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Physicochemical Assessment and Recovery Kinetics of Furfural from Agricultural Wastes Using Mineral and Acetic Acid

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Abstract Agricultural wastes rich in bioactive compounds consequently should be considered as raw materials rather than wastes. The use of agricultural wastes as raw materials can help to reduce production cost and contribute to the recycling of waste. Using the acid hydrolysis gravimetric method, furfural was produced and quantified from waste materials; corn cob, sawdust, and rice husk. The obtained results showed varied physicochemical properties of the waste materials, with the cellulose contents varying from 22.8% for sawdust, 38.7% for corn cob, and 30.1% for rice husk. The ash content was 6.9%, 8.5%, and 11.5% for sawdust, corn cob and rice husk respectively. Lignin varied from 16.0% for sawdust, 16.6% for corn cob and 21.8% for rice husk. Bulk density varied from 0.21 g/cm^3, 0.27 g/cm^3 and 0.29 g/cm^3 while the porosity varied from 73.9%, 73.0%, and 67.8% for sawdust, corn cob and rice husk respectively. There were variations in the furfural yield of the different agro-wastes with corn cob having the highest yield 26.1 g amounting to 68.1% of furfural), followed by rice husk (21.6 g; 62.6% of furfural) and then sawdust (19.5 g; 59.5% of furfural). The mineral acids (H_2SO_4<HCl<H_2PO_4) have higher yield compared to the acetic acid (CH_3COOH). There were variations in the quality characteristics of the furfural produced from different waste materials with the same specific gravity of 1.17 g/cm^3, solubility of 8.6%, 8.5% and 8.4%. The kinetics of furfural production indicated that the kinetics data were best fitted by the pseudo-first-order model and this suggests that during the course of the reaction, the concentration of water is nearly constant and therefore the reaction appears to be a first order.

Keywords: *agricultural wastes, distillation, furfural, kinetics*

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1. Introduction

The increasing human population, technological advancement towards green revolution and expansion of soil for agricultural production has led to increased agricultural production [1]. As well; the level of progress and prosperity is associated with profitable specialization in agriculture and industry [2].

Most agricultural wastes are released to the environment without proper disposal procedure and this may lead to environmental pollution and harmful effect on human and animal health. Most of the agro-industrial wastes are untreated and underutilized. This accounts for many reports of its disposal either by burning, dumping or unplanned land filling which in turn lead to different problems with climatic change that increases greenhouse gas emission [3,4]. The alarming rise in industrial pollution and agro-wastes has prompted experts to propose a solution based on the proper utilization of agro/industrial wastes to reduce pollution and obtain several economically important substances while also reducing reliance on fossil fuels for direct energy consumption [5].

Therefore, these wastes can be recycled to generate organic chemicals such as furfural. Furfural is an important organic chemical produced from agro/industrial wastes and residues containing carbohydrates known as pentosan [6]. It is a basic chemical, which can be utilized in a variety of industries such as; chemical industry, refining oil industry [7,8], food industry [9], and agricultural industry [5,10].

Furfural is one of the numerous furan derivatives formed from the hemicellulosic fraction of lignocellulosics. It is produced from natural dehydration of xylose obtained in large amounts in the hemicellulose fraction of lignocellulosic biomass. It is a heterocyclic and aromatic aldehyde consisting of a furan ring with an aldehyde side group. It is also known as 2-furancarboxyaldehyde, furaldehyde, 2-furanaldehyde, fural, and furfuraldehyde. Furfural is oily in appearance, has almond-like odour, and is a colourless liquid that turns yellow to dark brown in the presence of air [11]. This research work is based on the assessment of physicochemical properties and recovery kinetics of furfural from agricultural waste such as rice husk, sawdust, and corncob.

2. Materials and Methods

2.1. Sample Collection/Authentication

The analyzed samples including saw dust, rice husk and corn cob were collected from their different dump site in Okigwe in Okigwe Local Government Area, Imo State; Uzuakoli in Bende LGA Abia State and Ihie-Ukwu in Ugwunagbo LGA Abia State respectively, identified by Dr. Chikodi Okechukwu, a taxonomist in the department of Plant Science and Biotechnology, Abia State University Uturu and labeled accordingly. Extraneous materials were removed from each of the samples by hand picking. The collected samples were confirmed in the Department of Plant Science and Biotechnology. The experiments for the production of furfural from these samples were carried out at the Analytical laboratory, Umudike, Abia State, and Chemistry laboratory, Department of Pure and Industrial Chemistry, Abia State University Uturu.

