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Kinetic Study of Urban Sludge Using Iso-conversional Kinetic Analysis

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Abstract

Significant quantities of urban sludge generated by wastewater treatment plants pose serious eco-toxicological and environmental issues. Urban sludge collected at different stages of wastewater treatment is generally composed of non-biodegradable organic matter, micro-organisms, and mineral matter in the form of aluminum hydroxide, silica hydroxide, iron hydroxide, and calcium hydroxide. The most common uses of sewage sludge treatment are agriculture and landfill. However, they cause problems related to pollution and recovery of energy and nutrients from sewage sludge, which makes its usage as fertilizer doubtful. Therefore, thermal treatment methods handle these problems through energy recovery and pollutant destruction. In this context, we studied the urban sludge characteristics using X-ray diffraction (XRD), X-ray fluorescence (XRF), and thermal analysis. The results obtained showed that the studied samples contain different mineral fractions of 31% silica (SiO_2), 21.4% aluminum oxide (Al_2O_3), and 14.7% iron species, which make urban sludge promising in building materials. Through the heat treatment of raw and limed urban sludge, we observed a complex decomposition process, and the calculated activation energy using the isoconversional method proposed by Friedman showed a significant variation of over 10%, confirming the intricate nature of the sludge. Our findings underscore the need for a comprehensive approach to sludge management, optimizing its potential use and reducing the environmental impact.

Keywords

Urban sludge, Oxidation kinetics, Non-isothermal analysis, Peak-deconvolution, Malek

Introduction

Waste management is a crucial issue and an important area of research in the modern age [1, 2]. The treatment of sludge generated by drinking and wastewater treatment plants is an important branch of waste management that aims to address environmental problems caused by sludge [3]. Wastewater treatment plants cause significant production of urban residual sludge [4], the treatment and disposal of which involve significant economic, health, and technological restrictions [5]. Treatment of urban sludge is a significant challenge in wastewater management as it requires the development of new techniques and increased financial investment [6, 7].

The current methods used for sludge treatment include anaerobic digestion, composting, and land application [8]. Anaerobic digestion produces biogas as a source of renewable energy and a stabilized residue. Composting produces a stabilized residue that can be used as a soil amendment. Land application involves spreading the stabilized sludge on agricultural land as a fertilizer or soil amendment. Each method has its own advantages and limitations, and the choice of treatment method depends on the characteristics of the sludge and the specific goals of the treatment [9].On the other hand, proper heat treatment of sludge, particularly if it is enriched with organic matter, can yield a variety of benefits such as the production of energy, sustainable electricity [10], precious chemicals, and various construction materials [4, 5], including cement [7, 11], eco-cement [12], light aggregates, and ceramic products [8, 13].

The use of thermo-analytical techniques, specifically thermogravimetric analysis, for studying the combustion characteristics of sludge may provide valuable information on thermal treatment plants to follow. The advantages of thermogravimetric analysis include its ability to quickly assess the fuel value, determine the temperatures at which combustion starts and ends, and other characteristics such as maximum reactivity temperature, ash amount, and total combustion time. Thermal methods such as TGA (Thermogravimetric analysis), DTG (Derivative thermogravimetry), and DTA (Differential thermal analysis) have been used to study a variety of combustion areas. Thermal analysis is a set of methods that determine the selected physical properties of a substance under the influence of temperature. However, research on the combustion processes of sewage sludge has not been as extensive as research on coal or biomass due to its complex composition [14].

The primary objective of our study is to thoroughly characterize the sludge and investigate its complexity through thermal degradation processes, based on the calculation of the activation energy. In light of this, our study embarked on the examination of the mineral composition of raw and limed urban sludge materials using XRD and XRF. Following this, we delved into an investigation of the complex thermal behavior of both materials utilizing thermal analysis and thermal kinetics through isoconversional methods.

Materials and Method

Materials

Urban sludge was collected from the Bouragrag wastewater treatment plant in Rabat (Morocco). The samples were air-dried for a week, sieved to obtain a particle size of less than 2 mm, and then stored in a desiccator until use. The limed sludge was prepared by adding quicklime (CaO) to the raw sludge at a ratio of 2:1 (w/w) and mixing for 1 h. The mixture was then air-dried at room temperature to achieve a constant weight, ground, and sieved to obtain a particle size smaller than 2 mm. The reagents used were of analytical grade and were purchased from Merck (Darmstadt, Germany). All used materials are nanoscale materials.

