The recycled paper industry has increased significantly in the last few years, which consumes a large amount of water and energy, and thus produces an amount volume of wastewater. This wastewater had negative impact on the environment which must be treated to reduce the quantity and quality to avoid any impact on the environment [Bakraoui et al., 2020]. The paper mill effluents are rich in organic matters and currently treated using biological treatment systems [Cai et al., 2019]. Anaerobic digestion (AD) is a biological treatment which used to treat wastewater from recycled paper industry [Bakraoui et al., 2019b]. The process allowed reducing the concentration of the chemical oxygen demand COD in wastewater. The AD process produces two main products; the first one is methane that can be considered as renewable energy; and the second is the digestate which can be used in agriculture as a fertilizer, in addition to CO$_2$ and other gases. Prediction and optimization of bioreactor behavior has become easily achieved thanks to mathematical modeling of AD, which is considered a fast and inexpensive method [Zhen et al., 2015]. Approach consists in optimizing and having a clear idea on the recovery of at the laboratory scale for an integrated management of industrial waste. Therefore, the reliability of the kinetic model relies on the production of the correct results for the design and operation of the process [El-Mashad, 2013].
Appropriate dynamic modeling of anaerobic digestion is necessary to improve the performance of the digester and monitor the process. In this regard, the power of mathematical models is always evident in predicting performance under various operating conditions and different pre-treatment technologies [Mejdoub and Ksibi, 2015]. The application of kinetic modeling in the prediction of methane production using anaerobic digestion becomes more famous in literature [Beniche et al., 2020; El Gnaoui et al., 2020; Karouach et al., 2021; Lahboubi et al., 2020]. The kinetic models are used to describe the microorganism behavior under physical and chemical condition [Zwietering et al., 1990]. The methane production curves give an idea about the biodegradation of the substrate and inhibition factors [Ware and Power, 2017].

There are several kinetic models that study the degradation of organic matter and methanogenic production, in order to validate the most adequate model to the experimental results; four kinetic models have been studied. The first order model is the simplest model and calculated by the relationship between the concentration of the chemical oxygen demand (COD) or total volatile solid (TVS) and methane production [Blasius et al., 2020]. Beside that several studies have obtained valuable interpretations of anaerobic digestion kinetics using the first-order model, but it does not predict the maximum biological activity rate [Blasius et al., 2020]. The kinetic equation had been modified so that the mathematical parameters have biological meaning. The Gompertz equation was established to predict the bacterial growth rate, unless this equation contained mathematical parameters which did not have biological meaning [Lahboubi et al., 2020; Syaichurrozi et al., 2013]. Zwietering et al. had written the Gompertz equation in order to switch the mathematical to biological parameters [Zwietering et al., 1990]. These parameters define the maximum value reached, the maximum specific growth rate and the lag time. Usually the bacterial growth curve had an exponential shape. The maximum value reached is defined as the asymptote of the curve; the maximum specific growth is defined as the tangent in the inflection point and the lag time is defined as the x-axis intercept of this tangent [Zwietering et al., 1990]. The modified Logistic function assumes that methane production is proportional to the maximum rate methane production [Blasius et al., 2020]. Transference function model used for easily digestible substrate where there is no lag phase in biogas production [Panigrahi et al., 2020]. Pretreatment is an important step to improve the characteristics of the substrate to achieve better anaerobic digestion yields. At this a large number of pretreatment options, including ultrasonic, thermal, microwave, chemical, electrical and freeze/thaw methods, exist [Carlsson et al., 2012; Hamraoui et al., 2020; Kiran et al., 2014; Li et al., 2016; Marin et al., 2011]. As the study of Lahboubi et al. the results showed that the combined alkali-thermal pretreatment is 144 N mL/g VS was better than the alkali pretreatment 132 N mL/g VS, knowing that the methane potential of the control test was only 118.5 N mL/g VS using Date Palm Empty Fruit Bunch as a substrate and biochemical methane potential (BMP) tests [Lahboubi et al., 2021]. In the same context, Dong-Jin Kim et al. study concerning the effect of food waste pretreatment showed the reliability of the different types of pretreatment used (alkali-thermal, thermal, ultrasonic and alkaline pretreatment) on methane production [Naran et al., 2016]. Among these pretreatment methods mentioned above, thermal treatment is one of the most studied pretreatment methods. It has been successfully applied on an industrial scale [Carlsson et al., 2012; Cesaro and Belgiorno, 2014]. Among the advantages of thermal pretreatment are: acceleration of the hydrolysis step [Cesaro and Belgiorno, 2014], solubilization of organic compounds [Ariunbaatar, 2014; Kim et al., 2006], disinfection by sterilization [Chen et al., 2012] and reduction of exogenous pollution [Chen et al., 2014]. These effects increase methane production and reduce retention time [Appels et al., 2010]. The duration and temperature of the pretreatment depends mainly on the nature and composition of the substrate used. The pretreatment of the substrate before its treatment by anaerobic digestion has a good effect on the production of methane compared to the untreated substrate.