2.2. Sample Preparation

The test sample materials (rice husk, saw dust and corn cob) were first ridded of extraneous materials and then dried in the oven at 100°C for 24 hours. The dried samples were ground using laboratory Willy Mill, PLT-210 and sieved through 1mm test sieve to obtain the fine prepared sample used for the study.

2.3. Experimental Techniques

2.3.1. Basic Process

The production and quantification of Furfural in the waste materials was done using the acid hydrolysis gravimetric method as described by [12]. The production was done in a unified process as the two major steps were not separated rather transited from one to the other in a continuous process.

2.3.2. Determination of Composition of Test Materials

Each of the prepared samples (raw materials) was analyzed to determine their respective fibre content. The samples were subjected to compositional analysis using gravimetric method [13]. The method involved systematic extraction of the different fiber types at various stages of the process and the determination of the percentage of each fraction.

The formula below was used in each case:

$$\%\ fraction = \frac{dry\ wt\ of\ \ fraction\ extracted}{weight\ of\ \ sample} X \frac{100}{1} \quad (1)$$

2.3.3. Determination of Ash Content

Ash content was determined using the furnace incineration gravimetric method [14]. The ash content was calculated as shown below.

$$\%\ Ash = \frac{W2 - W1}{W} X \frac{100}{1} \quad (2)$$

W = weight of sample analyzed
W_1 = weight of empty crucible
W_2 = weight of crucible + ash.

2.3.4. Determination of Moisture Content

Moisture content was determined gravimetrically as described by [14]. The formula below was used to calculate the moisture content.

$$\%\ Moisture = \frac{W2 - W3}{W2 - W1} X \frac{100}{1} \quad (3)$$

W_1 = weight of empty moisture can
W_2 = weight of can + sample before during
W_3 = weight of can + sample dried to constant weight.

2.3.5. Determination of Bulk Density

This estimation was done gravimetrically using the method of [15]. The formula below was used for the calculation.

$$BD\left(g/cm^3\right) = \frac{\mathrm{W2 - W1}}{V} \quad (4)$$

V = Volume of the container
W_1 = Weight of empty container
W_2 = Weight if container tilted level with the material.

2.3.6. Determination of Porosity

The water pyenometer volumetric method [16] was employed. Porosity of the material was calculated as follows;

$$Porosity\ (\%) = \frac{V1 - V2}{V} \times \frac{100}{1} \quad (5)$$

V_1= Volume of the sample in cylinder + the added water
V_2= Final total volume of the sample and added water
V = Volume of the sample analysed.

2.3.7. Determination of Furfural Yield

In line with the methods as described by [12]. The yield of furfural in each case was calculated as follows;

$$\%\ Furfural\ yield = \frac{100}{W} \times W_2 - W_1 \quad (6)$$

Where;
W = weight of sample analyzed
W_1 = weight of empty beaker
W_2 = weight of beaker and Furfural distillate.

2.3.8. Determination of Percentage Concentration of Furfural

This was determined colorimetrically using the method described by [17]. In this regard, based on the stem house colour reaction of furfural with aniline acetic acid in which sodium chloride was used as colour stabilizer.

The furfural content of the mixture was calculated as shown below.

$$Furfural\ content = \frac{100}{W} \times \frac{Au}{As} \times C \times \frac{Vf}{Va} \quad (7)$$

A_u = Absorbance of distillate
A_s = Absorbance of standard
C = Concentration of standard
V_f=Total volume of distillate
V_a = Volume of distillate analyzed
W = Weight of sample analyzed.

2.4. Statistical Analysis

Triplicate data were analyzed by using one-way ANOVA (Analysis of Variance) using SAS version 9.3statistical software. Normality and homogeneity of variance assumptions were tested before data analysis. Comparison of treatment groups was conducted using Fisher's least significant difference (LSD) tested at p = 0.05 level for parameters that showed a significant difference.

3. Results

3.1. Physicochemical Properties of Waste Materials

The physicochemical properties of the waste materials used for the furfural production are presented in (Table 1). From the result, there were significant variations in the composition of the materials as well as their physical properties at the time of use. The corn cob had the least moisture content of 8.99 % while the saw dust had the highest of 9.79 % and rice husk had 9.38%. The cellulose part of the materials (hemicellulose and cellulose) made up to a range from 41.25% to 62.80 %, while the Lignin made up 15.95 % to 21.83 % of the materials.

