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

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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. In contrast, 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. The absorbent properties of the 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 the adsorption efficiency. Characterization before the adsorption process revealed that the prepared materials had a partially homogeneous surface with particles of irregular sizes and varied atomic compositions. The material prepared from limestone showed the highest performance, with reduction rates of 39%, 43%, and over 80% for COD, BOD, and heavy metals (Cr, Fe, Ni, Pb, and Zn), respectively. The results of the kinetic and isothermal models showed that the removal efficiency of COD was 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 pseudo-second-order and Freundlich models well adjusted the kinetic and isothermal models. These results confirm the potential of these low-cost adsorbents for sustainable environmental applications, with limestone exhibiting superior performance.

1. INTRODUCTION

Household waste is non-hazardous waste, including all waste from economic activities or households, and is guaranteed to be harmless. Waste production and management 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 owing to annual demographic increases, booming industrialization, accelerated urbanization, and large-scale consumption habits (Chen et al. 2020). Similar to many developing countries, Morocco has experienced rapid development over the last five decades, particularly in terms of population growth. Simultaneously, the quantity of household waste has undergone a similar evolution, mainly due to new production and consumption patterns, as well as a progressive rate of rural exodus and urbanization. Household waste production is estimated to be over 7 million tons per year.

To optimize solid waste management, local authorities have established strategies for collecting and handling waste, particularly in controlled or uncontrolled open dumps. When precipitation or other sources of moisture come into contact with waste accumulated in landfills, soluble compounds are generated through biological and physicochemical reactions. These degradation processes subsequently produce a heavily polluted effluent, known as leachate (Wang & Qiao 2024, Mor & Ravindra 2023). The compositional variability of these discharge compounds is explained by the influence of multiple physicochemical and environmental factors, such as the landfill's age, accumulated waste typology, and 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, are variable over time, and are influenced by several factors (El-Saadony et al. 2023, Gutiérrez-Mosquera et al. 2022). They are generally characterized by high pollution loads, both organic and inorganic. Organic load encompasses quantified compounds in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), volatile fatty acids, and various hydrocarbons and volatile organic compounds (VOCs) (Kjeldsen et al. 2002). The inorganic fraction is characterized by the presence of ammoniacal 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 & Hamoda 2020).

The structural diversity of this pollutant matrix is a fundamental determinant of ecosystem pollution and has significant health implications at the community level. These liquids, which are highly charged with pollutants, can infiltrate soils and contaminate groundwater (Ahouach et al. 2023). Moreover, pathogens can adversely affect water- 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 living near discharges (Daniel et al. 2021, Njoku et al. 2019).

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

Although conventional adsorbents are effective, their high costs limit 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 & Nasar 2024, Aljabarin 2023, Hussain & Ali 2021). These materials are abundant, inexpensive, sometimes derived from quarry waste, and have favorable physico-chemical properties for adsorption. Although these geological adsorbents have several advantages, they face limitations that restrict their large-scale use. Their adsorption power is always less important than that of commercial materials, such as activated carbon or synthetic zeolites (Foo & Hameed 2010). Moreover, their efficiency decreases in the presence of several competing ions, which reflects limited selectivity. Performance is also strongly conditioned by parameters such as pH, temperature, or initial concentration, which restricts their use in variable environments (Kordala & Wyszkowski 2024). Finally, the regeneration of the material 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 for the treatment of leachates from the controlled landfill of the city of Fez. This study aims to offer a sustainable and inexpensive alternative to commercial adsorbents. The novelty of this study lies in the use of these two materials, which have 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 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 of metals. The two materials obtained were characterized before and after the leachate treatment process using SEM, XRD, and FTIR to confirm and evaluate the reduction potentials of certain types of pollutants present in the leachates. The effect of temperature, contact time, and COD content of leachate on the COD reduction efficiency of both materials was evaluated. Kinetic models, including the pseudo-first and pseudo-second order, as well as the Langmuir and Freundlich isotherms, were 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 an 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 from around the city of Taza, Morocco (Fig. 1). The preparation of materials based on these rocks using physical processes involves several steps. The collected limestone and raw green schist were first cleaned and dried, and then crushed using a jaw crusher of the type FRITSCH PLUVERISETTE 1. After grinding 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 smaller than 100 µm. The material was then dried at 60°C for several hours. The materials produced from limestone and green shale were named T1 and T2, respectively. The two materials used in this study did not undergo any additional chemical modifications or treatments. 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.

