vibrations in minerals such as hydrated silicates. A broad band around 1000 cm^{-1} is generally attributed to vibrations of Si-O bonds in silicate minerals. Analyses of the IR spectra of T1 and T2 after treatment (figures 4.C and 4.D) showed the positional shift of certain peaks, the disappearance of others and the appearance of new peaks. In particular, the band between 1300-1500 cm^{-1} and the 1000 cm^{-1} band of T1 and T2 respectively were modified.

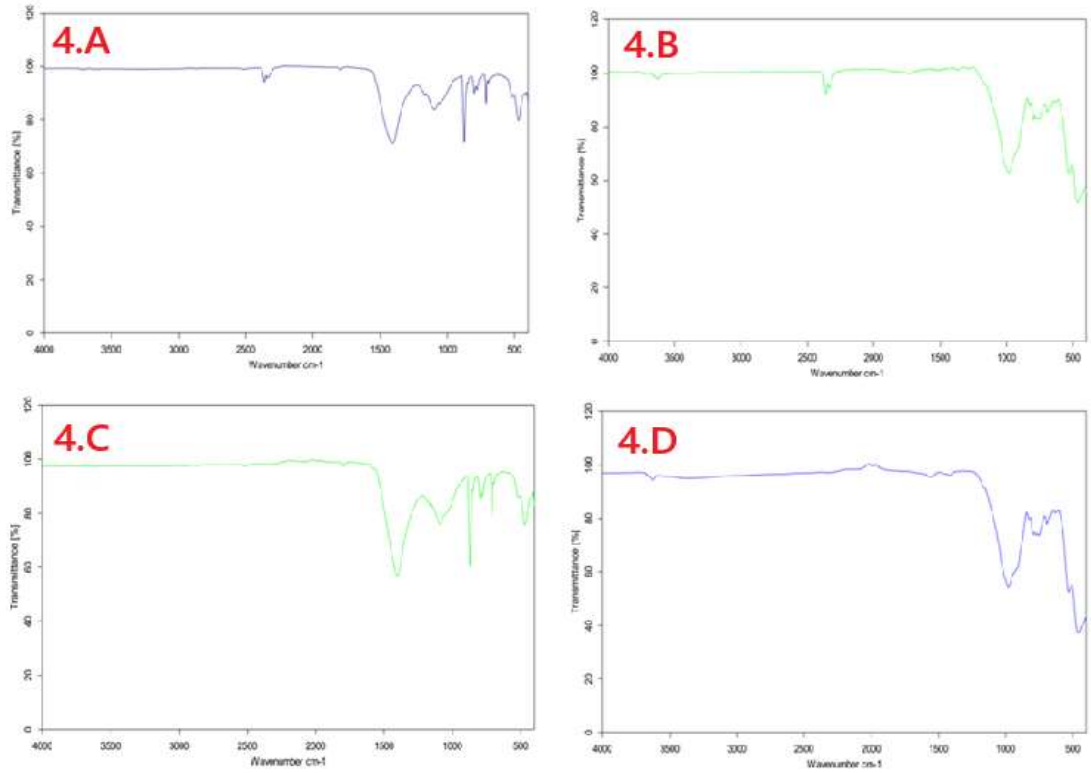

Fig. 4: FTIR spectrum of T1 and T2 before (4.A, 4.B) and after (4.C, 4.D) treatment.

3.2. Leachates Analysis

The pollution indicator parameters were analyzed in the aim to evaluate the physicochemical and metallic quality of the studied leachate. The results presented in table 3 of the leachate parameters analyzed show that it is highly polluted and does not meet discharge standards for several parameters, including pH, electrical conductivity, COD, NTK, suspended solids, chromium and other metallic elements. The basic pH of the effluent studied can be linked to low concentrations of VOCs due to the waste anaerobic degradation. Moreover, the pH value obtained of 8.2 is of the same order of magnitude as that found in other studies reported by El Jalil et al. (2020). Electrical conductivity (EC) reflects the concentration of ions present in leachates. The concentration obtained from the EC is 36.04 mS/cm, indicated a strong activity of mineralization, which is essentially related to the high concentrations of chloride ions present in domestic and industrial solid waste received by the landfill. This result is consistent with previous works (Zineb et al. 2020; Mor et al. 2018). Dissolved organic matter is represented by certain global parameters such as chemical oxygen demand (COD) and biological oxygen demand (BOD_5) (Mandal et al. 2017). Respective COD and BOD_5 values were 9088.5 and 1680.2 mg/L. These results far exceed the values set by Moroccan discharge standards. These high concentrations are largely due to the composition of the mixtures of putrescible waste and also to refractory organic compounds. Suspended Solids