Table 1. Physicochemical composition of the waste materials

Parameters	Corn cob	Rice husk	Saw dust
Cellulose (%)	38.77^{a}±0.40	30.08^{b}± 0.38	22.81^{c}±0.20
Hemi-cellulose (%)	24.03^{a}± 0.41	19.95^{b}± 0.08	18.44^{c}±0.05
Lignin (%)	16.59^{b}±0.57	21.83^{a}±0.14	15.99^{c}± 0.11
Ash (%)	8.51^{b}±0.08	11.51^{a}±0.06	6.86^{c}±0.05
Moisture content (%)	9.79^{a}±0.12	9.38^{ab}±0.04	8.99^{b}±0.43
Bulk density (g/cm^3)	0.27^{a}± 0.014	0.29^{a}±0.01	0.21^{b}±0.02
Particle density (g/cm^3)	0.286^{b}± 0.002	0.349^{a}± 0.02	0.166^{c}±0.00
Porosity (%)	73.00^{a}±0.88	67.76^{b}±0.88	73.89^{a}±0.49

Values shown are means of triplicate analysis mean ± standard deviation. Values in the same column with different superscript letters of the alphabet are not significantly different (P>0.05).

3.2. Furfural Yield and Concentration from the Waste Materials with Different Solvents

Table 2 shows the yield of furfural produced with sulphuric acid and acetic acid. The result showed significant variations in the furfural yields (furfural condensate) from the different test materials (saw dust, rice husk, and corn cob) with the two acids. The furfural yield (furfural condensate) with sulphuric acid was in the range of 19.50 g (saw dust) to 26.07 g (corn cob) while the yield with Acetic acid ranged from 11.10 g (saw dust) to 15.57 g (corn cob).

Table 2. Comparative estimation of furfural yield and concentration of furfural in the materials using H_2SO_4 and CH_3COOH

Samples	Furfural yield (g)	Furfural concentration (%)
H_2SO_4 saw dust	19.50^{c}± 0.66	59.46^{b}± 0.94
H_2SO_4 rice husk	21.57^{b}± 0.87	62.56^{b} ± 2.75
H_2SO_4 corn cob	26.07^{a}± 0.45	68.12^{a}± 1.14
CH_3COOH saw dust	11.10^{f}± 0.36	47.49^{e}± 1.67
CH_3COOH rice husk	13.33^{e}± 0.45	51.25^{d}± 2.31
CH_3COOH corn cob	15.57^{d}± 0.45	55.72^{c}± 0.60

Values shown are means of triplicate analysis mean ± standard deviation. Values in the same column with different superscript letters of the alphabet are not significantly different (P>0.05).

3.3. Furfural Recovery Deductions

Physical characteristics of the furfural recovered from the waste materials were determined and presented in (Table 3). There is no variation in the colour as well as the odour in the furfural produced from the different materials as all have a pleasant odour and amber colour. Aside from sawdust which has light variation in its furfural boiling point (162°C), there is no variation in the boiling point of furfural from rice husk and corn cob (161°C). This could be attributed to the presence of impurity in furfural from sawdust. There is a slight variation in their solubility which ranges from 8.42 g/100ml, 8.55 g/100ml, and 8.61 g/100ml for sawdust, rice husk, and corncob respectively. The specific-gravity (g/cm^3) of the recovered furfural is 1.17 for the three waste materials, this is indicative that furfural is denser than water.

Table 3. Physical characteristics of the furfural produced

Parameters	Sawdust	Rice husk	Corncob
Colour	Amber	Amber	Amber
Odour	Pleasant	Pleasant	Pleasant
Specific-gravity (g/cm^3)	1.17	1.17	1.17
Boiling point (°C)	162	161	161
Solubility (g/100ml) in Water	8.42	8.55	8.61

3.3.1. Effect of Sulphuric Acid Concentration and Effect of Salt on Furfural Yield

A plot of furfural yield versus concentration is presented in (Figure 1) which gives an illustration of furfural yields of the three materials as affected by acid concentration. From the result, the optimum yield was obtained at acid concentration of 5.5 M (molar concentration) with yield of 19.2 g, 22.1 g and 26.3 g for saw dust, rice husk and corn cob respectively. There was a progressive increase in the yield from concentration of the sulphuric acid from 4.0 M to 5.5 M.