Characterization

Infrared measurements were performed at room temperature with a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer with a resolution of 4 cm^{-1} in the spectral range 400 - 4000 cm^{-1}, adopting the KBr pellet technique. The XRD of the urban sludge was collected using a Schimadzu 6100 powder diffractometer with a monochromatic beam (λ_{Cuk} = 1.541838A°). The pattern was collected at room temperature in a range of 10 - 70° (2θ) with a scan rate of 2° (2θ/min). For the ATG/ATD thermal analyses, the simultaneous measurements were carried out on a Labsys^{TM} (1F) Setaram device, under non-isothermal conditions in an air atmosphere with a flow rate of 30 ml/min. A 5 mg sample was placed in an Alumina crucible, and the analysis was performed in a temperature range of 30 - 600 °C with different heating rates. The chemical analysis of the urban sludge was carried out by XRF using the Panalytical PW 4400/24 analyzer. The samples were prepared in bead form using lithium tetraborate as a flux. The chemical analysis by SEM-EDX (Scanning electron microscope-Energy dispersive X-ray spectroscopy) was carried out by the QUATTRO S-FEG-Thermofisher scientific device.

Solid state kinetic analysis of thermal processes

The thermal decomposition of the raw and limed urban sludge was studied using the iso-conversional kinetic analysis method. The kinetic parameters were determined using the Friedman's isoconversational differential method [15]. Isoconversional methods are used to examine the variation of the activation energy as a function of the progress of the decomposition reaction, to estimate the effective values of the activation energies for the processes involved, which is represented by the following equation:

$$\ln\left(d\alpha/dt\right)_{\alpha,\beta} = -E_\alpha / RT_{\alpha,\beta} + \ln Af\left(\alpha\right)$$

Where, dα/dt: Conversion rate (min^{-1}), α: Conversion degree, E_α: Activation energy at defined α value ($kJ.mol^{-1}$), R: Universal gas constant, T: Instantaneous temperature, A: Pre-exponential factor, and f(α): The kinetic model.

Results and Discussion

XRF analysis

The results of the XRF analysis of the raw and limed urban sludge are summarized in table 1. The data shows that the major constituents of the raw urban sludge are SiO_2, Al_2O_3, and Fe_2O_3, which together make up more than two-thirds of

Table 1: Chemical composition of raw urban sludge.

Constituents	Raw urban sludge (%)	Limed urban sludge (%)
SiO_2	30.98	8.92
Al_2O_3	21.43	3.53
Fe_2O_3	14.67	1.33
CaO	2.19	44.82
MgO	2.19	1.16
SO_3	0.96	0.52
K_2O	2.28	0.44
TiO_2	0.85	0.26
MnO	0.29	0.07
P_2O_5	7.11	2.25
SrO	0.042	0.028
L.O.I.*	16.92	36.50

Note: *L.O.I. at 1000 °C.

the sludge composition. The limed urban sludge, on the other hand, contains a much higher percentage of CaO (44.82%) due to the addition of lime in the latter. Accordingly, the percentage of the other minerals lowered compared to the raw sludge. SiO_2 is a major component of sand, which is commonly found in raw water sources. Similarly, Fe_2O_3 and Al_2O_3 are commonly found in the materials and chemicals that are used during the wastewater treatment process, such as coagulants and flocculants [15]. The loss on ignition (L.O.I.) values for the raw and limed sludge are 13.92% and 36.50%, respectively. The higher L.O.I. value for the limed urban sludge may be due to the loss of OH species from lime. Overall, the XRF analysis provides valuable information about the mineral composition of the urban sludge samples.

XRD analysis

The XRD patterns of the raw sludge and limed sludge are shown in figure 1. The raw urban sludge displays the major crystalline phases of SiO_2, $CaCO_3$, and Al_2O_3. The main crystalline phase in the raw sludge was SiO_2, while the main crystalline phase in the limed sludge was $Ca(OH)_2$ and $CaCO_3$. Additionally, the urban sludge exhibits a broad hump between 15 - 35° 2θ which is indicative of a high quantity of organic matter. The absence of the broad hump observed in the limed sludge is due to its lower quantity of organic matter when compared to the raw urban sludge [16]. The thermal treatment at 900 °C of raw urban sludge gave the XRD pattern represented in figure 1c, which showed the appearance of several new phases, including Fe_2O_3, Fe_3O_4, $KAlSi_2O_6$, and Ca_3SiO_5. These new phases likely formed due to the high temperature treatment of the raw sludge. The obtained results are consistent with other studies that have reported the formation of Fe_2O_3 and Fe_3O_4 phases during the thermal treatment of sewage sludge. In addition, the appearance of $KAlSi_2O_6$ suggests the formation of a new crystalline phase that was not present in the original sludge.

