

**PROCESS PARAMETER OPTIMIZATION OF WASHING
PRETREATMENT FOR INORGANIC REMOVAL FROM
RICE HUSK**

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Dissertation submitted in partial fulfillment of the requirements for the degree of Master
of Science

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May 2020

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ABSTRACT

Rice husk is particularly known as one of the most common agricultural waste and the usage of rice husk in energy applications is typically via the combustion process. Using agricultural waste for combustion application can lead to slagging, corrosion and fouling of boilers due to some problematic elements such as K and Cl. Water washing removes those problematic elements from rice husk and hot water washing treatment improves the removal efficiency of those alkali oxides, halides and total ash content. Further, hot water washing pretreatment has been identified as an effective method compared to acid treatment and alkali treatment.

This study is aimed at optimizing the washing parameters; washing temperature, time and water to biomass ratio. Effectiveness of washing was directly evaluated by conductivity measurements and the removal of inorganic elements. The second order kinetic model was successfully applied for the leaching of K and Cl species and the kinetic parameters were obtained.

Washing temperature has significant effect on Si removal, a considerable effect on K removal and a very weak effect of Cl removal. Moreover, water/biomass ratio has an appreciable effect on K removal, a very weak effect on Cl removal whereas almost no effect of Si removal. Washing temperature of 65 °C and water to biomass ratio of 100 was selected as the optimum process conditions. At the selected optimum conditions, about 84% of K and 81% of Cl can be removed while Si removal is insignificant. Within 10 minutes leaching time, 97% of leachable Cl and 81% leachable K can be removed.

Key words: Rice husk, Washing, Alkali, Leaching kinetics

ACKNOWLEDGEMENT

The Research project is a core module offered for postgraduates of Sustainable Process Engineering, Department of Chemical and Process Engineering, University of Moratuwa. I take this opportunity to express my sincere gratitude to those who helped throughout the project.

My sincere gratitude goes to Prof.Mahinsasa Narayana, the former course coordinator of the MSc. in Sustainable Process Engineering for the valuable guidance and the encouragement.

My special thanks go to Dr.(Mrs.)Duleeka Gunarathne, supervisor of the research project, for her immense support, guidance and inspiration throughout this project.

I would like to convey my gratitude Prof.P.G.Rathnasiri, in charge of Environmental laboratory for giving me the laboratory facilities to do my research work and I thank to the laboratory staff of the Environmental laboratory.

Last but not least, I would appreciate to all who gave valuable support to success my research project.

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NOMENCLATURE

Abbreviations

L/S ratio - Liquid over Solids ratio

ICP-OES - Inductively Coupled Plasma Optical Emission Spectroscopy

ICP-MS - Inductively Coupled Plasma Mass Spectroscopy

Symbols

$C_{i,s}$ - Equilibrium concentration of species i (mg/L)

$C_{i,t}$ - Concentration of species i in water at a leaching time t (mg/L)

k_i - First order leaching rate constant of species i (s^{-1})

k - Second order leaching rate constant ($L\ mg^{-1}\ s^{-1}$)

h - Initial leaching rate ($mg\ L^{-1}\ s^{-1}$)

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CHAPTER 1. INTRODUCTION

Concerns over pollution and climate changes, issues surrounding energy supply and consumption are growing. Increase of global energy consumption will shortage of fossil fuels in the upcoming decades. Therefore, non-renewable energy sources such as oil, natural gas and coal usage is limited. According to the International Energy Agency (IEA) data reveal that, global energy demand could increase more than 50% by 2030 from current demand.

The use of renewable energy sources such as solar, wind and biomass energy is becoming increase. Biomass is one of the renewable energy sources used in worldwide not only in Sri Lanka. Researchers characterize various types of biomass in different ways, but it can be simply categorized into four main types; agriculture crops and waste materials, woody plants, food waste and manure.

Agricultural waste consists of animal waste, food processing waste and crop waste (corn stalk, peels of fruits and vegetables, rice husk, saw dust, coconut husk, oil palm shell, neem bark etc.). Silica is the major element of agricultural waste ash and silicon content varies 36-98wt% of ash in rice husk, sugarcane leaves and corn husk [1]. Alkali and alkaline earth metal oxides present with some trace elements in agricultural waste ash.

There are three main thermo-chemical processes used for conversion of biomass to energy such as combustion, gasification and pyrolysis. The most common application of agricultural waste is combustion in boilers and furnaces. High maintenance cost derived from severe sintering, slagging, fouling and corrosion risk should be expected due to the presence of alkali oxides such as Na_2O , K_2O , CaO , MgO and chlorides in biomass, especially in agricultural waste. According to the literature, alkali metals and chlorides can be effectively removed by hot water washing treatment. Therefore, slagging, fouling and corrosion risk can be reduced significantly.

In this study, the effect of washing rice husk with water was investigated in laboratory scale to optimize the washing medium temperature, washing time and L/S ratio for effective removal of alkali oxides and chlorides in rice husk.

1.1 Research Objectives

This study is aimed at finding how the rice husk can be upgraded by washing pretreatment in technically and economically feasible way. Following objectives were chosen to reflect the anticipated aim:

- To optimize the washing parameters; washing temperature, washing time and water to biomass ratio on the removal of mineral matter from rice husk.
- To evaluate the leaching kinetics of mineral matter in the rice husk.

CHAPTER 2. LITERATURE REVIEW

2.1 Selection of Biomass

Biomass is an organic material derived from plants and animals. There are many biomass types ex: wood waste, agriculture crops and food waste, animal manure and human sewage [2].

Rice is grown in more than a hundred countries worldwide. Total harvested area is approximately 158 million hectares, annually producing more than 700 million tons resulting around 470 million tons of milled rice. Nearly 640 million tons of rice is grown in Asia, representing 90% of global production. Mainly Asian region produce requirement amount of consumption. Global rice consumption is increasing with the population growth. In 2018, approximately one third of total paddy produces by China. In 2018/2019 year about 4.5 million tons of rice import to China and India export 12.5 million tons of rice worldwide. Thailand was the second largest rice exporter and export 10.3 million tons of rice worldwide. In 2018/2019 year, the total production of milled rice of worldwide about 481.1 million tons.