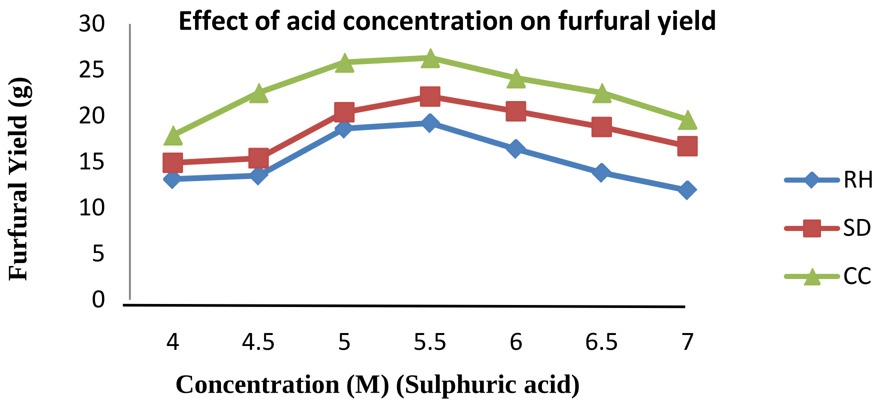

Figure 1. Effect of acid concentration on furfural yield (Key: RH = Rice husk, SD = Sawdust, CC = Corn cob)

3.3.2. Effect of Salt on Furfural Yield

A plot of furfural yield against amount of salt is presented in (Figure 2) which shows the furfural yield in the different test materials with different amounts of salt (NaCl). The addition of NaCl increased the yield of furfural from 59% to 68% and 47% to 56% for sulphuric and acetic acid respectively. For all the test material, furfural yield was highest at 7.5 g. As the amount of salt increases, the furfural yield also increases until at 10.0 g the yield starts to decrease. And meanwhile corn cob has the highest yield followed by saw dust and then rice husk has the lowest yield (CC< RH<SD) as shown in (Figure 2) below.

3.3.3. Effect of Different Acids on Furfural Yield

The yield of furfural was compared with different acids using 7.5 g of salt. From the result as shown in (Figure 3), H_2SO_4 acid had the best yield of 19.1 g, 22.5 g, 26.1 g for all the materials saw dust, rice husk and corn cob respectively followed by HCl, then H_2PO_4 while CH_3COOH has the least of 11.5, 13.4 and 15.8 for saw dust, rice husk, and corn cob respectively. The mineral acids (H_2SO_4<HCl<H_2PO_4) have higher yield compared to the organic acid (CH_3COOH). From the result, it can be deduced that corn cob among the three materials used for the experiment has the best and highest furfural yield for both mineral and organic acid.

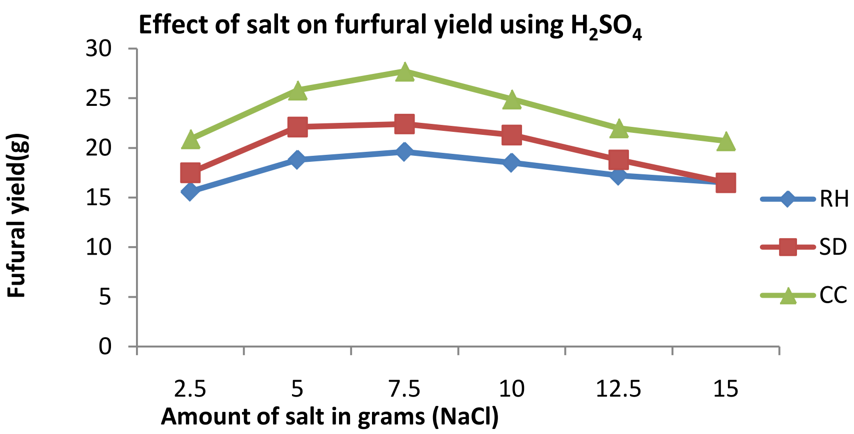

Figure 2. Effect of salt on furfural yield using H_2SO_4 (Key: RH = Rice husk, SD = Sawdust, CC = Corn cob)