(SS) also show a very high value 2089.42 mg/L, far from the value required by the Moroccan standard. The high levels of SS in leachate are due to the incomplete decomposition of waste, leaching of solid particles (organic and mineral), which could reflect the increase in lixiviate mineralization. Similarly, the total Kjeldahl nitrogen (NTK) content in the leachate analyzed was found to be high at 1080 mg/L. NTK, which includes ammoniacal nitrogen (NH_4^+) and organic nitrogen, is a key indicator of the overall nitrogen load in the leachate. Compared to national standards and results observed in other studies, these measured values are within the orders of magnitude typical of leachates (Benaddi et al. 2022; Merzouki et al. 2015). With regard to the analysis of metallic elements, Fe and Cr have the highest values, with respective concentrations of 34.15 mg/L and 5.12 mg/L, that are higher than the national standards for surface water and water intended for irrigation, Ni also has a high level at 4.36. The other elements Al, Pb and Zn, are present in low concentrations. The results of this study are similar to those of other works that reported the presence of heavy metals in leachates (Shadi et al. 2020; Hernández-García 2019). Elements such as Ni, Fe, Cr, Zn, Pb and Al detected in the leachate from the Fez landfill site are mainly found in the decomposition of industrial electronic and domestic waste. These metallic components are harmful and durable, and can threaten health and the environment, particularly lead, chromium and nickel, which remain dangerous even at low levels.

Table 3: Results of physicochemical parameters from leachate controlled landfill in Fez.

Parametres	Unit	Leachate	MLDS*
pH	--	8.2	5.5-9.5
EC	mS/cm	36.04	2.7
SS	mg/L	2089.42	100
COD	mg/L	9088.5	500
BOD_5	mg/L	1646.82	100
NTK	mg/L	1080.2	40
Al	mg/L	3.19	10
Cr	mg/L	5.12	2
Fe	mg/L	34.15	5
Ni	mg/L	4.36	5
Pb	mg/L	0.42	1
Zn	mg/L	2.86	5

*: Moroccan Liquid Discharges Standards (MLDS, 2018).

3.3. Leachate Treatment

This part aims to determine the variation of the physicochemical parameters (pH, COD, BOD_5, NTK, Al, Cr, Fe, Ni, Pb and Zn) of leachate treated by the T1 and T2 materials. Table 4, shows the reduction rate of the physicochemical parameters of leachate treated by T1 and T2. Removal rates were calculated for each parameter after 24 hours of treatment. The results obtained following treatment of the leachate by T1 and T2 show a variable efficiency depending on the physicochemical parameters studied. These results reveal significant differences in terms of abatement efficiency between T1 and T2 applied to the leachate treatment. Generally, adsorption on T1 and T2 led to a significant reduction of various pollutants, confirming the potential of these materials as a low-cost processing medium. pH analyses before and after treatment revealed distinct effects depending on the material's type. The initial leachate had a slightly basic pH. After treatment on T1, the pH raised slightly from 8.2 to 9.02. This result is consistent with other works (Aziz et al. 2004; Aziz et al. 2001) which attributes the pH raise to the presence of CO_3 in limestone. However, after treatment by T2, the pH slightly decreased, reaching a value of 7.4. This pH decrease can be due to ion exchange of the basic cations in the leachate and the sites available in the green shale mineral matrix. T1 showed a higher COD adsorption capacity (39.20 %) than T2 (30.10 %). This indicates a partial interaction between the organic compounds present in the leachate and the T1 surface. Similarly, BOD_5 showed the same variations with a removal rate of around 41-43%, indicating that biodegradable compounds are retained by both T1 and T2 materials. These results are consistent with those of Aluko and Sridhar (2013), who used a process combining biofiltration and sequencing of batch reactors (SBR) and (Halim et al. 2010) who compared zeolite with other adsorbents such as activated carbon and a composite material for COD removal from leachate. Furthermore, the reduction in ammoniac nitrogen was rather modest for both T1 and T2. The concentration of NTK fell from 1080.2 mg/L to 841.56 mg/L for T1 and 880.51 mg/L for T2, corresponding to a reduction of 22.09 % for T1 and 18.48 % for T2 respectively. This is due to the weak attraction of limestone and green shale for ammonium ions without specific exchangers' intervention. The results of the analysis of heavy metals after treatment show that both materials are highly effective against heavy metals. Indeed, the removal rate of Cr, Ni, Pb and Zn reached up to 100 % for T1, compared with 60 to 90 % for T2. This maximal reduction of heavy metals on the T1 material can be explained by the high cation exchange capacity of the limestone and also by a better chemical affinity for metals thanks to surface interactions reinforced by the large number of active sites available on the limestone surface. These results are in agreement with other studies (Foul et al. 2009; Aziz et al. 2004; Aziz et al. 2001) which highlighted a significant improvement in metal reduction by limestone. On the other hand, these results indicate that limestone can be used as a low-cost and available

material, which justifies its use to replace certain expensive adsorbents and can contribute significantly to improve leachate quality.