Sri Lanka is an agricultural country. Rice is cultivated as a main agricultural crop. Rice is the most important crop in Sri Lanka occupying approximately 34% of the total cultivated area. On average 560,000 ha are cultivated during Maha and 310,000 ha during Yala are resulting the average annual rice production about 870,000 ha. Currently Sri Lanka's rice production approximates 95% from the total consumption. Rice husk is one of the most common agricultural wastes. The husk is an outer shell of the grain and separated during the milling process. In this study rice husk used as biomass because it is easily found, lightweight, dry foam after milling, storage is simple and easy to transport. Husk contains almost about 75% volatile organic compounds that can burn in the combustion process and approximately 25% is converted to ash (The Energy Efficiency Guide for Industry in Asia).

2.2 Composition of Rice Husk and Deposition Problems During Combustion

Rice husk contains mainly organic substances such as cellulose, lignin and hemicellulose contain high percentage and other components of nitrogen and some compounds form by inorganic ions [2].

Table 2. 1: Rice husk composition [3]

Ultimate Analysis (Dry basis)						
C	H	N	S	Cl	O	HHV
38.8	4.8	0.5	0.05	0.1	35.5	15.8
Proximate Analysis (As received basis or dry basis)						
Moisture		Ash		Volatile matter		Fixed carbon
4		20.3		63.5		16.2

Table 2. 2: Rice husk ash composition [4]

Content, % wt.							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅
93.4	0.05	0.06	0.31	0.35	1.4	0.1	0.8

During the combustion process impurities in the form of inorganic materials apart from the organic materials undergo changes in their chemical form by combining with other constituents in the combustion regime. Various effects can occur, such as furnace wall corrosion, wall deposition, slagging, fouling, high temperature deposition in super heaters and high temperature corrosion in super heaters, low temperature corrosion and metal wastage due to erosion. The alkali content of biomass reduces the ash fusion temperature [5].



Figure 2. 1: Slagging and fouling problems in boilers

High temperature corrosion in boiler firing is mainly due to the presence of impurities like alkali metals, chlorine and sulfur. Essential elements for plant growth are Si, Ca, K, Al, Fe, Na, Mg, Ti, P and S [6-8]. Alkali sulphates with chlorides are responsible in slagging, fouling and corrosion. Due to inorganic compounds corrosion, slagging and fouling in furnaces resulting high cost of repair and maintenance [9, 10].

Deposit of inorganic constituents on exhaust duct in the furnace cause for fouling, it reduces the heat exchange efficiency and increase the pressure balance difficulties in the furnace. Slagging cause due to form of a melted glass layer. Ferric oxides and Potassium oxide cause for thickness of glass layer and it interact with metal surface within the furnace increase corrosion of furnace [11]. Convective heat transfer rate reduces due to fly ash in the gas stream. Thus, the efficiency of the combustion process decreases [12].

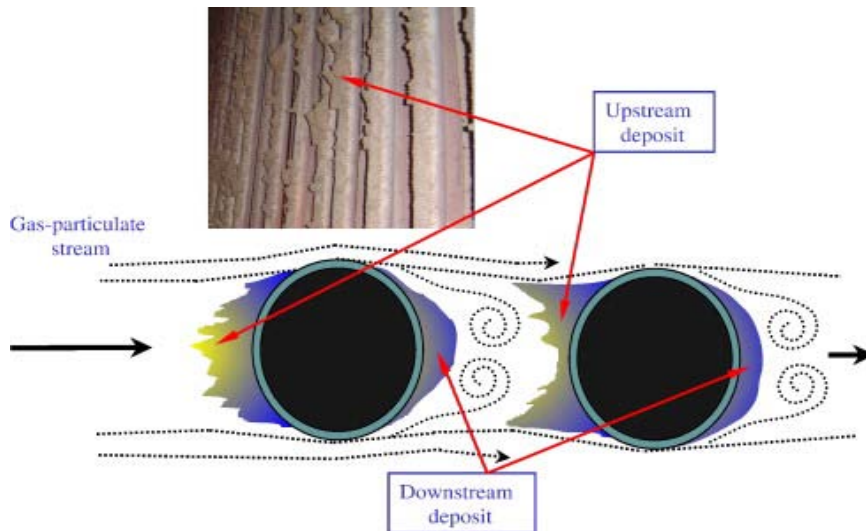


Figure 2. 2: Gas stream inside the furnace

2.3 Ash Forming Elements of Biomass [13]

Potassium(K)

Potassium is one of the most important ash forming elements in biomass-fired boilers. Potassium is highly affected on sintering, fouling and corrosion. Potassium present in both soluble and insoluble portions. The insoluble portion is inert and the soluble portion consists in salts as an ions and organic form bound in K ions.

During the combustion process K is released and easily combines with other elements. There are three types of primary vapors: K (g), KOH (g) and KCl(g). If the chlorine is present dominant vapor is KCl(g). If sulphur is present KCl(g) condense as KCl aerosol particles. Condensed KCl(l/s) is melting at the furnace temperature at 770°C. KCl is highly corrosive and the presence in super heater metal surfaces is problematic.

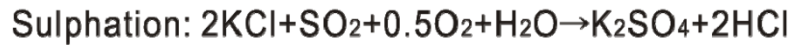
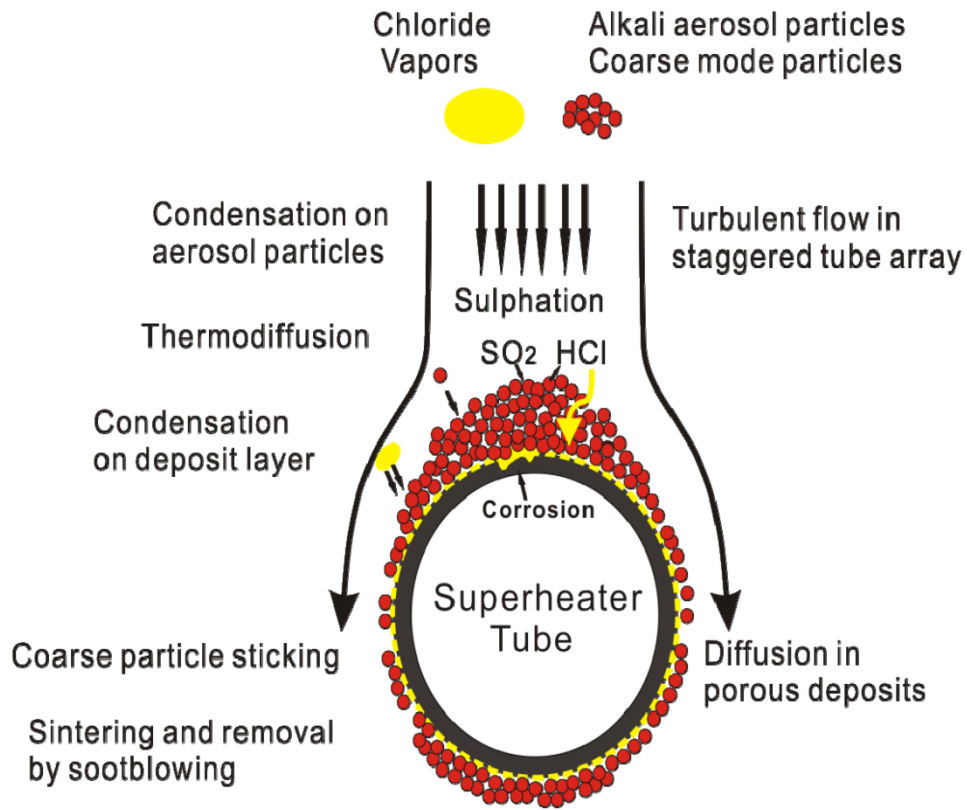