Table 1: Physicochemical parameters analysis methods.

Parameters	Unit	Analysis methods
pH	--	Multi-parameter Consort C561
EC	mS.cm^{-1}	
SS	mg.L^{-1}	Filtration method
COD	mg.L^{-1}	Colorimetric
BOD$_5$	mg.L^{-1}	OXITOP
NTK	mg.L^{-1}	Mineralization
Al	mg.L^{-1}	ICP-AES
Cr		
Fe		
Ni		
Pb		
Zn		

2.2. Leachate Sampling and Characterization

Leachate collection was carried out at the landfill site of Fez City (Morocco), which extends over 120 hectares and accommodates more than 800 tons of mixed municipal solid waste streams daily. The leachate samples intended for physicochemical and heavy metal analyses were collected in 500 mL polyethylene bottles, labeled, and transported in a temperature-controlled cooler at 4°C to the laboratory. The multiparametric instrument Consort was used to perform local measurements of the electrical conductivity (EC) and

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

pH. All physicochemical analyses were conducted following the techniques suggested by Rodier et al. (2009), and the parameters are listed in Table 1.

2.3. Experimental Study of Leachate Treatment

To assess the efficacy and performance of T1 and T2 materials for leachate treatment, 75 mL of leachate was brought into contact with 5 $g.L^{-1}$ of T1 or T2 in a closed reactor, and each solution was stirred at 300 rpm. Following a 24 h contact period, the suspension was centrifuged at 5000 rpm for 10 min. The final concentrations of physicochemical parameters and heavy metals were determined in the supernatant using the methods described above. The adsorption experiments were conducted at room temperature without a temperature control device, and no pH adjustments were made to evaluate the natural behavior of the materials under actual leachate conditions. The reduction rate R (%) and adsorption capacity q_e ($mg.g^{-1}$) of the various physicochemical parameters (pH, COD, BOD_5, NTK, Ni, Fe, Cr, Zn, Pb, and Al) were determined using Equations (1) and (2), respectively:

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

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

Where C_i and C_e are the initial and equilibrium concentration parameters in solution, respectively ($mg.L^{-1}$), 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 and then mixed with 5 $g.L^{-1}$ of T1 or T2. Sample mixtures with varying concentrations were stirred for 24 h at 300 rpm at room temperature. Every two hours of contact, the suspension was centrifuged for five minutes at 5000 rpm and filtered, and the filtrate was analyzed colorimetrically to determine the COD. The monitoring of this indicator was carried out because of its relevance in assessing the effectiveness of treatment procedures and compliance with the 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):

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

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

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

Where: k_2 is the pseudo-second order adsorption rate constant ($g.mg^{-1}.min^{-1}$).

The kinetic model is mainly used in a linear form because fewer calculations are required to determine the model parameters. Error analysis for a kinetic model using a nonlinear model consists of evaluating the accuracy and reliability of the model used to estimate the parameters of the adsorption models. The application of the model can also be verified using error analysis techniques such as the sum of squares error (SSE), which is a measure of the difference between the experimental values and the 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 equation (Zand & Abyaneh 2020).

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 $g.L^{-1}$ of T1 or T2, together with a crude leachate sample (75 mL), were added to the system in batches for 6 h and maintained at various temperatures (25, 30, and 40°C). For each adsorbate, the residual concentration ($C_{e)}$ was determined.

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

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

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

Where: C_e ($mg.L^{-1}$) is the adsorbate concentration in the liquid phase at equilibrium, q_e ($mg.g^{-1}$) is the adsorption capacity at equilibrium, q_{max} ($mg.g^{-1}$) is the maximum adsorption capacity, K_L, K_f and n are constants of Langmuir and Freundlich models.