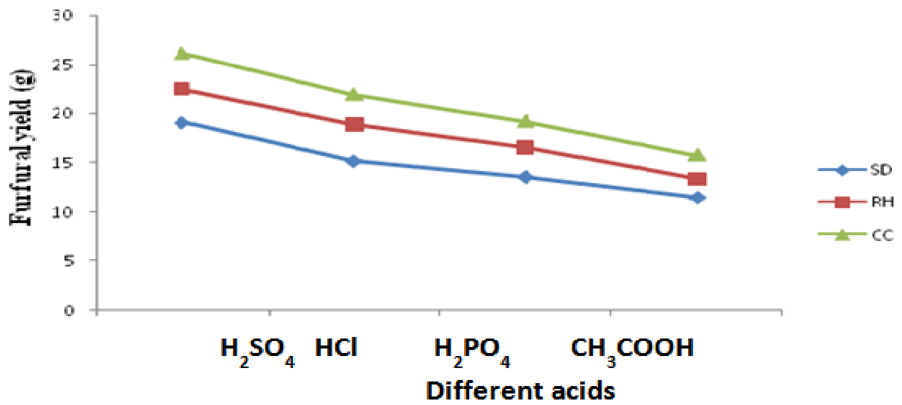

Figure 3. Effect of different acids on furfural yield

3.4. Kinetic Studies

This study also investigated how experimental conditions influenced the speed of chemical reaction and yield. In this respect, pseudo-first-order kinetic model and pseudo-second-order kinetic model were considered.

Pseudo-first-order model

Pseudo-first-order kinetic equation [18] is given as;

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad (8)$$

Where q_t is the quantity of furfural distilled at time t (g), q_e is the total quantity of furfural distilled (g), K_1 is the pseudo-first-order rate constant (min^{-1}), and t is the time (min). From equation (8), log (q_e-q_t) was plotted against time as shown in Figure 4a, 5a & 6a for sawdust, rice husk and corncob respectively. The pseudo-first-order rate constant (k_1) determined from the model, q_{cal} and R^2 value are presented as shown in Table 4.

Pseudo -second – order model

Pseudo - second - order kinetic equation [18] is given as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

q_e is the total quantity of furfural distilled (g), and k_2 is the rate constant of the pseudo–second-order model (g/mg min), t is time (min). The plot of t/q_t as a function of time gives a linear relationship as seen in Figure 4b, Figure 5b & Figure 6b for sawdust, rice husk and corncob respectively. From the equation (9), slope $1/q_e$ and the intercept $1/(k_2 q_e^2)$, k_2, the second-order rate coefficient.

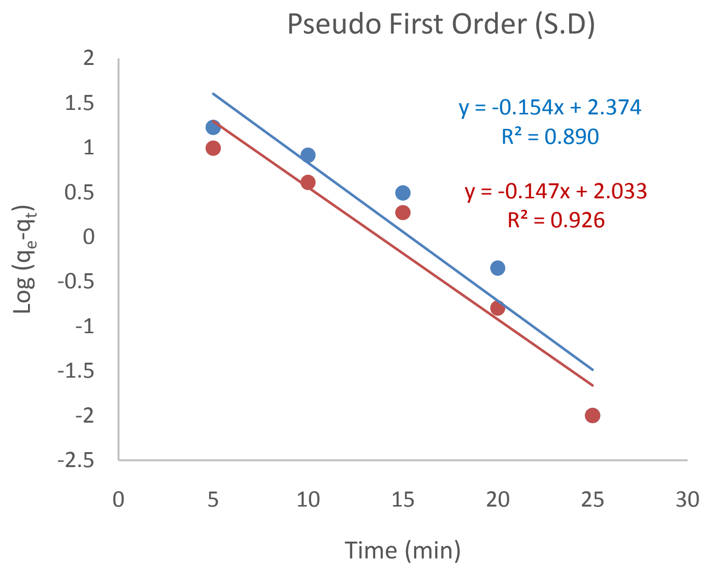

Figure 4a. Pseudo-first order kinetics for furfural recovery in sawdust. Blue line and dots depict H_2SO_4 and red line and dots depict CH_3COOH