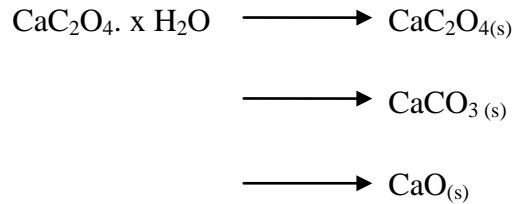
Figure 2. 3: Reactions inside the furnace

Sodium(Na)

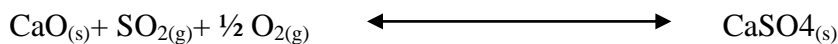
Sodium is another element present in most types of biomass. Sodium concentration is lower than potassium concentration and it has similar reactions described in potassium.

Calcium(Ca)

Calcium is partially organically bound and present as crystal types such as various forms of calcium oxalates. During the combustion process organically bound Ca compounds convert into CaO. Calcium oxide has a high melting point of 2570⁰C and low vapor pressure. Organic calcium release as CaO_(s) small solid particles. CaC₂O₄ form CaO as following reaction in the furnace.

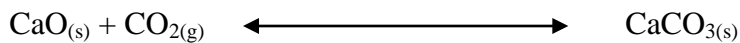


Ca present in some silicate minerals and it is insoluble in selective leaching tests. Forms of calcium silicate are inert during the combustion process and effect to form flue gases. To absorb sulphur during combustion process limestone can be used. But naturally occurring CaO in biomass is different from the CaO produced from limestone. Oxide particles of limestone are larger and the reactive surface area is smaller, thus particles less reactive in flue gases. CaO react with free Sulphur dioxide from flue gases as follows.

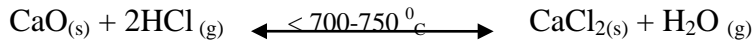
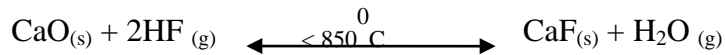


If the above reaction happened SO₂ is not available for sulfation of alkali chlorides. Lime stone can be used to reduce sulfation.

Following reaction occurs at the temperature between 600⁰C- 800⁰C. Temperature below 800⁰C, sintering occurs and CaO particles deposit on some surfaces and form hard deposits.



CaO also react with HF and HCl as follows;



Magnesium(Mg)

Mg is naturally present in some biomasses with low concentrations. Mg has similar reactions as Calcium in low temperature. But in the combustion process MgO is an inert compound. Mg causes low temperature corrosion in boilers. MgO react with SO₃ below 200°C it is called acid dew point corrosion.

Chlorine (Cl)

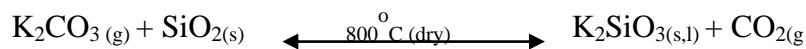
Chlorine is present as chloride salt in biomass. Chloride salts are soluble in leaching tests. Chlorine is present both organic and inorganic compounds. Organic chlorine compounds contain in PVC (Poly Vinyl Chloride) polymers and it is insoluble in leaching tests.

In combustion process, chlorine release as chloride vapors such as NaCl, KCl, ZnCl, PbCl and gaseous HCl. At the temperature between 700°C to 850°C alkali chlorides release from the fuel. Metal chlorides react with SO₂ and release HCl with metal sulfates. Alkali chlorides remain in flue gases may form particles and make fly ash more corrosive than chloride free fly ash.

Silicon (Si)

Silicon is normally present as silica (SiO₂) or as minerals of silicates. Silicon is relatively inert and insoluble in leaching analysis. In the combustion process, various metals combine with silicates and produce high melting ash. Straw is one of the agricultural residues containing high concentration of Si and K equally distributed in the fuel organic matrix. K and Si differently soluble in leaching test. K is relatively high soluble and Si remains as residue fraction. During combustion Si reacts with K and form low melting silicates it causes major sintering and fouling problems. Silica and its silicates indirectly affect for fouling and corrosion properties of fly ash while reacting with ash forming elements K, Na and Ca.

Alkali vapors such as KOH, KCl & K₂CO₃ react with SiO₂ and form alkali silicates.



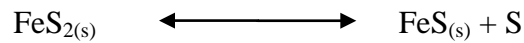
Aluminium (Al)

Aluminium is present in biomass; either organically bound Al or precipitated Al-salts. Al₂O₃ is an inert compound not significantly participates to form ash. Clay or other impurities contain biomass fuels when Al present in the form of silicates. Aluminium is insoluble in leaching test and a portion remains as residual fraction. Al₂(SO₄)₃ form is acid-soluble and decompose to alumina (Al₂O₃) in the combustion process. Alkali vapors KOH and KCl react with Al-silicate and form K-Al-silicates.

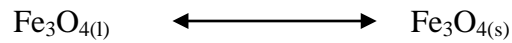
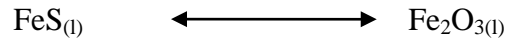
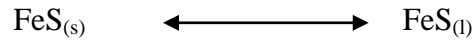
Iron (Fe)

Iron present in biomass fuels in many forms such as organically bound (Fe^{2+}), partially dissolved in the aqueous phase and partly precipitate as $\text{Fe}(\text{OH})_2$. Organically bound (Fe^{2+}) soluble in ammonium acetate and $\text{Fe}(\text{OH})_2$ soluble in acid.