3. RESULTS AND DISCUSSION

3.1. Characterization of Materials

SEM and EDX analysis: SEM was used to determine the morphological features and surface porosity of the investigated material. The developed porosity makes it possible to enhance the number of active sites on which different types of pollutants can be fixed (Davarnejad et al. 2020). The SEM analysis results for T1 and T2 before treatment are shown in Figs. 2A and 2B, respectively, while Figs. 2C and 2D show the results for T1 and T2 after the treatment. 2 also shows the chemical compositions of T1 and T2 before and after treatment. These results show that the surfaces of T1 and T2 are partially homogeneous with a fragmented and rough structure, which may indicate natural weathering and high porosity. These results also indicate the presence of carbonate crystals at the limestone level. 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, sample T2 mainly contained 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 revealed 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

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

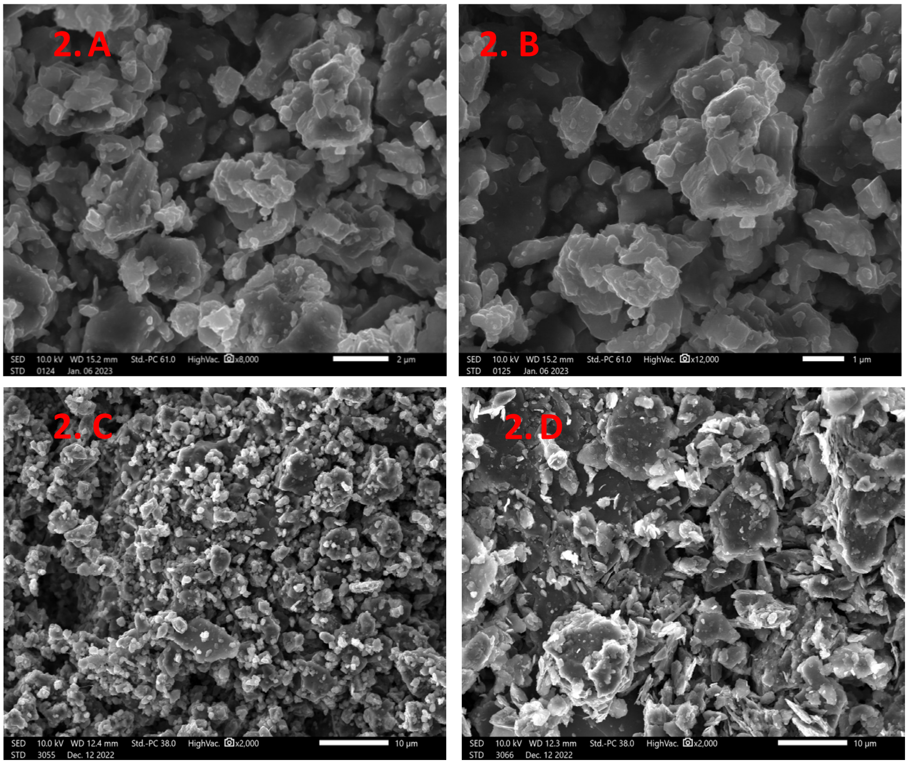

Fig. 2: Image of the T1 and T2 observed by Scanning Electron Microscopy (SEM) before (2.A, 2.B) and after (2.C, 2.D) treatment.

various pollutants or by chemical reactions or interactions with the effluent elements (Figs. 2C and 2D). These results are consistent with the EDX analysis (Table 2), which indicates an increase in carbon and the presence of chlorine and certain heavy metals such as aluminum and iron. Overall, these results corroborate the decrease in organic load and heavy metals from leachate samples treated with both T1 and T2.

X-ray diffraction: XRD was used to determine the mineralogical composition and crystalline arrangement of the samples. Figs. 3A and 3B show the X-ray diffraction patterns of the two materials, T1 and T2, with several marked diffraction peaks. The spectral analysis of T1 mainly revealed the presence of an intense peak at 29.43° corresponding to calcite ($CaCO_3$), while the peaks identified at 26.60° and 50.14° corresponded to the presence of quartz (SiO_2), which indicated that the T1 material was essentially calcite, with a negligible amount of quartz. 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 the presence of chlorite marked by the peak 25.30°. Figs. 3C and 3D of T1 and T2 after treatment show slight variations in peak intensities. The characteristic limestone peaks at 20.96°, 29.5°, and 43.30° exhibit minor intensity changes following treatment. Additionally, the peaks observed at 36° and 39° suggest the presence of other calcite phases or secondary mineral components. Similarly, the XRD pattern of the green shale after treatment revealed the presence of more chlorite and less quartz than that of the raw T2 material. Therefore, the differences observed between the two samples are probably due to the leachate treatment. This treatment can introduce additional phases or disrupt the structure of minerals present in limestone and green shale.