The main objective of this work is to study the effect of thermal pre-treatment on the kinetic parameters of anaerobic digestion of the RPPS effluent. In particular, these kinetic parameters were compared in order to propose the best model to fit the experimental results in terms of methane production rate and lag phase. Our study is based on a previously published work by our team [Bakraoui et al., 2019]. This research study was about the methane production from RPPS using...
semi-continuous anaerobic digestion under mesophlic conditions. The sludge was collected from industrial wastewater from the manufacture of recycled pulp and paper sludge in Morocco [Bakraoui et al., 2019]. To our knowledge, no study has been conducted to report the kinetic modeling of methane yields from thermally pretreatment for the study effluent. The novelty of this work is the study the impact of thermal pretreatment of RPPS on the kinetic parameters since there are no studies dealing with these kinetic parameters for such industrial waste.

MATERIALS AND METHODS

The data used in this work was collected from a previous study on producing methane from RPPS semi-continuous anaerobic digestion under mesophlic conditions [Bakraoui et al., 2019]. The data used are the methane production of the untreated and pretreated substrate. Table 1 resumes the cumulative methane production without and with thermal pretreatment for RPPS for each added load [Bakraoui et al., 2019].

Kinetic modeling

In this study, four mathematical models of methane production were optimized using experimental data of sludge from the RPPS without and with a thermal pretreatment at 120 °C and for 24 minutes.-Experimental data on the cumulative methane yield for the different added load 0.50, 1, 1.5, 2, 2.5, 3 g VS/L without and with thermal pretreatment were used to estimate the kinetic parameters. In the present study, modified Gompertz, transference function, logistic function and first order models were applied to predict the methane production and evaluate the kinetic parameters [Bakraoui et al., 2019].

The equations models

First-order model. The first order kinetic model of methane production was used to kinetically characterize each set of experiments as described by Borja et al [Borja et al., 1995]. This kinetic model adjusts the experimental methane production volumes over time for low substrate concentrations. According to this model, the volume of cumulative methane \( P \) (mL, at 1 atm, 0 °C) at a given time \( t \) (h) corresponds to the following equation:

\[
P(t) = A \cdot (1 - \exp(-Kt))
\]

where: \( A \) (mL) is the maximum methane volume cumulative at an infinite digestion time and \( K \) is the specific kinetic constant of methane production (h^{-1}).

Modified Gompertz model. To describe a growth curve of bacteria in a batch culture, many mathematical models have been proposed. Among them, the Gompertz equation has been found to be the most appropriate model, and is written as follows [Altas, 2009]:

\[
P(t) = A \cdot \exp\left(-\exp\left(\frac{\mu e}{A} (\lambda - t) + 1\right)\right)
\]

where: \( P(t) \) is the cumulative methane production (mL), \( A \) is the methanogenic potential (mL), \( \mu \) is the maximum rate of methane production (mL/h), \( \lambda \) is the duration of the lag phase (h), \( e \) is \( \exp(1) \) and \( t \) is the time when the cumulative methane \( P(t) \) is measured (h). \( A, \mu \) and \( \lambda \), are important parameters that affect the characteristics of methane production.

Logistic model. The logistic model present a linear relationship between specific growth rate and biomass concentration could be considered as a specific case and may not be valid for all constraints. A modified form of logistic equation was

| Added load (g VS/L) | Cumulative methane production without pretreatment (NmL) | Cumulative methane production with thermal pretreatment (NmL) |
|--------------------|----------------------------------------------------------|---------------------------------------------------------------|
| 0.5                | 103                                                      | 80                                                            |
| 1                  | 139                                                      | 165                                                           |
| 1.5                | 156                                                      | 174                                                           |
| 2                  | 255                                                      | 176                                                           |
| 2.5                | 257                                                      | 240                                                           |
| 3                  | 361                                                      | 323                                                           |
| 3.5                | –                                                        | 495                                                           |

Table 1. Cumulative methane production without and with thermal pretreatment for each added load [Bakraoui et al., 2019]
used to describe cell growth kinetics by presenting an inhibitory effect which explains the deviation of growth from the exponential ratio. The equation of logistic model thus found is as follows [Bakraoui et al., 2019a]:

\[ P(t) = \frac{A}{1 + \exp\left(\frac{4\mu}{A} (\lambda - t) + 2\right)} \]  

where: \( P(t) \) is the cumulative methane production (mL), \( A \) is the methanogenic potential (mL), \( \mu \) is the maximum rate of methane production (mL/h), \( \lambda \) is the duration of the lag phase (h) and \( t \) is the time when the cumulative methane \( P(t) \) is measured (h).