Table 4. Analysis result of physicochemical parameters before and after treatment of leachate by T1 and T1.

Parametres	Unit	leachate	Treatment by T1	%R (T1)	Treatment by T2	%R (T2)
pH		8.2	9.02	--	7.4	--
COD	mg/L	9088.5	5525.25	39.20	6352.86	30.10
BOD5	mg/L	1646.82	960.80	41.66	930.07	43.52
NTK	mg/L	1080.20	841.56	22.09	880.51	18.48
Al	mg/L	3.19	< 0.01	100	< 0.01	100
Cr		5.12	0.01	99.73	2.05	60.05
Fe		34.15	2.16	93.69	6.37	81.34
Ni		4.36	0.02	99.46	0.59	86.54
Pb		0.42	< 0.01	100	0.08	80.95
Zn		2.86	< 0.01	100	0.26	90.91

Note. *<0.001: The limit value obtained by the ICP is 0.001. Values below this limit cannot be detected.

3.3.1. Contact Time's effect and Kinetic Models:

The adsorbate's initial concentration and contact time play a crucial role in the adsorption process. Figure 5, illustrates the variation of the COD reduction rate (R %) of the raw leachate samples (EC1, EC2 and EC3) by adsorption on T1 and T2. The results show that after 8 hours of adsorption on T1, the reduction rate of COD (R %) was between 35 and 40 %, but it did not exceed 32 % on T2. Therefore, T1 based on limestone is more efficient than T2 based on green shale. On another note, the adsorption curves show similar patterns, starting with an initial phase around of about 5 hours, where the reduction rate is about 15-30 %. This is followed by second step until equilibrium is reached at around 12 hours, with final efficiencies of 30 to 38 %. This kinetics suggests a physicochemical adsorption mechanism involving first the occupation of the most energetic sites, then a slower intra-particulate diffusion. The effect of the initial concentration of COD manifests itself differentially depending on the type of material. The increase in initial concentration tends to create a higher mass transfer driving force, which leads to slightly lower removal efficiencies at the end of treatment. This phenomenon can be attributed to the increased competition between the organic load and the active sites responsible for reduction, as well as to the possible inhibition of reduction mechanisms by accumulation of intermediate products. The

variability observed between the different curves for each material therefore confirms the influence of the morphology and mineralogical composition of the materials as well as the pollutant load to be treated.

The kinetic study of adsorption provides information regarding the adsorption mechanism and the transfer mode between liquid/solid. Different models can be used to test the kinetics of adsorbent interactions. These models depend on the physical and chemical characteristics of the adsorbing material. The linear plot of log (q_e - q_t) versus t of the pseudo-first order model yields a line with a slope of (-k_1) and the y-intercept (logq_e). Thus, k_2 and q_e of the pseudo-second order model are calculated from the y-intercept and the slope of the linear graph of t/qt versus t, such that q_e = 1/slope and k_2 = slope²/y-intercept (Al-Anber and Al-Anber 2008). Table 5, presents the different parameters of adsorption kinetics. Comparative analysis of the two kinetic models shows that adsorption on T1 and T2 mainly follows second-order kinetics. Furthermore, the pseudo-second order model is distinguished by higher correlation coefficients (R^2) and lower SSE values than those obtained with the pseudo-first order model. A remarkable agreement between the experimental adsorption capacity (q_{exp}) and the theoretical capacity (q_{cal}) was also observed, confirming the predominance of a chemisorption mechanism (Mahmoudy et al. 2024). The rate constant K_2 decreases significantly with increasing concentration, reflecting notable differences in the availability and accessibility of active sites (Dawood and Sen 2012). These results confirm that the pseudo-second order model is better suited for the removal of COD on T1 and T2.