Fourier transform infrared spectroscopy: FTIR is an analysis technique based on the vibrational properties of interatomic 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 products T1 and T2 before and after leachate treatment. Figs. 4A and 4B and 4C and 4D 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}. The band between 780 and 840 cm^{-1} is generally related to the out-of-plane deformation of CO_3^{2-}, indicating the presence of calcite. The bands between 1200 and 1250 cm^{-1} are attributed to the silicates. A broad band between 1300 and 1500 cm^{-1} is attributed to the asymmetric stretching of carbonate (CO_3^{2-}), confirming the presence of calcite ($CaCO_3$). Similarly, three bands were detected in the T2 spectrum (Fig. 4B). 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 the vibrations of Si-O bonds in silicate minerals. Analyses of the IR spectra of T1 and T2 after treatment (Figs. 4C and 4D)

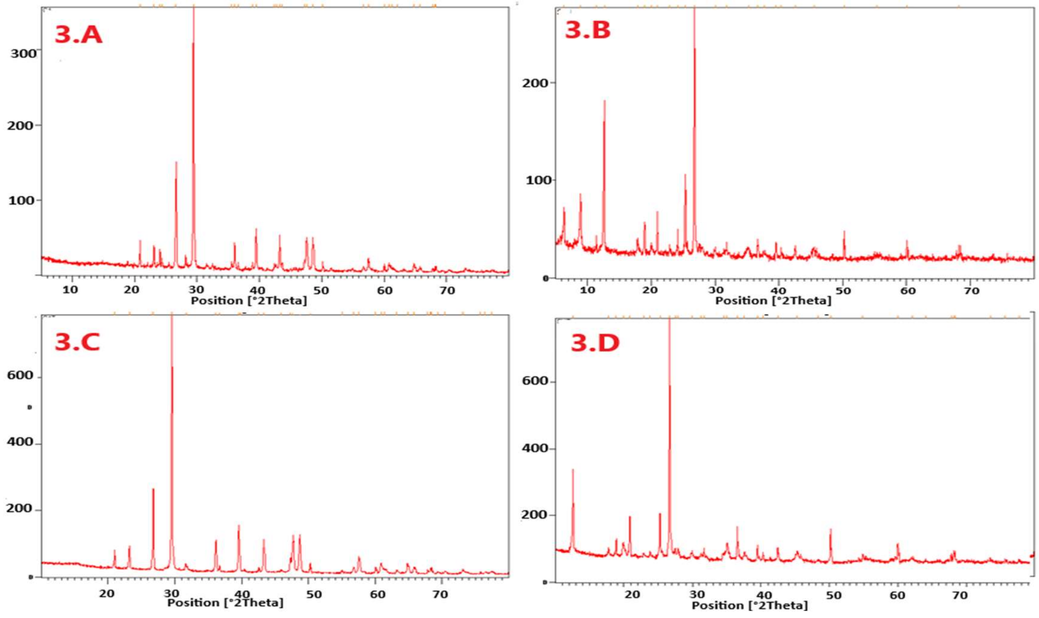

Fig. 3: X-ray diffraction of T1 and T2 before (3.A, 3.B) and after (3.C, 3.D) treatment.