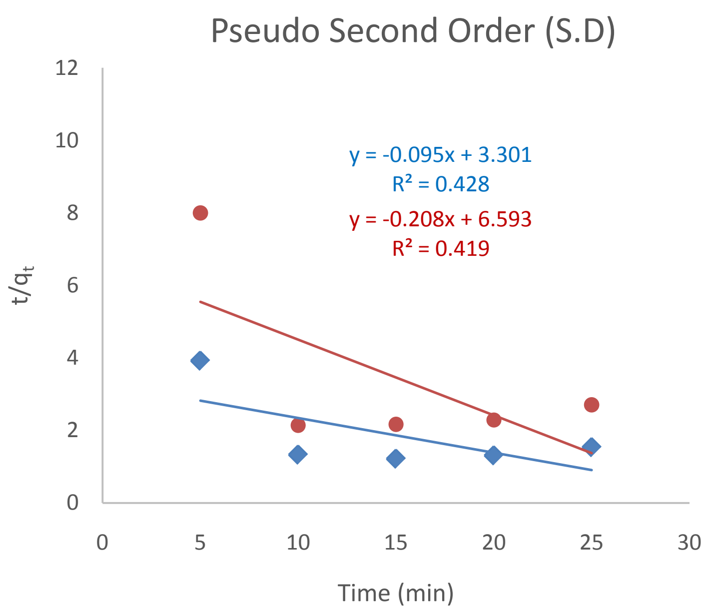

Figure 4b. Pseudo-second order kinetics for furfural recovery in sawdust. Blue line and dots depict H_2SO_4 and red line and dots depict CH_3COOH

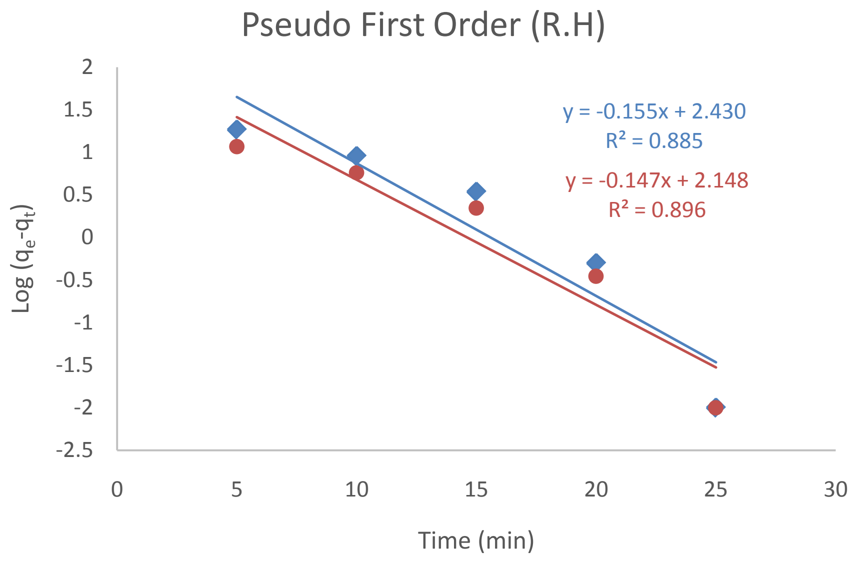

Figure 5a. Pseudo-first order kinetics for furfural recovery in rice husk. Blue line and dots depict H_2SO_4 and red line and dots depict CH_3COOH

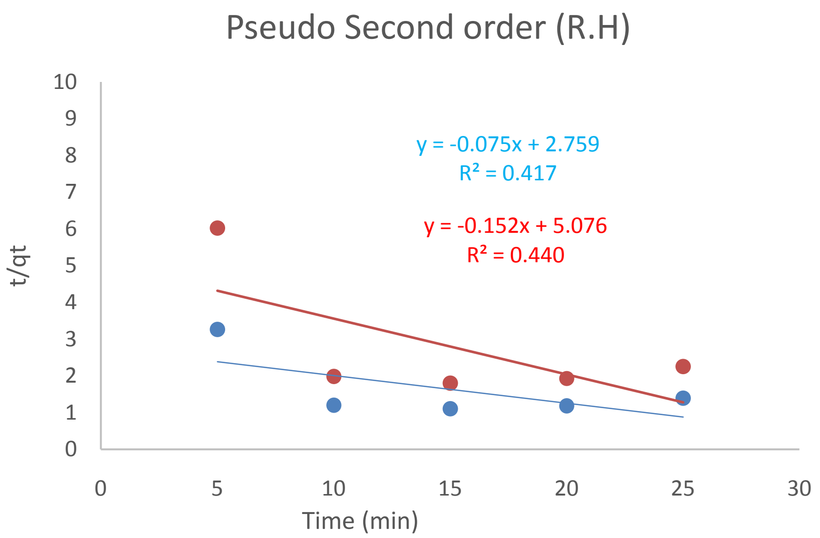

Figure 5b. Pseudo-second order kinetics for furfural recovery in rice husk. Blue line and dots depict H_2SO_4 and red line and dots depict CH_3COOH