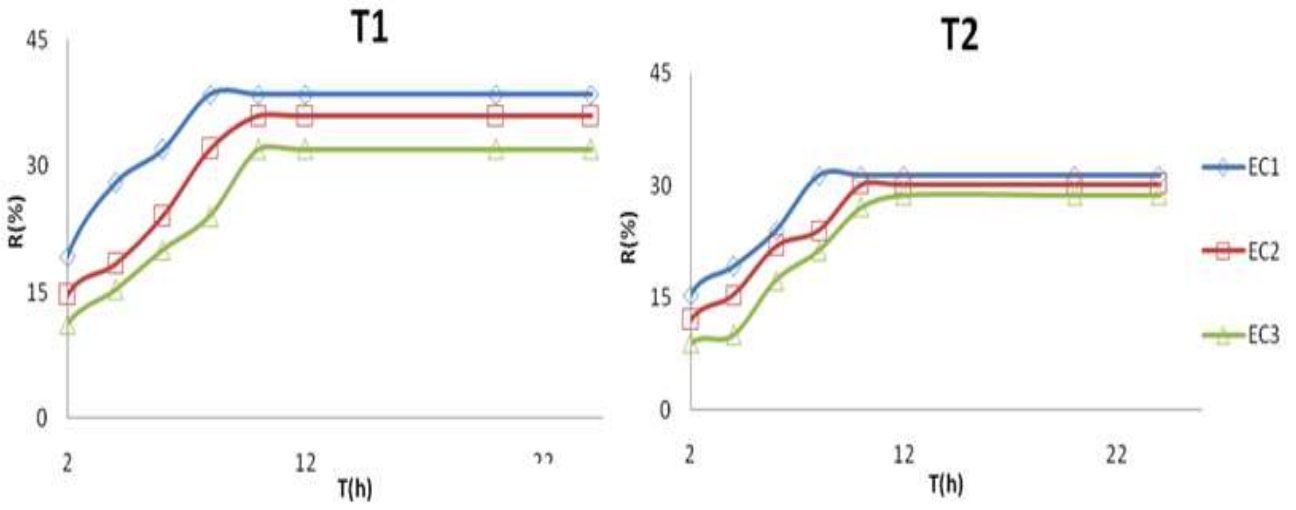

Fig. 5: Effect of contact time's on COD removal rate by T1 and T2.
(EC1, EC2 and EC3 = 2010, 2300 and 2540 mg/L, m = 5g/L, V=75ml).

Table 5: Adsorption kinetics parameters

				First-order			Second-order			
		q_{eexp}	q_{ecal}	K_1	R^2	SSE	qe cal	K_2	R^2	SSE
T1	EC1	49.29	73.96	0.31	0.76	8.23	50.68	0.14	0.95	0.47
	EC2	49.65	50.81	0.12	0.98		49.94	0.10	0.96	
	EC3	48.95	49.77	0.10	0.92		48.88	0.04	0.88	
T2	EC1	41.90	50.93	0.21	0.85	3.02	40.30	0.13	0.95	1.02
	EC2	39.72	39.36	0.12	0.91		38.91	0.08	0.92	
	EC3	39.16	37.54	0.08	0.89		41.67	0.02	0.85	

3.3.2. Adsorption Isotherms

The efficiency and adsorption capability of the two materials under study are assessed using the Langmuir and Freundlich adsorption isotherms. The parameters of the two adsorption models and the associated correlation coefficients (R^2) are shown in table 6. The high correlation coefficients obtained from the Freundlich model (R^2 = 0.99) for the two adsorbents show that adsorption preferentially occurs in multi-layeron heterogeneous active sites with non-uniform energy levels (Orugba et al. 2024), giving this model a better representation of the observed phenomenon. Furthermore, this result is confirmed by the heterogeneity factor 1/n, whose value is between 0 and 1. According to these results the maximum adsorption capacity of material T1 is q_{max} = 9.90 mg/g which is higher than that of material T2 (q_{max}= 6.49 mg/g). Showing that T1 is the most suitable for high-load pollutant treatments. This synergy demonstrates how surface property optimization affects thermodynamic performance simultaneously.