In combustion process iron oxides such as FeO , $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ and Fe_2O_3 can be formed. In high temperature, iron compounds deposit in boilers. In boilers cause slagging problems in intermediate steps while FeS_2 gradually oxidize to iron oxides.



pyrrhotite



magnetite

2.4 Washing Treatments

2.4.1 Acid treatments

Some inorganic constituents are insoluble in water, but some are highly soluble in dilute acids such as nitric acid, hydrochloric acid and acetic acid. Acid leaching treatment can remove more inorganic constituents compared to water washing.

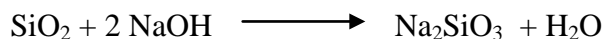
Alkali emission has been compared by using acid leaching and hot water leaching of wood waste and wheat straw. At the temperature between 200-500 °C, water reduced the alkali emission by 5-30%, while acid reduced the alkali emission by 70% [14].

To study the removal rate of alkali metals, HNO₃, H₃PO₄ and de-ionized water have been used. Concentration of HNO₃ acid (0.5, 2.0 and 5.0 kmolm⁻³) and concentration of 0.5kmolm⁻³ H₃PO₄ acid solutions were used as acid leaching solutions. Leaching by HNO₃ acid solutions increase the removal Na, K by 66% to 81% with increasing of HNO₃ concentration. The removal percentage of Na, K around 73% by using de-ionized water and removal as same as 2.0 kmolm⁻³ HNO₃ leaching. The highest alkali metal (Na and K) removal rate was observed by using 0.5kmolm⁻³ H₃PO₄ acid leaching and it is around 93% [15].

However, this dilute acid treatment requires a neutralization step for both washed biomass and washed liquid due to the lower pH. This leads to additional costs for the treatment process [16].

2.4.2 Alkali treatments

Majority of rice husk contain silica (SiO₂) and other oxides contain in small amount [17, 18]. Some research studies based on removal of silica from rice husk by using sodium hydroxide [19]. Silica removes by alkali treatment as follows:



The combination of high temperature and high sodium hydroxide concentration leads high ash removal. More than 90% of ash removal by using 13% sodium hydroxide at the temperature of 57.5°C has been reported. At 50°C washing temperature, 1:5 sodium hydroxide: husk ratio could be able to remove nearly all soluble silica within 3 hours.

However, the retention of organic matter was just 63%, which is not beneficial [20]. Almost all the silica removed by reflux for 6h (3 runs, 2h each) with the alkali treatment. The cost associated with the reagents and additional neutralization steps as well as the high loss of organic matter limit the use of this process as a pretreatment technology.

2.4.3 Water washing treatment

Water washing is an effective pretreatment method to remove trouble some elements from biomass. In laboratory scale studies showed that there were some washing techniques such as water spraying, water flushing and water soaking [21].

Solubility of inorganic constituents can be categorized as follows [22].

- Salts of K^+ , Na^+ , Ca^{2+} , Cl^- , HPO_4^{2-} , $H_2PO_4^-$, SO_4^{2-} can be removed by hot water treatment.
- Some organic compounds combined with metal cations K, Na, Mn, Ca, Mg, Fe and Al are form ion exchange with ammonium acetate solutions.
- Amino acids and proteins are insoluble and slightly soluble in water. Organic form of phosphorus partially soluble in acids.
- Silica and different calcium oxalates slightly soluble in water. In acidic solutions calcium salts are highly soluble.
- Selective leaching process is leaching of different constituents in different pH of solvents such as water, ammonium acetate and acids.

The water washing technology of biomass can leach substantial amount of potassium, chlorine and sulfur [21]. Over 90% of alkali content is in water soluble form [14, 23-25] and water washing pretreatment is an effective method of remove alkali and ash from herbaceous biomass [26]. The effectiveness depends on material characteristics, L/S ratio and temperature of washing solution, leaching duration and particle size.

Water to biomass ratio

Different washing methods (spray, soak, rain wash) applied to rice straw and inorganic removed percentage given in the Figure 2.4. Soaked and rain washed samples show better removal compared to sprayed samples [23].

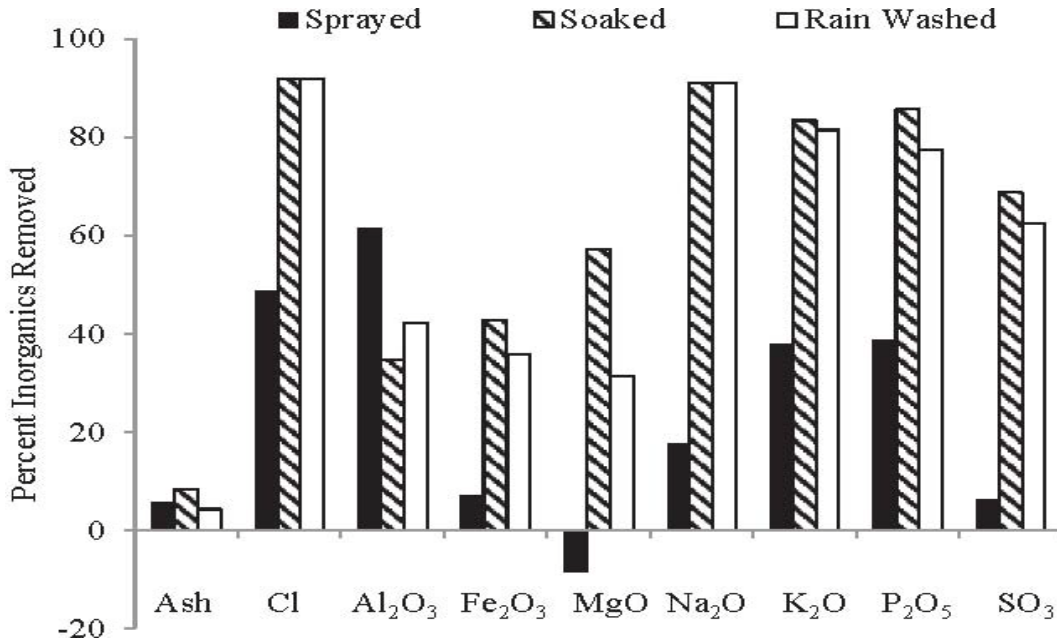


Figure 2. 4: Comparison of washing methods applied for rice straw

A study on multiple washing of Sorghum biomass has revealed that most effective triple wash can increase the ash removal from 14% to 20% compared to single wash. When it comes to halogen removal, double wash has shown the same performance as soaking [5].