**Transference model.** A transfer function is defined as the relationship between the output signal of a control system and the input signal, for all possible input values. This modified model has been implemented in the adaptation of anaerobic digestion data [Blasius et al., 2020]. The equation thus found is as follows:

\[ P(t) = A \cdot \left[ 1 - \exp\left(\frac{\mu \cdot (\lambda - t)}{A}\right)\right] \]  

where: \( P(t) \) is the cumulative methane production (mL), \( A \) is the methanogenic potential (mL), \( \mu \) is the maximum rate of methane production (mL/h), \( \lambda \) is the duration of the lag phase (h) and \( t \) is the time when the cumulative methane \( P(t) \) is measured (h).

The Table 2 resumes the different equations for the kinetic models.

**RESULTS AND DISCUSSIONS**

**Kinetic modeling curves result**

In order to describe the evolution over time of anaerobic digestion process, different kinetic models have been developed. The kinetic models used in this study allow us to explore the methane production rate, the lag phase and the simulated methane production, which lead to describe the anaerobic digestion process. Figure 1 shows the cumulative experimental and simulated methane production as a function of time for 0.5 g VS/L added load for untreated and pretreated substrate.

As shown in Figure 1, the experimental methane production results are close to the first order model from the beginning of the production until 20 hours. Moreover, between 20 and 40 hours, the cumulative volume follows the same pattern as the modified Gompertz model. Then beyond 40 hours of production, the cumulative volume reaches the maximum at 103 N mL. The closest model to the experiment is the transference function (Fig. 1a). On the other hand, the cumulative volume of methane with pretreatment of the RPPS recognized a correspondence of the experimental values with the kinetic models used. With a maximum value of the cumulative methane of 80 N mL; low compared to the production without pretreatment. This decrease is due to a bad adaptation of the substrate with the selected pretreatment (Fig. 1b). Passing to load of 1 g VS/L of untreated substrate, we can see that at the beginning of the experiment, the methane production curve follow the same logistic and first order models. From the 30 hours of production the cumulative methane after thermal pretreatment, for 1 g VS/L load, the values obtained follow the same rate as the kinetic models except for a few during production (Fig. 2b). The effect of thermal pretreatment is well visualized on the 1.5 g VS/L; methane production increased from 156 to 174 NmL without and with pretreatment respectively. Bakraoui et al. [2019a] shows the logistic model predicted the methane production volume like the experimental within loads added of 2.5 g VS/L using 4 kinetic models for recycled pulp and paper sludge.

| Model              | Equation                                      | References          |
|--------------------|-----------------------------------------------|---------------------|
| First order        | \( P(t) = A \cdot (1 - \exp(-K^\ast t)) \)    | [Borja et al., 1995]|
| Logistic function  | \( P(t) = \frac{A}{1 + \exp\left(\frac{4\mu}{A} (\lambda - t) + 2\right)} \) | [Bakraoui et al., 2019a]|
| Transference function | \( P(t) = A \cdot \left[ 1 - \exp\left(\frac{\mu \cdot (\lambda - t)}{A}\right)\right] \) | [Blasius et al., 2020]|
| Modified Gompertz  | \( P(t) = A \cdot \exp\left(-\exp\left(\frac{\lambda}{A} (\lambda - t) + 1\right)\right) \) | [Altaş, 2009]       |
Effect of pretreatment on kinetic model parameters