Table 6: Langmuir and Freundlich isotherm constants and correlation coefficients

	Langmuir			Freundlich		
	q_{max}	K_L	R^2	K_F	1/n	R^2
T1	9.90	0.10	0.92	0. 45	0.67	0.99
T2	6.49	0.15	0.95	0.50	0.45	0.99

In order to compare the results obtained in this study with those of previous studies, a comparative analysis of data published in the literature was carried out. Existing studies show considerable variability in the removal rates obtained by adsorption applied to leachates. For example, Genethliou et al. (2021) reported a COD reduction rate of 23.68 % during the simultaneous adsorption of ammoniacal nitrogen, COD, and color from a sanitary leachate using natural zeolite. Similarly, Lim et al. (2016) achieved a 43 % reduction in COD by combining a sequential anaerobic reactor (ASBR) with a zeolite adsorption stage. These variations in performance mainly reflect differences in the nature and structure of the adsorbents, the physicochemical characteristics of the leachates (pH, organic load, ionic composition, presence of metals). Despite this

heterogeneity, the results obtained in this study are in line with those usually observed for low-cost natural adsorbents. They also confirm that the chemical complexity of leachates and the persistent presence of refractory organic compounds often make it necessary to combine several complementary processes, with adsorption representing a relevant but insufficient step on its own to meet strict regulatory standards.

Limits and Prospects

With a view to future development, this study is part of an approach aimed at establishing a predictive model based on kinetic and isothermal adsorption models in order to anticipate the performance of the materials studied under different operating conditions. Although the results obtained highlight promising adsorption potential, the in-depth evaluation of the long-term durability, regeneration, and reuse of natural adsorbents from local resources remains a limitation of this work and constitutes a priority area for research. In this regard, further investigations incorporating successive adsorption–desorption cycles, as well as a more detailed analysis of operating parameters (temperature, contact time, pollutant load), would optimize performance and provide a better understanding of the process's applicability on a larger scale. These future developments would help consolidate the relevance of these materials as an environmentally friendly, economically accessible, and potentially renewable alternative to commercial adsorbents for the treatment of contaminated water.

4. CONCLUSIONS

The optimal management of leachates is generally guided by their properties and by technical feasibility. In this study, two adsorbent products based on limestone rocks and green shale derived from local Moroccan geological resources as natural adsorbents were characterized and evaluated for leachate treatment. The originality of this work lies in the use of abundant and inexpensive materials, combined with a kinetic and isothermal approach that makes it possible to describe and predict their adsorption behavior with respect to organic load. The results revealed that the material prepared from limestone has a higher efficiency than green shale for most of the physicochemical parameters analyzed, which opens up concrete prospects for their integration into treatment schemes adapted to the economic and environmental constraints of Morocco and regions with similar contexts. The results of kinetic and isotherm modeling the COD adsorption demonstrate that a number of parameters, including initial concentration, contact time and temperature, influence the adsorption process. Kinetic modeling and adsorption isotherms were best fitted by the pseudo-second order model and Freundlich model, respectively. In addition, these data demonstrate that limestone can serve as

an economic and accessible material, justifying its use as a substitute for certain expensive adsorbents. This choice can contribute significantly to improving the quality of leachates and other industrial effluents. However, before large-scale application, further studies are needed, including assessments of the regeneration and durability of adsorbents over multiple cycles, as well as pilot-scale validation. These developments will confirm the technical feasibility and optimize the integration of these materials into sustainable and economically viable leachate treatment systems.

Author Contributions: Conceptualization, I.E, A.B, and K.F.B.; Methodology, I.E, A.B, and I.T., Validation, A.B. and K.F.B., software, I.T, J.N, and M.B.A.; Writing—Original Draft Preparation, I.E, I.T, J.N. and M.B.A.; Writing—Review And Editing, A.B. and K.F.B.; Supervision, A.B. and K.F.B.; project administration, A.B.; funding acquisition, Not applicable. All authors have read and agreed to the published version of the manuscript.

Funding: "This research received no external funding"

Institutional Review Board Statement: "Not applicable"

Informed Consent Statement: "Not applicable"

Acknowledgments: A special thanks to the Fez city's controlled landfill and the staff of the USMBA' Innovation Center of Fez for their kindness and commitment.

Conflicts of Interest: "The authors declare no conflicts of interest".

REFERENCES

1. Abdel-Shafy, H. I., Ibrahim, A. M., Al-Sulaiman, A. M., and Okasha, R. A. 2024. Landfill leachate: Sources, nature, organic composition, and treatment: An environmental overview. *Ain Shams Engineering Journal*, 15(1), 102293. [https://doi.org/10.1016/j.asej.2023.102293]
2. Achak, M., Hafidi, A., Mandi, L., and Ouazzani, N. 2014. Removal of phenolic compounds from olive mill wastewater by adsorption onto wheat bran. *Desalination and Water Treatment,* 52(13-15), 2875-2885. [https://doi.org/10.1080/19443994.2013.819166]
3. Ahamad, Z., and Nasar, A. 2024. Polypyrrole-decorated bentonite magnetic nanocomposite: a green approach for adsorption of anionic methyl orange and cationic crystal violet dyes from contaminated water. *Environmental Research*, 247, 118193. [https://doi.org/10.1016/j.envres.2024.118193]