Two biomass types, Lupines and Nardus have been used to observe the leaching behavior of different water to biomass ratios: (1:2, 1:4, and 1:8). In lupines material, water to biomass ratio of 1:8 has resulted the lowest concentration of N, K and Cl. In Nardus material S, K and Cl concentrations has significantly lowered for 1:4 and 1:8 water to biomass ratios [27].

Temperature

The effect of temperature on water washing of biomass has been studied by washing six biomass fuels; (wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood and rice hull) using de-ionized water for different water temperatures; (303K, 333K, 363K). Before and after ash composition measurements have shown that potassium and chlorine content of biomass can be effectively removed in high percentages for all temperature [3].

Two types of biomass, the empty fruit bunch (EFB) and palm kernel shell (PKS) have been washed for a 5-min leaching duration at different temperatures (25⁰C, 40⁰C, 55⁰C) using distilled water. Alkali metals, alkaline earth metals and transition metals removal has been increased with temperature up to 40⁰C(except Fe and Mg) as shown in the Figures 1.5 and 1.6 [28].

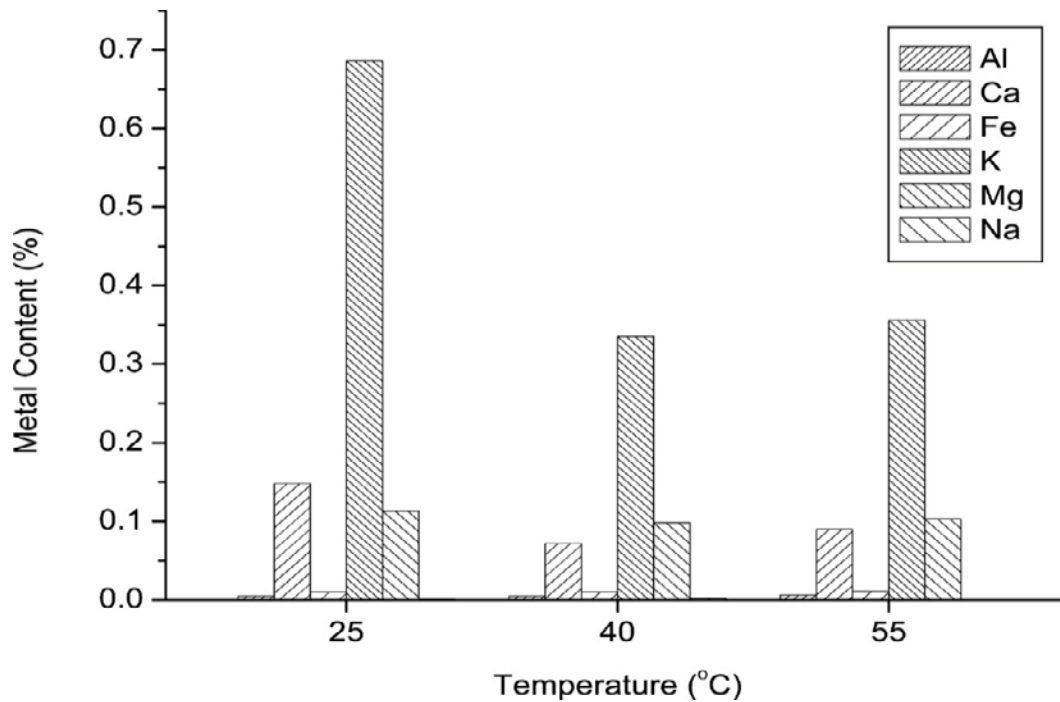


Figure 2. 5: Leached metal content percentages of EFB biomass particles

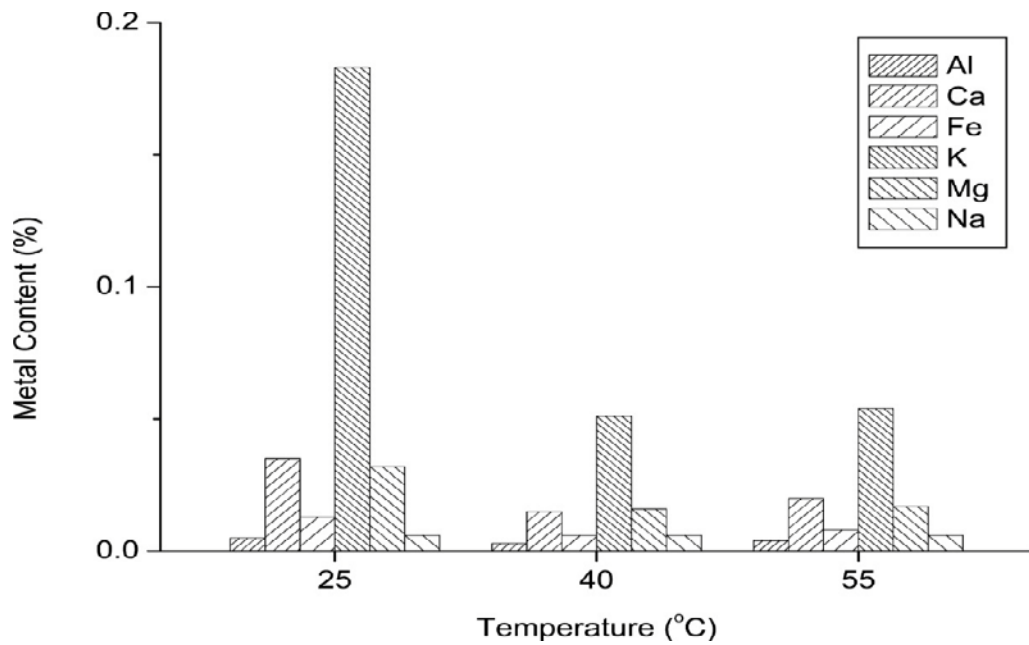


Figure 2. 6: Leached metal content percentages of PKS biomass particles

Leaching Time

Influence of time on the leaching process has been studied using batch reactor at room temperature. In a study of *Eucalyptus loxophleba* (mallee) samples (150-250µm), potassium, sodium and chloride has been removed more than 90% within first few minutes and equilibrium reached less than five minutes as can be seen from the Figure 2.7 [3].