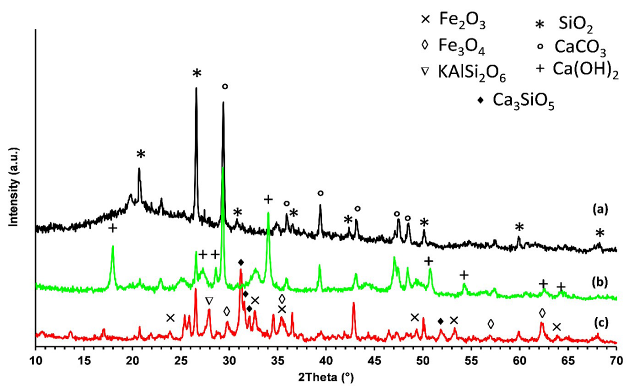

Figure 1: XRD diffractogram of raw and limed sludge.

FTIR spectroscopy

The FTIR spectrum of the raw sludge is shown in figure 2. A broad band observed at 3460 cm^{-1} is attributed to the hydrogen vibrations of the OH groups. Strong peaks at 2921 cm^{-1} and 2851 cm^{-1} indicate symmetrical and asymmetrical stretching vibrations of the aliphatic groups, after calcination

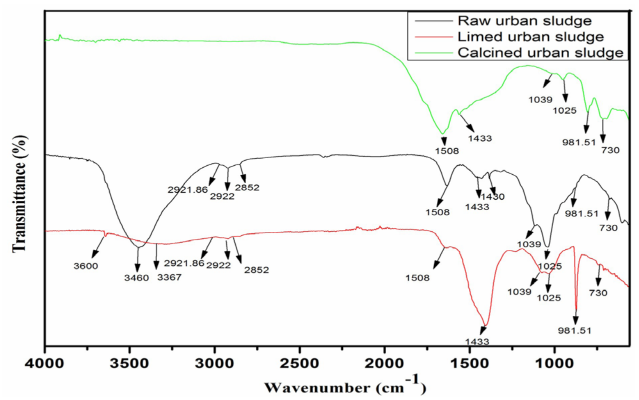

Figure 2: FTIR spectrum of raw and limed sludge from the city of Dakhla.

these peaks completely disappeared [17]. The peak at 1508 cm^{-1} is due to the presence of C=C, while the bands at 1433 and 1430 cm^{-1} are attributed to the presence of C-O in amides I. The bands at 1025 and 1039 cm^{-1} are caused by the presence of -C-O and -O-H deformation of COOH [18]. After calcination these peaks have decreased, the peaks located at 981 and 730 cm^{-1} are associated with the presence of Si-H bonds for the raw urban sludge and after calcination. In the FTIR spectrum of the limed urban sludge, the doublets observed at 3620 and 3367 cm^{-1} correspond to the presence of hydrogen -OH vibrations. The well-defined doublets observed at 2922 and 2852 cm^{-1} indicate the presence of the symmetric and asymmetric stretching vibrations of the aliphatic groups. The peak observed at 1508 cm^{-1} is attributed to the angular deformation of H-O-H. The intense peak at 1433 cm^{-1} is due to the formation of $CaCO_3$, while the peak at 1433 cm^{-1} is attributed to the presence of calcite. The peak at 1025 and 1039 cm^{-1} is due to the presence of -C-O, and the strongest peak at 981.5 cm^{-1} and the peak located at 730 cm^{-1} are also attributed to the Si-O valence vibration. These observations are consistent with previous studies on the characterization of limed sludge by FTIR spectroscopy [16].

SEM-EDX analysis

The micrographs obtained by SEM are presented in figure 3. The SEM observation of raw urban sludge shows a disordered structure with the presence of large granular phases and pores [19]. In contrast, the SEM images of limed urban sludge display an assembly of crystals in the form of hexagonal plates, with some elongated or reduced to simple diamonds, and of different sizes. The observed morphology is typical of the crystal structure of $Ca(OH)_2$ and $CaCO_3$. The crystals are evenly distributed in the matrix, suggesting a homogenous distribution of the lime and good mixing during the liming process.