4. Ahouach, Y., Baali, A., Boushaba, A., Hakam, O., Azennoud, K., Lyazidi, A., and Chen, T. W. 2023. Impact of the controlled dump of fez city (Morocco): evaluation of metallic trace elements contamination in the sediments. *Water*, 15(6), 1209. [https://doi.org/10.3390/w15061209]

5. Al-Anber, M., and Al-Anber, Z. A. 2008. Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron. *Desalination*, 225(1-3), 70-81. [https://doi.org/10.1016/j.desal.2007.07.006]

6. Aljabarin, N. 2023. Chemical adsorption of iron ions from drinking water using Jordanian zeolitic tuff. *Desalination and Water Treatment*, 281, 196-203. [https://doi.org/10.5004/dwt.2023.29133]

7. Aluko, O. O., and Sridhar, M. K. 2013. Evaluation of leachate treatment by trickling filter and sequencing batch reactor processes in Ibadan, Nigeria. *Waste management research, 31*(7), 700-705. [https://doi.org/10.1177/0734242X13485867]

8. Al-Yaqout, A., and Hamoda, M. F. 2020. Long-term temporal variations in characteristics of leachates from a closed landfill in an arid region. *Water, Air, Soil Pollution*, *231*(6), 319. [Https://doi.org/10.1007/s11270-020-04688-7]

9. Aziz, H. A., Othman, N., Yusuff, M. S., Basri, D. R. H., Ashaari, F. A. H., Adlan, M. N., and Perwira, M. 2001. Removal of copper from water using limestone filtration technique: determination of mechanism of removal. *Envronment international*, *26*(5-6), 395-399. [https://doi.org/10.1016/S0160-4120(01)00018-6]

10. Aziz, H. A., Yusoff, M. S., Adlan, M. N., Adnan, N. H., and Alias, S. 2004. Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter. *Waste management*, *24*(4), 353-358. [https://doi.org/10.1016/j.wasman.2003.10.006]

11. Benaddi, R., Ferkan, Y., Bouriqi, A., and Ouazzani, N. 2022. Impact of landfill leachate on groundwater quality–a comparison between three different landfills in Morocco. *Journal of Ecological Engineering*, *23*(11), 89-94. [https://doi.org/10.12911/22998993/153006]

12. Chen, D. M. C., Bodirsky, B. L., Krueger, T., Mishra, A., and Popp, A. 2020. The world's growing municipal solid waste: trends and impacts. *Environmental Research Letters*, *15*(7), 074021. [DOI 10.1088/1748-9326/ab8659]

13. Daniel, A. N., Ekeleme, I. K., Onuigbo, C. M., Ikpeazu, V. O., and Obiekezie, S. O. 2021. Review on effect of dumpsite leachate to the environmental and public health implication. *GSC Advanced Research and Reviews*, *7*(2), 051-060. [https://doi.org/10.30574/gscarr.2021.7.2.0097]

14. Davarnejad, R., Afshar, S., and Etehadfar, P. 2020. Activated carbon blended with grape stalks powder: properties modification and its application in a dye adsorption. *Arabian Journal of Chemistry*, *13*(5), 5463-5473. [https://doi.org/10.1016/j.arabjc.2020.03.025]

15. Dawood, S., and Sen, T. K. 2012. Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. *Water research*, *46*(6), 1933-1946. [https://doi.org/10.1016/j.watres.2012.01.009]

16. El Jalil, M. H., Elkrauni, H., Khamar, M., Bouyahya, A., Elhamri, H., Cherkaoui, E., and Nounah, A. 2020. Physicochemical characterization of leachates produced in the Rabat-Salé-Kénitra Region landfill technical center and monitoring of their treatment by aeration and reverse osmosis. In *E3S Web of Conferences* (Vol. 150, p. 02013). EDP Sciences. [https://doi.org/10.1051/e3sconf/202015002013]

17. El Khomri, M., El Messaoudi, N., Dbik, A., Bentahar, S., and Lacherai, A. 2020. Efficient adsorbent derived from Argania Spinosa for the adsorption of cationic dye: kinetics, mechanism, isotherm and thermodynamic study. *Surfaces and Interfaces*, 20, 100601. [https://doi.org/10.1016/j.surfin.2020.100601]

18. El-Saadony, M. T., Saad, A. M., El-Wafai, N. A., Abou-Aly, H. E., Salem, H. M., Soliman, S. M., and AbuQamar, S. F. 2023. Hazardous wastes and management strategies of landfill leachates: A comprehensive review. *Environmental Technology Innovation*, *31*, 103150. [https://doi.org/10.1016/j.eti.2023.103150]

19. Fayoud, N., Younssi, S. A., Tahiri, S., and Albizane, A. 2015. Etude cinétique et thermodynamique de l'adsorption de bleu de méthylène sur les cendres de bois (Kinetic and thermodynamic study of the adsorption of methylene blue on wood ashes). *J. Mater. Environ.* Sci, 6(11), 3295-3306.