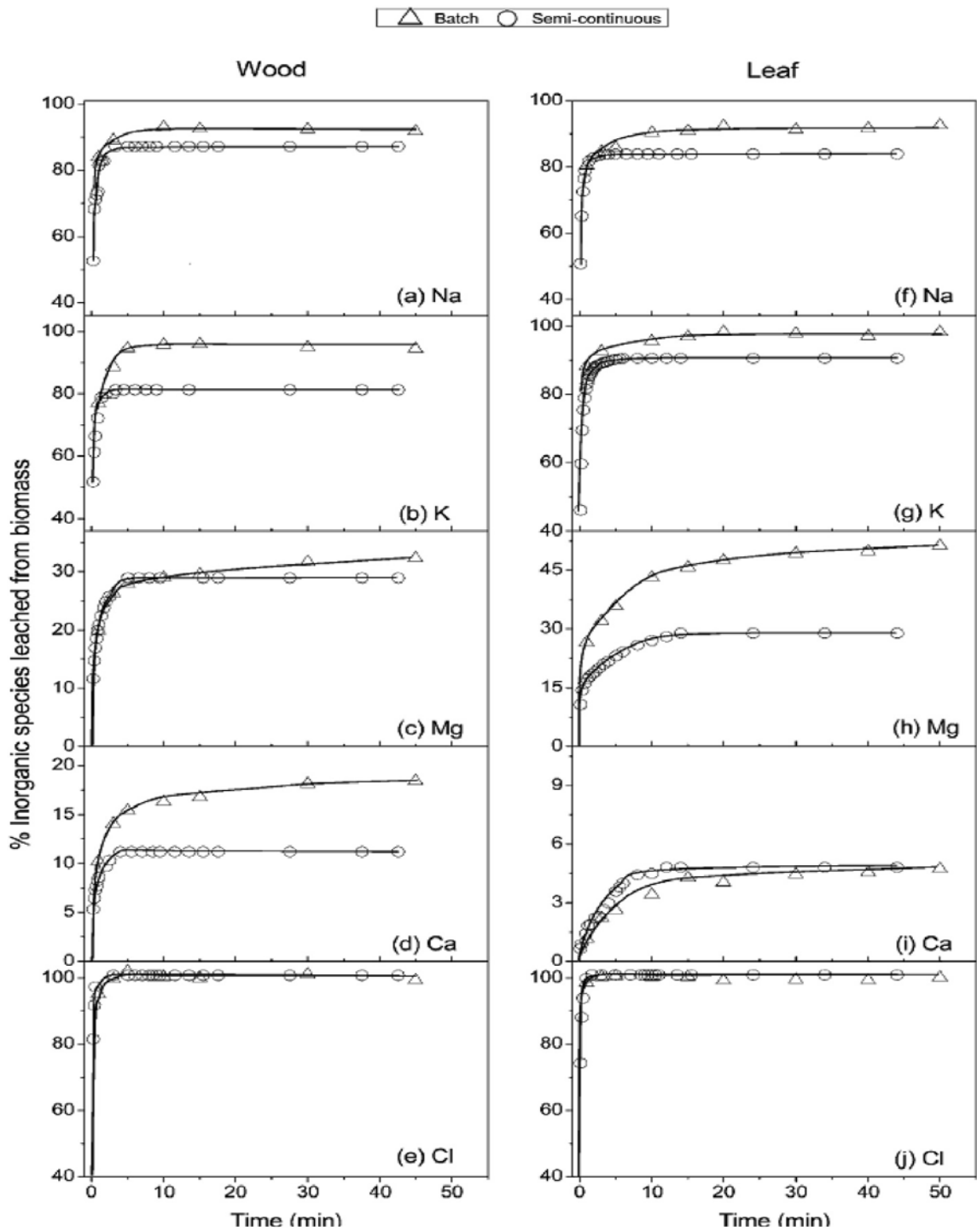


Figure 2. 7: Leached percentages of inorganic ions on mallee wood and leaf

Particle Size

Two types of palm residues EFB and PKS have been studied for the effect of particle size on water leaching. In 4-0.149mm range leaching of small particle size biomass has shown higher ash removal due to higher surface area [28].

2.5 Leaching Kinetics

In order to predict short-and long-term release rates of inorganic matter, the kinetic behavior of inorganic leaching is described by kinetic models [29].

First order kinetic model and second order kinetic model has been used to describe the leaching kinetics.

First order kinetic model:

$$\frac{d C_{i,t}}{dt} = k_i (C_{i,s} - C_{i,t})$$

If the species i follows and first order model, $-\ln \left(\frac{C_{i,s} - C_{i,t}}{C_{i,s}} \right)$ vs time should be a straight line.

The first order kinetic model is not suitable for processes having two distinct leaching steps; relatively fast initial leaching process and slower residual leaching process.

Second order kinetic model:

$$\frac{d C_{i,t}}{dt} = k(C_{i,s} - C_{i,t})^2$$

Integrating the equation applying boundary conditions $t=0$ to t and $C_{i,t} = 0$ to $C_{i,t}$;

$$C_{i,t} = \frac{C_{i,s}^2 kt}{1 + C_{i,s} kt}$$

Rearranging the equation as $y = mx + c$;

$$\frac{t}{C_{i,t}} = \frac{t}{C_{i,s}} + \frac{1}{kC_{i,s}^2}$$

Initial leaching rate h ; $h = kC_{i,s}^2$

2.6 Research Gap

According to the literature review carried out, few studies consider on hot water washing of rice husk [21, 31]. According to those studies; water washing effectively removed potassium, sulfur and chlorine content of biomass. Even though there are several washing parameters such as temperature, water/biomass ratio, time and particle size, that affect the washing performance, washing medium temperature effect has been studied only for rice husk washing [21]. When considering the industrial applications, mainly focus on water, energy, space and duration for the washing pretreatment need to be optimized in order to minimize the pretreatment cost. Further, elemental wise leaching kinetics is also important for the design of proper pretreatment process.

CHAPTER 3. MATERIALS AND METHODOLOGY

3.1 Materials

Dry rice husk with particle size ranging from 2.8-5.6mm was used in all the experiments. Rice husk was collected before encounter any rain washing. The ash content of rice husk was analyzed and was 19.95% before the washing pretreatment.