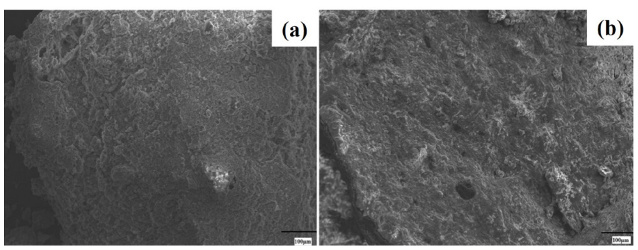

Figure 3: SEM micrographs of the sludge: **(a)** raw and **(b)** limed.

TGA/DTG analysis

The TGA and DTA analysis of both raw and limed urban sludge provides valuable information about their thermal behavior (Figure 4). Below 200 °C, the losses recorded for both raw and limed sludge are mainly due to the release of humidity, as indicated by the TGA curve. The first endothermic peak observed in the DTA analysis at 100 °C corresponds to the evaporation of free water. Between 230 °C and 500 °C, the significant mass loss observed in the TGA curve is due to the release of volatile matter from organic compounds, including the degradation of proteins, carbohydrates, and lipids, which is confirmed by the second exothermic peak observed in the DTA curve [15]. The mass loss observed between 530 °C and 600 °C in the TGA curve corresponds most probably to the Boudouard reaction, as supported by the broad exothermic peak observed in the DTA curve at 550 °C, as previously reported in the literature [20]. The latter was absent in the case of limed urban sludge, which may be attributed to its lower content in organic matter. The addition of lime likely neutralizes acids present in the sludge, alters the pH, and potentially precipitates and binds some of the organic matter, which consequently reduces the carbon content available for the Boudouard reaction. The observed behavior of raw and limed sludge provides valuable insights into how lime treatment affects the thermal behavior and organic content of urban sludge. Such information can be useful for the optimization of sludge treatment and disposal processes [21, 22]. Finally, the mass loss observed above 630 °C is probably due to the decomposition of the carbonates, such as $CaCO_3$, to give CaO with the release of CO_2, as observed in the TGA curve, and confirmed by the endothermic peak in the DTA curve between 630 and 830 °C.

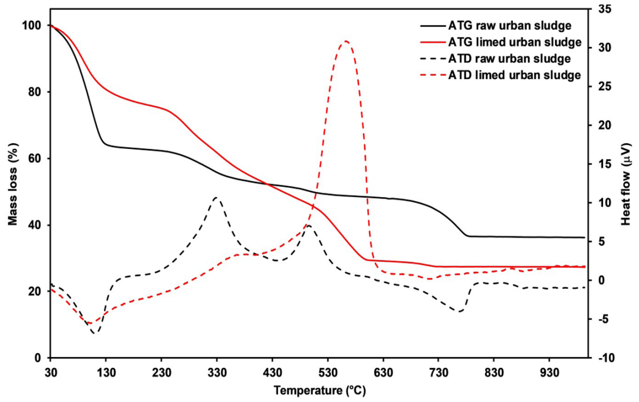

Figure 4: TGA/DTG analysis of raw (In black) and limed (In red) urban sludge at 20 °C/min.

Thermal degradation kinetics

Figure 5 shows the TGA/DTG curves of raw and limed sludge under air atmosphere at different heating rates (20, 15, and 10 °C/min). As first observation the curves shift to higher temperatures as the heating rate increases, which is due to the reduced temperature exposure time, as frequently observed in many inorganic and organic solids [23, 24]. On the other hand, for the raw urban sludge, the DTG curves exhibit a flared peak with a shoulder at low temperature, indicating

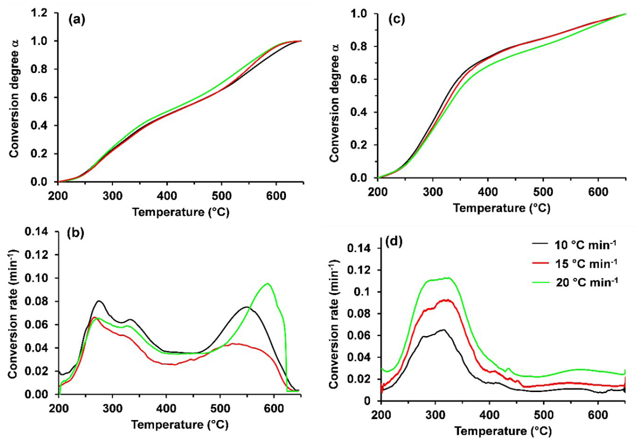

Figure 5: Kinetic curves of α and $d\alpha/dt$ as a function of temperature at different heating rates for limed sludge **(a** and **b)** and raw sludge **(c** and **d)**.