20. Foo, K. Y., and Hameed, B. H. 2010. An overview of dye removal via activated carbon adsorption process. *Desalination and Water Treatment,* 19(1-3), 255-274. [https://doi.org/10.5004/dwt.2010.1214]

21. Foul, A. A., Aziz, H. A., Isa, M. H., and Hung, Y. T. 2009. Primary treatment of anaerobic landfill leachate using activated carbon and limestone: batch and column studies. *International Journal of Environment and Waste Management*, *4*(3-4), 282-298. [https://doi.org/10.1504/IJEWM.2009.027397]

22. Genethliou, C., Triantaphyllidou, I. E., Giannakis, D., Papayianni, M., Sygellou, L., Tekerlekopoulou, A. G., Vayenas, D. V. 2021. Simultaneous removal of ammonium nitrogen, dissolved chemical oxygen demand and color from sanitary landfill leachate using natural zeolite. *Journal of hazardous materials, 406, 124679.* [https://doi.org/10.1016/j.jhazmat.2020.124679]

23. Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., and Suhas. 2009. Low-cost adsorbents: growing approach to wastewater treatment a review. *Critical reviews in environmental science and technology*, *39*(10), 783-842. [https://doi.org/10.1080/10643380801977610]

24. Gutiérrez-Mosquera, L. F., Arias-Giraldo, S., and Zuluaga-Meza, A. 2022. Landfill leachate treatment using hydrodynamic cavitation: exploratory evaluation. *Heliyon*, *8*(3). [https://doi.org/10.1016/j.heliyon.2022.e09019]

25. Halim, A. A., Aziz, H. A., Johari, M. A. M., and Ariffin, K. S. 2010. Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. *Desalination*, *262*(1-3), 31-35. [https://doi.org/10.1016/j.desal.2010.05.036]

26. Hernández-García, A., Velásquez-Orta, S. B., Novelo, E., Yáñez-Noguez, I., Monje-Ramírez, I., and Ledesma, M. T. O. 2019. Wastewater-leachate treatment by microalgae: Biomass, carbohydrate and lipid production. *Ecotoxicology and Environmental safety*, *174*, 435-444. [https://doi.org/10.1016/j.ecoenv.2019.02.052]

27. Hussain, S. T., and Ali, S. A. K. 2021. Removal of heavy metal by ion exchange using bentonite clay. *Journal of Ecological Engineering*, 22(1), 104-111.

28. Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., and Christensen, T. H. 2002. Present and long-term composition of MSW landfill leachate: a review. *Critical reviews in environmental science and technology*, *32*(4), 297-336. [https://doi.org/10.1080/10643380290813462]

29. Kordala, N., and Wyszkowski, M. 2024. Zeolite properties, methods of synthesis, and selected applications. *Molecules*, *29*(5), 1069. [https://doi.org/10.3390/molecules29051069]

30. Lim, C.K., Seow, T.W., Neoh, C.H., Md Nor, M.H., Ibrahim, Z., Ware, I., Mat Sarip, S.H., 2016. Treatment of landfill leachate using ASBR combined with zeolite adsorption technology. *3 Biotech. 6, 195.* [http://dx.doi.org/10.1007/s13205-016-0513-8]

31. Mahmoudy, G., Dabagh, A., El-Habacha, M., Lagdali, S., Assouani, A., Soulaiman, I., and Zerbet, M. 2024. Preparation and characterization of biomaterial for phosphate ion removal: Kinetics, isotherms and thermodynamics studies. *Desalination and Water Treatment*, *317*, 100062. [https://doi.org/10.1016/j.dwt.2024.100062]

32. Mandal, P., Dubey, B. K., and Gupta, A. K. 2017. Review on landfill leachate treatment by electrochemical oxidation: Drawbacks, challenges and future scope. *Waste Management*, *69*, 250-273. [https://doi.org/10.1016/j.wasman.2017.08.034]

33. Merzouki, H., Hanine, H., Lekhlif, B., Latrache, L., Mandi, L., and Sinan, M. 2015. Physicochemical characterization of leachate discharge Fkih Ben Salah from Morocco. J. Mater. Environ. Sci, 6(5), 1354-1363.