Table 3.1 shows the elemental composition of raw rice husk ash. Assuming all the elements in ash are in their stable oxide forms, the balance was taken as SiO₂.

Table 3. 1: Ash composition

Element	Composition mg/g ash	Composition mg/g biomass
Fe	0.746	0.149
Ca	3.810	0.760
Mg	0.899	0.179
Na	0.472	0.094
K	15.200	3.032
Al	1.160	0.231
Ti	0.010	0.002
P	1.980	0.395
Si	449.171	89.6
Cl	N/A	1.075

Electrical conductivity of 1 μ S/cm de-ionized water was taken as the liquid washing medium.

3.2 Washing Apparatus

Figure 3.1 shows the washing apparatus used for the experiments. A temperature-controlled water bath was used and a portable conductivity meter was used to measure the conductivity of washing water at definite time intervals.



Figure 3. 1: Schematic diagram of the water washing experimental setup

3.3 Methodology

3.3.1 Study the effect of washing temperature

- The test was carried out keeping the same water to biomass ratio (L/S ratio) of 100(600 ml water: 6 g husk).
- Beakers with de-ionized water were kept inside the water bath until they attain the required temperature; room temperature (30⁰C), 50⁰C, 65⁰C and 75⁰C and then the rice husk samples were introduced.

- Within the time duration of 90 minutes, samples were stirred with a glass rod every two minutes and electrical conductivity of water was measured every five minutes.
- Finally, the optimum temperature was selected using electrical conductivity values.

3.3.2 Study the effect of L/S ratio

- Five samples were prepared to test different L/S ratios of 20,40,60,80 and 100. Here, the liquid volume was same (600 ml) and solid mass was varied accordingly.
- Five beakers were kept in hot water bath of 65⁰Ctemperature. After adding the samples to the beakers, the test was carried out for 90 minutes similar to the previous case. Optimum L/S ratio was selected using electrical conductivity values.

3.3.3 Study the effect of washing time

- Using optimum L/S ratio and optimum temperature, the test was carried out for different time intervals; 5 minutes, 10 minutes, 15 minutes, 30 minutes, 60 minutes and 90 minutes similar to the previous cases.

3.3.4 Composition analysis

- After each test, samples were taken from the water bath and filtered. (see Figure 3.2).
- Filtered effluents were analyzed elemental wise at the room temperature using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).
- A raw rice husk sample was also analyzed to quantify the initial elemental concentrations using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

- Amount of Cl determined by titration method.

Table 3.2 summarizes the operating conditions of the test runs.

Table 3. 2: Operating conditions

Controlling parameter	Range	Fixed parameters
Temperature	30,50,65,75 (°C)	Water/biomass: 100 Time: 90 minutes
Water/biomass	20,40,60,80,100 (w/w)	Temperature: 65 °C Time: 90 minutes
Time	5,10,15,30,60,90 (minutes)	Temperature: 65 °C Water/biomass: 100

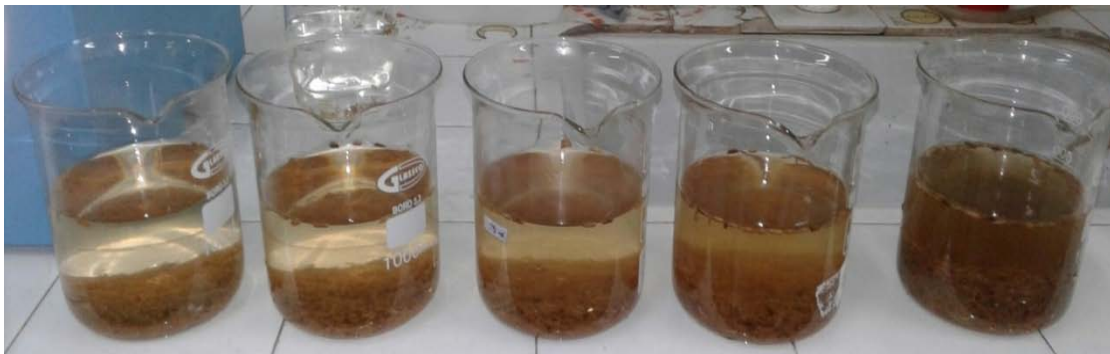


Figure 3. 2: Test samples after the experiment with changing L/S ratio

3.4 Second Order Kinetic Model for Leachate: [30]

$$\frac{dC_{i,t}}{dt} = k(C_{i,s} - C_{i,t})^2$$

where k is in $\text{g mg}^{-1}\text{s}^{-1}$, $C_{i,s}$ and $C_{i,t}$ are in mg/g .

Integrating the rate law applying boundary conditions of $t = 0$ to t and $C_{i,t} = 0$ to $C_{i,t}$:

$$C_{i,t} = \frac{C_{i,s}^2 kt}{1 + C_{i,s} kt}$$

Above equation can be rearranged in $Y = mX + C$ form as follows;

$$\frac{t}{C_{i,t}} = \frac{t}{C_{i,s}} + \frac{1}{kC_{i,s}^2}$$

Initial leaching rate h ; $h = kC_{i,s}^2$

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Leaching Behavior

This study is based on the electrical conductivity values of washed water of fixed time intervals. Electrical conductivity of de-ionized water was measured before adding biomass in to the beakers and it was constant ($1\mu\text{S}/\text{cm}$) irrespective of the temperature. Electrical conductivity is directly proportional to the ionic content of a solution. Three parameters were studied; washing temperature, L/S ratio and washing time.

4.1.1 Effect of temperature

The change of electrical conductivity with time (per gram of washed rice husk), in five minutes time span up to 90 minutes, for four different temperatures is represented in Figure 4.1. The room temperature was considered as 30°C .