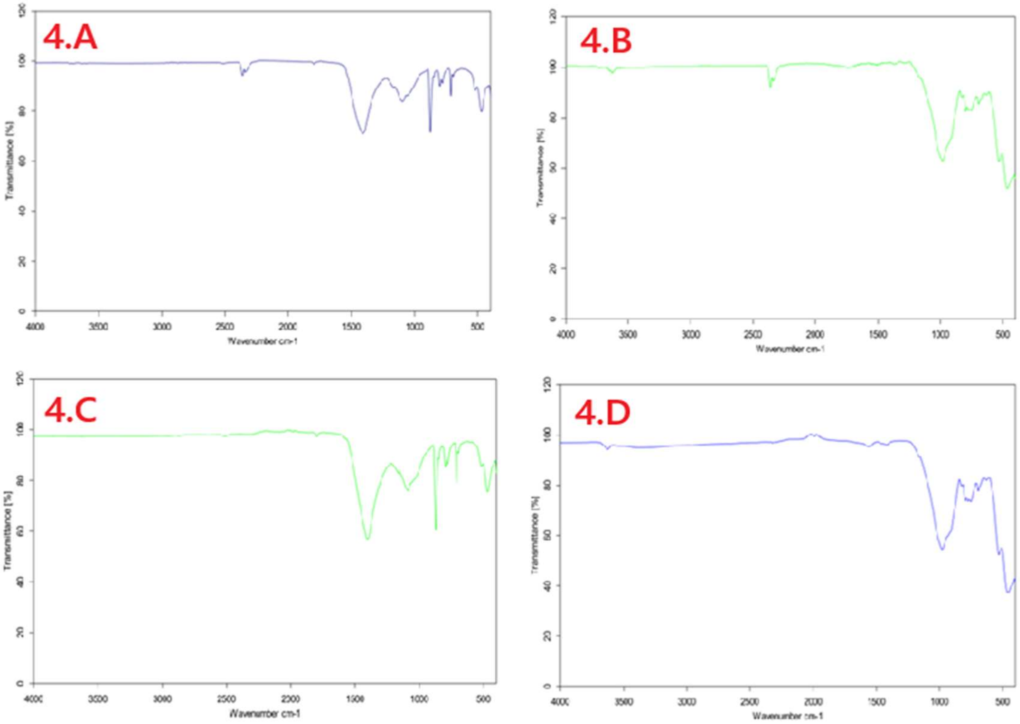

Fig. 4: FTIR spectrum of T1 and T2 before (4A, 4B) and after (4C, 4D) treatment.

show 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 were modified.

3.2. Leachate Analysis

Pollution indicator parameters were analyzed to evaluate the physicochemical and metallic qualities 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 waste anaerobic degradation. Moreover, the pH value 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 in leachates. The EC concentration was 36.04 mS.cm^{-1}, indicating a strong mineralization activity, 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 studies (Zineb et al. 2020, Mor et al. 2018). Dissolved organic matter is represented by certain global parameters, such as chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) (Mandal et al. 2017). Respective COD and BOD_5 values were 9088.5 and 1680.2 mg.L^{-1}. These results far exceeded the values set by the Moroccan discharge standards. These high concentrations are largely due to the composition of the mixtures of putrescible waste and refractory organic compounds. Suspended Solids (SS) also show a very high value, 2089.42 mg.L^{-1}, far from the value required by the Moroccan standard. High levels of SS in the leachate are due to the incomplete decomposition of waste and leaching of solid particles (organic and mineral), which could reflect an increase in lixiviate mineralization. Similarly, the total Kjeldahl nitrogen (TKN) content in the leachate was high at 1080 mg.L^{-1}. NTK, which includes ammoniacal nitrogen (NH_4^+) and organic nitrogen, is a key indicator of the overall nitrogen load in leachate. Compared to national standards and results observed in other studies, these measured values were 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^{-1} and 5.12 mg.L^{-1}, which 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, were present at low concentrations. The results of this study are similar to those of other studies that reported the presence of heavy metals in leachates (Shadi et al. 2020, Hernández-García,

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

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

*: Moroccan Liquid Discharges Standards (MLDS 2018).

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 electronics 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.