34. Miao, L., Yang, G., Tao, T., and Peng, Y. 2019. Recent advances in nitrogen removal from landfill leachate using biological treatments–A review. *Journal of environmental management*, *235*, 178-185. [https://doi.org/10.1016/j.jenvman.2019.01.057]

35. Mor, S., and Ravindra, K. 2023. Municipal solid waste landfills in lower-and middle-income countries: Environmental impacts, challenges and sustainable management practices. *Process Safety and Environmental Protection*, *174*, 510-530. [https://doi.org/10.1016/j.psep.2023.04.014]

36. Mor, S., Negi, P., and Khaiwal, R. 2018. Assessment of groundwater pollution by landfills in India using leachate pollution index and estimation of error. *Environmental nanotechnology, monitoring management*, *10*, 467-476. [https://doi.org/10.1016/j.enmm.2018.09.002]

37. Njoku, P. O., Edokpayi, J. N., and Odiyo, J. O. 2019. Health and environmental risks of residents living close to a landfill: A case study of Thohoyandou Landfill, Limpopo Province, South Africa. *International journal of environmental research and public health*, *16*(12), 2125. [https://doi.org/10.3390/ijerph16122125]

38. Nourmoradi, H., Avazpour, M., Ghasemian, N., Heidari, M., Moradnejadi, K., Khodarahmi, F., and Moghadam, F. M. 2016. Surfactant modified montmorillonite as a low cost adsorbent for 4-chlorophenol: Equilibrium, kinetic and thermodynamic study. *Journal of the Taiwan Institute of chemical engineers*, *59*, 244-251. [https://doi.org/10.1016/j.jtice.2015.07.030]

39. Orugba, H. O., Sinebe, J. E., Chukwuneke, J. L., Okoro, V. I., Enyi, C. L., and Ani, O. I. 2024. Adsorption of cadmium from wastewater with activated carbons derived from pig fur biowaste: A comparative study of in-situ and ex-situ activation routes. *Heliyon*, 10(18). [https://doi.org/10.1016/j.heliyon.2024.e37768]

40. Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., and Moulin, P. J. J. O. H. M. 2008. Landfill leachate treatment: Review and opportunity. *Journal of hazardous materials*, *150*(3), 468-493. [https://doi.org/10.1016/j.jhazmat.2007.09.077]

41. Rodier, J., Bazin, C., Broutin, J. P., Chambon, P., Champsaur, H., and Rodi, L. 2009. Water analysis, 9th edit. *Dunod, Paris, France*, *1579*.

42. Shadi, A. M. H., Kamaruddin, M. A., Niza, N. M., Emmanuela, M. I., Shaah, M. A., Yusoff, M. S., and Allafi, F. A. 2020. Characterization of stabilized leachate and evaluation of LPI from sanitary landfill in Penang, Malaysia. *Desalination and Water Treatment*, *189*, 152-164. [https://doi.org/10.5004/dwt.2020.25468]

43. Sharma, A., Grewal, A. S., Sharma, D., and Srivastav, A. L. 2023. Heavy metal contamination in water: consequences on human health and environment. In *Metals in water* (pp. 39-52). Elsevier. [https://doi.org/10.1016/B978-0-323-95919-3.00015-X]

44. Sun, S., Ren, J., Liu, J., Rong, L., Wang, H., Xiao, Y., and Su, X. 2022. Pyrite-activated persulfate oxidation and biological denitrification for effluent of biological landfill leachate treatment system. *Journal of Environmental Management*, *304*, 114290. [https://doi.org/10.1016/j.jenvman.2021.114290]

45. Wang, J., and Qiao, Z. 2024. A comprehensive review of landfill leachate treatment technologies. *Frontiers in Environmental Science*, *12*, 1439128. [https://doi.org/10.3389/fenvs.2024.1439128]

46. Zand, A. D., Abyaneh, M. R. 2020. Adsorption of Lead, manganese, and copper onto biochar in landfill leachate: implication of non-linear regression analysis. *Sustainable Environment Research, 30(1), 18.* [https://doi.org/10.1186/s42834-020-00061-9]

47. Zineb, H., Latifa, M., Salah, S., and Laila, S. 2020. Removal of pollution by intensive aeration technology for landfill leachate treatment. *Journal of Health and Pollution*, *10*(28), 201212. [https://doi.org/10.5696/2156-9614-10.28.201212]