The thermal pretreatment carried out on this experiment results in a good evolution of the key parameters studied in the previous paragraph. In this part we will establish the kinetic models of AD to visualize as closely as possible the variations of the parameters of these kinetic models with and without pretreatment of the substrate.
Table 3 represents the kinetic parameter results for all added loads with and without thermal pretreatment. Figure 4 represents the comparison of the maximum cumulative methane without and with thermal pretreatment for each added loads. According to the Table 3 and (Fig. 4a), we notice that the experimental cumulative methane production is close to the simulated using the transference function, especially for the last loads (2, 2.5, 3 g VS/L) without pretreatment. On the other hand, the experimental cumulative methane production is close to the logistic model with thermal pretreatment (Fig. 4b). Figure 5 and 6 shows the evolution of lag phase and methane production rate respectively for each load added with and without pre-treatment for the different kinetic models used for this study. Concerning the evolution of lag phase, for the untreated substrate we notice that for the first added charge of 0.5 g VS/L, the lag phase is large compared to the other charges and it is close to zero for the charge of 3 g VS/L. We also notice that the transference and logistic models paces are close to each other compared to Modified Gompertz model (Fig. 5a). However the lag phase is almost negligible for the different loads added with thermal pre-treatment of the substrate for the different kinetic models studied. For the last kinetic parameter methane production rate $\mu$ there is a remarkable increase at the level of the last added load of 3 g VS/L with a value of 58.55 N ml/h (Fig. 6a). However the $\mu$ value does not exceed 10 N ml/h with thermal pre-treatment due to the accumulation of volatile fatty acids in the digester for higher loads (Fig. 6b). This increase is due to the presence of a large amount of soluble carbohydrates and proteins, which are the result of improved hydrolysis at a higher temperature [Zhang and Yang, 2009].

![Fig. 4.](image)

Fig. 4. Maximum cumulative experimental methane production as a function of added load for different kinetic models; (a): without pretreatment; (b): with thermal pretreatment

![Fig. 5.](image)

Fig. 5. Evolution of a lag phase as a function of added load for different kinetic models; (a): without pretreatment, (b): with thermal pretreatment
Fig. 6. Evolution of methane production rate as a function of added load for different kinetic models; (a): without pretreatment, (b): with thermal pretreatment

Table 3. Kinetic parameters model for Modified Gompertz, Transference function, Logistic function and First order for different added loads with and without pretreatment