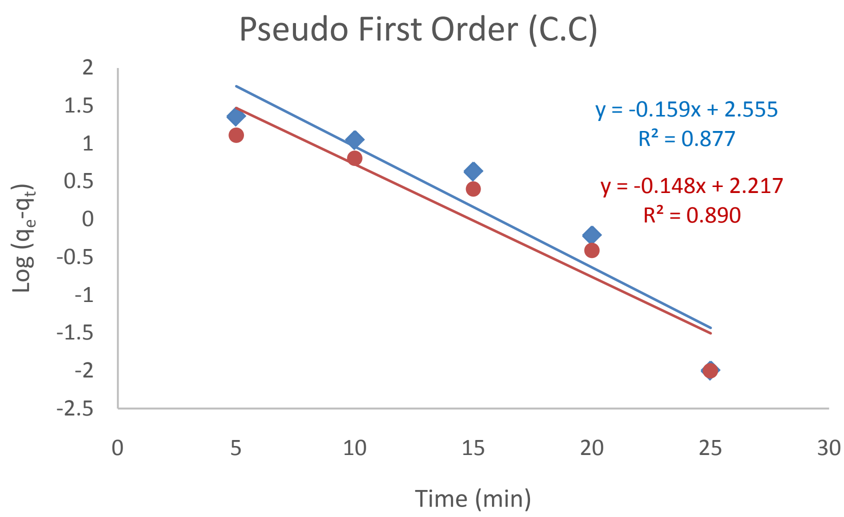

Figure 6a. Pseudo-first order kinetics for furfural recovery in corncob. Blue line and dots depict H_2SO_4 and red line and dots depict CH_3COOH

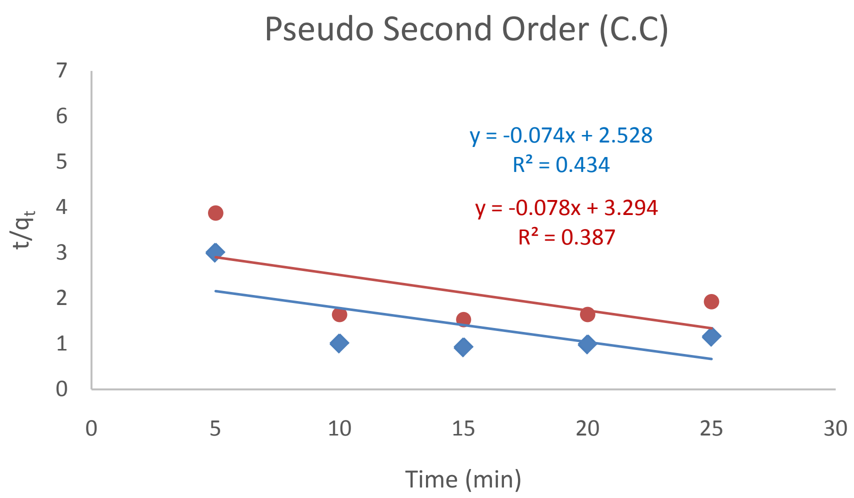

Figure 6b. Pseudo-second order kinetics for furfural recovery in corncob. Blue line and dots depict H_2SO_4 and red line and dots depict CH_3COOH

Table 4. Calculated values of constants and variables in pseudo-first and second order kinetic for the waste materials

Kinetic Models	Constants	Values	
		H_2SO_4	CH_3COOH
PFO_{RH}	k_1	0.36	0.34
	q_{cal}	269.15	140.6
	R^2	0.88	0.9
PFO_{SD}	k_1	0.35	0.34
	q_{cal}	236.59	107.89
	R^2	0.89	0.93
PFO_{CC}	k_1	0.37	0.34
	q_{cal}	358.92	164.82
	R^2	0.88	0.9
PSO_{RH}	k_2	0	0.01
	q_{cal}	13.33	6.58
	R^2	0.42	0.44
PSO_{SD}	k_2	0	0.01
	q_{cal}	10.53	4.81
	R^2	0.43	0.42
PSO_{CC}	k_2	0	0
	q_{cal}	13.51	12.82
	R^2	0.43	0.39