3.3. Leachate Treatment

This section aims to determine the variation in the physicochemical parameters (pH, COD, BOD_5, NTK, Al, Cr, Fe, Ni, Pb, and Zn) of leachate treated with T1 and T2 materials. Table 4 shows the reduction rates of the physicochemical parameters of the leachate treated with T1 and T2. The removal rates were calculated for each parameter after 24 h of treatment. The results obtained following the treatment of the leachate by T1 and T2 showed variable efficiencies depending on the physicochemical parameters studied. These results revealed significant differences in abatement efficiency between T1 and T2 applied to leachate treatment. Generally, adsorption on T1 and T2 led to a significant reduction in various pollutants, confirming the potential of these materials as low-cost processing media. pH analyses before and after treatment revealed distinct effects depending on the type of material. The initial leachate had a slightly basic pH value. After treatment at T1, the pH increased slightly from 8.2 to 9.02. This result is consistent with other studies (Aziz et al. 2004, Aziz et al. 2001), which attributed the increase in pH 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 attributed to the 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 approximately 41-43%, indicating that both T1 and T2 materials retained biodegradable compounds. These results are consistent with those of Aluko and Sridhar (2013), who used a process combining biofiltration and sequencing 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 ammonia nitrogen was modest for both T1 and T2. The concentration of NTK decreased from 1080.2 mg.L^{-1} to 841.56 mg.L^{-1} for T1 and 880.51 mg.L^{-1} 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 the intervention of specific exchangers. The results of the analysis of heavy metals after treatment showed that both materials were highly effective

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

Parameters	Unit	leachate	Treatment by T1	%R [T1]	Treatment by T2	%R [T2]
pH		8.2	9.02	--	7.4	--
COD	mg.L^{-1}	9088.5	5525.25	39.20	6352.86	30.10
BOD5	mg.L^{-1}	1646.82	960.80	41.66	930.07	43.52
NTK	mg.L^{-1}	1080.20	841.56	22.09	880.51	18.48
Al	mg.L^{-1}	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.

against heavy metals. Indeed, the removal rates of Cr, Ni, Pb, and Zn reached 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 a better chemical affinity for metals due 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. Conversely, 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 improving leachate quality.

3.3.1. Contact Time's Effect and Kinetic Models

The initial concentration and contact time of the adsorbate play crucial roles in the adsorption process. Fig. 5 illustrates the variation in 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 h 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, which is based on limestone, is more efficient than T2, which is based on green shale. On another note, the adsorption curves show similar patterns, starting with an initial phase of approximately 5 h, where the reduction rate is approximately 15-30 %. The second step followed this until equilibrium was reached at approximately 12 h, with final efficiencies of 30–38 %. This kinetic behavior suggests a physicochemical adsorption mechanism involving the occupation of the most energetic sites, followed by slower intraparticle diffusion. The effect of the initial COD concentration differed depending on the type of material. The increase in the initial concentration tends to create a higher mass transfer driving force, which leads to slightly lower removal efficiencies at the end of the treatment. This phenomenon can be attributed to the increased competition between the organic load and the active sites responsible for reduction, as well as the possible inhibition of reduction mechanisms by the accumulation of intermediate products. The variability observed between the different curves for each material confirms the influence of the morphology and mineralogical composition of the materials, as well as the pollutant load to be treated.