the presence of two types of organic matter. In addition, the observed large peak at higher temperature corresponds to the Boudouard reaction as mentioned above. The Boudouard reaction is a carbon-carbon redox reaction where carbon monoxide is reduced to carbon-by-carbon dioxide. The fact that this reaction is observed in raw sludge suggests a high carbon content, and potentially also the presence of carbon monoxide and carbon dioxide gases that could be generated during the thermal decomposition of the organic matter in the sludge. However, the behavior of organic matter in limed urban sludge is different, and no Boudouard reaction peak is observed due to the low percentage of organic matter present in the sample.

To gain further insights into the thermal kinetics of the oxidation reaction, the isoconversional method was applied to the DTG curves of the raw and limed urban sludge samples. The determination of the activation energy ($E\alpha$) was carried out using the Friedman isoconversional method, which does not require assuming a mechanistic function $f(\alpha)$ and avoids integral approximations of the temperature integral [22]. At least three experiments with different heating rates (β) are needed to apply this method. As shown in figure 6, the E_α values were determined in the α interval between 0.2 and 0.8 [25], and the obtained results exhibited a complex pattern for both sludge samples, characterized by a progressive increase

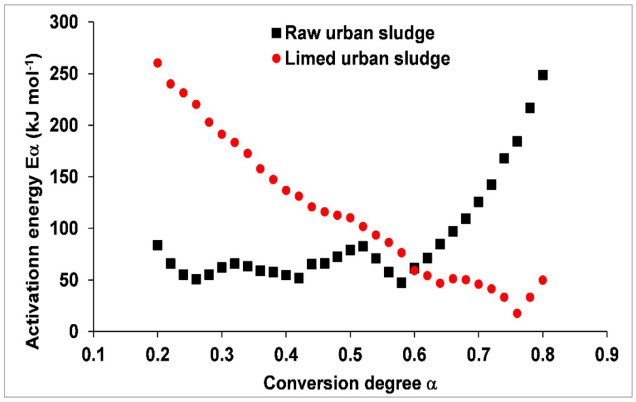

Figure 6: Variation of apparent activation energy Eα as a function of α for raw and limed urban sludge.

for raw sludge. This might suggest that the raw sludge is more resistant to decomposition as the oxidation reaction progresses, requiring higher energy input. Contrarily, a decreasing trend was observed for limed sludge. The liming process involves the addition of lime to the sludge, which can alter the chemical and physical properties of the sludge. The decrease in activation energy might be due to the lime facilitating the breakdown of organic matter or altering the reaction pathway, making the oxidation reaction easier as it proceeds. On the other hand, the study also revealed that the $E\alpha$ values varied significantly, exceeding 10% for both raw and limed sludge. This large variation suggests that the oxidation reaction mechanism of the urban sludge is indeed complex, and it may not be governed by a single reaction process but rather a series of simultaneous or sequential reactions [23]. This finding aligns with the observed complex thermal kinetics reported for various biomass materials, including sludge [23, 24].

Conclusion

The production of urban sludge during wastewater treatment processes presents a challenge for the management of this waste material. This study aims to contribute to the valorization of urban sludge in cement manufacturing by characterizing the raw and limed urban sludge resulting from the Bouregreg wastewater treatment plant. The addition of lime to urban sludge had a significant effect on its composition, resulting in a higher percentage of CaO and lower percentage of organic matter in limed sludge compared to raw sludge. XRD analysis showed that the main crystalline phase in limed sludge was $Ca(OH)_2$ and $CaCO_3$, while raw sludge was dominated by SiO_2. SEM micrographs indicated a well-organized crystal structure in limed sludge, while raw sludge displayed a disordered morphology. TGA/DTA analysis showed that the thermal behavior of raw and limed sludge is quite different, with the Boudouard reaction observed in raw sludge but not in limed sludge due to the low percentage of organic matter in the latter. Isoconversional kinetic analysis revealed that the oxidation mechanism of urban sludge is complex and cannot be described by a single reaction process. Overall, these findings suggest that the addition of lime can improve the properties of urban sludge, making it a valuable resource for various applications. However, further research is needed to fully understand the behavior of urban sludge and to optimize its utilization.

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Conflict of Interest

The authors declare that they have no competing interests.

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