Values in the table were calculated using equation (8) and equation (9), and extracted from Figure 4a, Figure 4b, Figure 5a, Figure 5b, Figure 6a, and Figure 6b. PFO: Pseudo-first order, PSO: Pseudo-second order, RH: Rice husk, SD: Sawdust, CC: Corncob

4. Discussion

The near similar moisture content of these materials corn cob, rice husk and sawdust could be attributed to the fact that all were dried in the oven under the same conditions. However, the slight difference was perhaps due to variations in the ability of different material particles to absorb and hold water from the atmosphere (hygroscopic moisture). The moisture content of corn cob 9.79% was similar to the values 8-9% as reported by [19], and higher than 6.38% as reported by [20]. These variations could be attributed to differences in collection, storage, and drying procedures. Rice husk contained the highest ash content (11.51 %), possibly due to the abundance of mineral constituents which agrees with previous works [21]. Factors such as; particle size distribution, particle shape, shaking and pressing determine the porosity of biomass samples [22]. In this study, the porosity of the materials are high as compared to previous study [20], this could be because of its particle size as a result of the grinding procedure.

Corn cob contained the highest amount of fibre which possibly contributed to its high moisture content; also this is in agreement with [21]. The composition of these test raw materials is indicative that they encompass the pentosans present in the hemicelluloses and which results in furfural production [5]. There are also other minor constituents like the ash content which depicts the minerals in the raw materials. The raw materials therefore present a good source of furfural production for the test production trials.

The results from (Table 2) show that the mineral acid reduces excessive cellulose degradation. Also, the concentration of furfural in the distillate varied. The result therefore reveals that the different materials had varied levels of furfural yield. This can be attributed to the level of pentosan in the different materials that can be hydrolyzed to produce pentose for furfural production. From the result in Table 2, it shows that corn cob has the highest level of pentosan as compared to rice husk and sawdust.

These physical properties of the furfural recovered from the samples are in agreement with [23]. From (Figure 1), the sudden decrease in yield from 6.0 M could be attributed to side reactions, such as degradation of furfural or polymerization of intermediate, and furfural. This shows that the optimum concentration is 5.5 M. The increase in production with acid concentration agrees with the findings of [24] with hydrochloric acid. Previous studies have shown that organic salts enhance xylose monomer degradation; also chloride ions enhance furfural formation from D-xylose [25]. NaCl decreases the pH of the solution providing H^+ for the acid catalytic dehydration of xylose [26]. In our study, the addition of NaCl increased the yield of furfural from 59% to 68% and 47% to 56% for sulphuric and acetic acid respectively.

A result obtained by [27] indicated that furfural yield increased with increase in NaCl up to an optimum after which yield dropped. As the amount of salt increases, the furfural yield also increases until at 10 g when the yield starts to decrease. This decrease in furfural yield could be attributed to polymerization, and furfural decomposition which leads to formation of other products [27]. From the result in (Figure 3), it can be deduced that corn cob among the three materials used for the experiment has the best and highest furfural yield for both mineral and organic acid**.**

Kinetic modelling does not only elucidates the distilling rate estimation but also leads to suitable rate expressions characteristic of possible reactions. Pseudo-first-order kinetic model and pseudo-second-order kinetic model were investigated in this study [28]. The (Table 4) shows that the data is best fitted with a pseudo-first-order model with higher R^2 values>0.8. Optimum adjustment is obtained with k_1 because it gives the best coefficient of correlation. k_1 fits the data well because it provides the higher R^2 value which satisfies the condition $R^2>0.8$ [29]. It can be deduced from these that corncob possesses the highest rate of conversion of pentosan for furfural production followed by rice husk, then sawdust.

Agricultural wastes rich in bioactive compounds and components as in (Table 1) consequently should be considered as raw materials rather than wastes. The use of agricultural wastes as raw materials can help to reduce production cost and contribute to the recycling of wastes [30]. The yield of furfural with acetic acid which is eco-friendly is slightly but significantly lower. There are potentials of improving the yield through effective manipulation of the production processes towards optimization to increase the yield. Variations in production temperature, distillation time, as well as acid concentration have prospects to improve the yield. With the foregoing, it is possible to replace sulphuric acid with acetic acid which is an eco-friendly alternative. The study of the kinetics of furfural production has the potential of opening a research drive for an increased in-depth understanding of furfural production from wastes.

Statement of Competing Interest

The authors declare that they have no competing interests.

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