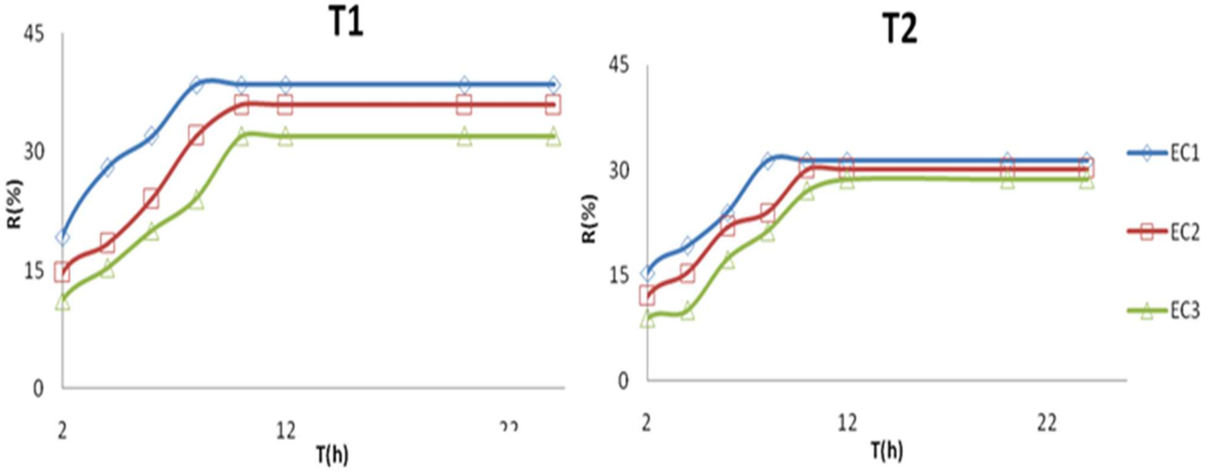

Fig. 5: Effect of contact times on COD removal rate by T1 and T2.
(EC1, EC2 and EC3 = 2010, 2300 and 2540 mg.L^{-1}, m = 5 g.L^{-1}, V=75 mL).

Table 5: Adsorption kinetics parameters.

		q_{eexp}	First-order				Second-order			
			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	

A kinetic study of adsorption provides information regarding the adsorption mechanism and transfer mode between liquid and solid. Different models can be used to test the kinetics of adsorbent interaction. These models depend on the physical and chemical characteristics of the adsorbent. The linear plot of log (q_e - q_t) versus t for the pseudo-first-order model yields a line with a slope of ($-k_1$) and a y-intercept ($\log q_e$). 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 & Al-Anber 2008). Table 5 presents the different adsorption kinetics parameters. Comparative analysis of the two kinetic models showed that adsorption on T1 and T2 mainly followed second-order kinetics. Furthermore, the pseudo-second-order model was 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 theoretical capacity (q_{cal}) was also observed, confirming the predominance of the 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 the active sites (Dawood & Sen 2012). These results confirm that the pseudo-second-order model is better suited for the removal of COD on T1 and T2.

3.3.2. Adsorption Isotherms

The efficiency and adsorption capabilities of the two materials were assessed using the Langmuir and the Freundlich adsorption isotherms. The parameters of the two adsorption models and their associated correlation coefficients (R^2) are listed in Table 6. The high correlation coefficients obtained from the Freundlich model ($R^2 = 0.99$) for the two adsorbents indicate that adsorption preferentially occurs on multilayers on heterogeneous active sites with non-uniform energy levels (Orugba et al. 2024), providing a better representation of the observed phenomenon. Furthermore, this result was confirmed by the heterogeneity factor 1/n, whose value was between 0 and 1. According to these results, the maximum adsorption capacity of material T1 was q_{max} = 9.90 $mg.g^{-1}$, which was higher than that of material T2 (q_{max} = 6.49 $mg.g^{-1}$). This shows that T1 is the most suitable for high-load pollutant treatment. 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

To compare the results obtained in this study with those of previous studies, a comparative analysis of the data published in the literature was performed. Existing studies show considerable variability in the removal rates obtained by the adsorption of 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 and the physicochemical characteristics of the leachates (pH, organic load, ionic composition, and presence of metals). Despite this heterogeneity, the results obtained in this study are consistent with those typically observed for low-cost natural adsorbents. They also confirmed that the chemical complexity of leachates and the persistent presence of refractory organic compounds often necessitate the combination of several complementary processes, with adsorption representing a relevant but insufficient step on its own to meet strict regulatory standards.

3.4. 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, an in-depth evaluation of the long-term durability, regeneration, and reuse of natural adsorbents from local resources remains a limitation of this study 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 environmentally friendly, economically accessible, and potentially renewable alternatives to commercial adsorbents for the treatment of contaminated water.

4. CONCLUSIONS

Their properties and technical feasibility generally guide the optimal management of leachates. 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 study 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 that prepared from 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 the kinetic and isotherm modeling of COD adsorption demonstrated that several parameters, including initial concentration, contact time, and temperature, influenced the adsorption process. The pseudo-second-order and the Freundlich models, respectively, best fit the kinetic modeling and adsorption isotherms. These data also demonstrate that limestone can serve as an economic and accessible material, justifying its use as a substitute for certain expensive adsorbents. This choice can significantly improve 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 and 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 for the future.

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