| Kinetic models         | Added loads (gVS/L) | Maximum cumulative methane production A (ml) | Methane production rate μ (ml/h) | Lag phase λ (h) | Constant of the specific rate K (h⁻¹) |
|------------------------|---------------------|---------------------------------------------|---------------------------------|-----------------|---------------------------------------|
|                        |                     | without pretreatment | with pretreatment | without pretreatment | with pretreatment | without pretreatment | with pretreatment | without pretreatment | with pretreatment |
| Modified Gompertz      | 0.5                 | 101                          | 79                      | 5.85            | 8.51                  | 16.6              | 0.33                | -                | -                |
|                        | 1                   | 120                          | 160                     | 5.30            | 14.73                 | 0.56              | 0.21                | -                | -                |
|                        | 1.5                 | 171                          | 179                     | 3.29            | 4                    | -                 | 2.09                | 0.32              | -                |
|                        | 2                   | 252                          | 182                     | 11              | 4                    | 0.03              | 0.83                | -                | -                |
|                        | 2.5                 | 243                          | 253                     | 29.72           | 5.02                  | 1.57              | 0.95                | -                | -                |
|                        | 3                   | 359                          | 323                     | 39.1            | 9.05                  | 1.07              | 0.76                | -                | -                |
|                        | 3.5                 | -                            | 503                     | -              | 9.71                  | -                 | 0.84                | -                | -                |
| Transference function  | 0.5                 | 105                          | 79.23                   | 2.93            | 9.58                  | 6.67              | 0.95                | -                | -                |
|                        | 1                   | 120.7                        | 160                     | 4.75            | 16.2                  | 0.08              | 0.08                | -                | -                |
|                        | 1.5                 | 157.6                        | 172                     | 3.46            | 4.02                  | 3.93              | 1.04                | -                | -                |
|                        | 2                   | 254                          | 175                     | 9.12            | 4.118                 | 0.05              | 2.16                | -                | -                |
|                        | 2.5                 | 256                          | 241                     | 8.72            | 5.29                  | 0.04              | 0.17                | -                | -                |
|                        | 3                   | 360                          | 317                     | 58              | 9.18                  | 1.76              | 0.21                | -                | -                |
|                        | 3.5                 | -                            | 474                     | -              | 10.2                  | -                 | 0.45                | -                | -                |
| Logistic function      | 0.5                 | 104                          | 79                      | 3.06            | 9.58                  | 7.61              | 0.95                | -                | -                |
|                        | 1                   | 120                          | 160                     | 4.72            | 16.27                 | 0.0827            | 0.0781              | -                | -                |
|                        | 1.5                 | 154                          | 172                     | 3.69            | 4.02                  | 5.46              | 1.0433              | -                | -                |
|                        | 2                   | 254                          | 175                     | 9.10            | 4.11                  | 0.43              | 2.16                | -                | -                |
|                        | 2.5                 | 255                          | 241                     | 9.48            | 5.29                  | 0.48              | 0.17                | -                | -                |
|                        | 3                   | 360                          | 317                     | 58.55           | 9.18                  | 1.76              | 0.21                | -                | -                |
|                        | 3.5                 | -                            | 474                     | -              | 10.23                 | -                 | 0.4550              | -                | -                |
| First order equation   | 0.5                 | 146                          | 80                      | -              | -                    | -                 | -                  | -                | 0.0207            | 0.1322            |
|                        | 1                   | 124.76                       | 162                     | -              | -                    | -                 | -                  | -                | 0.0704            | 0.1335            |
|                        | 1.5                 | 241                          | 199                     | -              | -                    | -                 | -                  | -                | 0.0160            | 0.0291            |
|                        | 2                   | 254                          | 208                     | -              | -                    | -                 | -                  | -                | 0.0907            | 0.0266            |
|                        | 2.5                 | 258                          | 275                     | -              | -                    | -                 | -                  | -                | 0.0831            | 0.0292            |
|                        | 3                   | 366                          | 336                     | -              | -                    | -                 | -                  | -                | 0.1230            | 0.0456            |
|                        | 3.5                 | -                            | 576                     | -              | -                    | -                 | -                  | -                | -                | 0.0250            |
study of Zhang et al. [2016], about the Kinetics of combined thermal pretreatment and anaerobic digestion of waste activated sludge from sugar and pulp industry using reaction curve and first order models, the results show that the maximum methane production was achieved at day 1 and the lag phase is negligible in the anaerobic digestion of pretreated sludge. Moreover, in a study about multicriteria decision model and thermal pretreatment of hotel food waste for robust output to biogas, using the modified Gompertz equation and Logistic function, Gandhi et al. [2018] shows that the decrease of lag phase from 0.5 to 0.0 for untreated and thermal pretreatment respectively. The results of the above studies are similar to our own, namely the methane production rate is increased from 4.72 to 16.27 N ml/h for untreated and thermal pretreated RPPS respectively. The lag phase is also decreased in all kinetic models used with the best results observed in load 1.5 g VS/L using logistic function from 5.46 to 1.04 h (from untreated RPPS). In general, the increase of temperature affect positively the influence of the methanogenic production; however there can be undesirable effects during anaerobic digestion such as the increase of volatile fatty acid levels which directly influences the studied parameters. For this reason we can conclude that the best added load that gave us more satisfactory results are 1 g VS/L and 1.5 g VS/L for thermal pretreatment of RPPS and the model closest to the experiment results is the logistic function.

CONCLUSION

The kinetic modeling proposes several kinetic parameters that describe the anaerobic digestion process of RPPS. These parameters are: maximum cumulative methane production; methane production rate and lag phase. In this study, four kinetic models are applied to fit experimental results of previous study of producing methane from RPPS with and without thermal pretreatment. These models are: modified Gompertz model, transference function, logistic function and first order equation. The main results are observed with the pretreated added load of 1 g VS/L using logistic function; the methane production rate is increased from 4.72 to 16.27 N ml/h (from untreated RPPS). The thermal pretreatment decreases the lag phase in all kinetic models used with the best results observed in load 1.5 g VS/L using logistic function from 5.46 to 1.04 h (from untreated RPPS). In general, the increase of temperature affect positively the influence of the methanogenic production; however there can be undesirable effects during anaerobic digestion such as the increase of volatile fatty acid levels which directly influences the studied parameters. For this reason we can conclude that the best added load that gave us more satisfactory results are 1 g VS/L and 1.5 g VS/L for thermal pretreatment of RPPS and the model closest to the experiment results is the logistic function.

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### Table 4. Comparative study of the studied kinetic parameters with other studies

| Operational conditions and kinetic parameters | Our study | Zhang Jian study | Paras Gandhi study |
|----------------------------------------------|-----------|------------------|--------------------|
| Pretreatment used                            | Thermal pretreatment | Thermal pretreatment | Thermal pretreatment |
| Substrate                                    | Recycled pulp and paper sludge | waste activated sludge from sugar and pulp industry | Hotel food waste |
| Kinetic models                               | Modified Gompertz, transference function, first order model and logistic function | Reaction curve and first order model | Multicriteria decision model |
| Lag phase ($\lambda$(h))                     | 1.04      | Negligible      | 0                  |


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