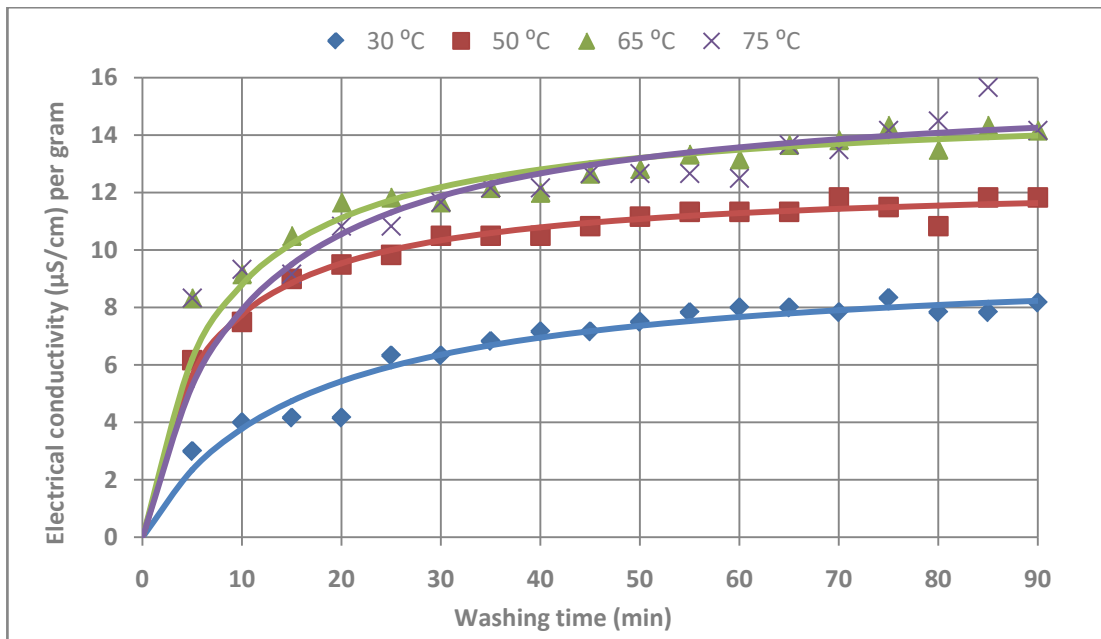


Figure 4. 1: Electrical conductivity per gram Vs Washing time.

According to the Figure 4.1, the electrical conductivity is increasing with temperature. The trends of electrical conductivity values are almost same at the temperatures of 65°C and 75°C.

In order to analyze the leaching behavior in more details, a second order kinetic linearized equation was applied to all the temperature cases as shown in the Figure 4.2. The calculated kinetic parameters and corresponding R^2 values are summarized in the Table 4.1 where k is the overall leaching rate constant, h is the initial leaching rate at time equals to zero (at the time starts to leach), C_s is the saturated leaching capacity and R^2 is the goodness of fit. All the R^2 values are above 0.98. It suggests that the proposed second order kinetic model successfully represent the ash leaching behavior with respect to different temperatures. Further, for 90 minutes of washing time, the modeled leaching capacity was compared with the experimental leaching capacity in the Table 4.2 which also shows a good agreement.

Table 4. 1: Calculated kinetic parameters for different temperature

	30 °C	50 °C	65 °C	75 °C
$k (cm \mu S^{-1} s^{-1})$	11.1×10^{-5}	22.2×10^{-5}	15.4×10^{-5}	10.5×10^{-5}
$h (\mu S cm^{-1} s^{-1})$	0.010	0.034	0.035	0.026
$C_s (\mu S cm^{-1})$	9.66	12.42	15.11	15.85
R^2	0.9813	0.9959	0.9952	0.9836

Table 4. 2: Leaching capacity values at 90 minutes for different temperature

Temperature	30 °C	50 °C	65 °C	75 °C
Model $C_{90} (\mu S cm^{-1})$	8.17	11.83	14.17	14.17
Experimental $C_{90} (\mu S cm^{-1})$	8.24	11.64	13.99	14.26

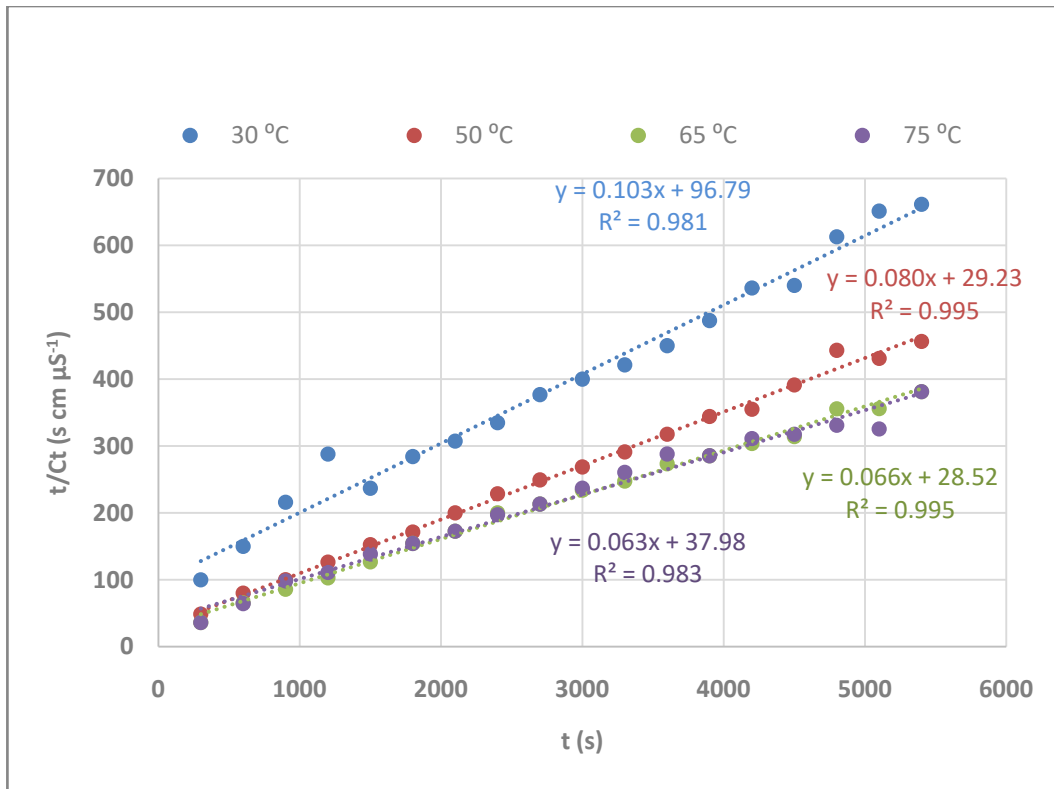


Figure 4. 2: t/Ct Vs time

According to the Table 4.1, the overall leaching rate constant k is increasing up to 50 °C and decreasing thereafter. However, the initial leaching rate h is highest at 65 °C. The saturated leaching capacity is increasing with the temperature and levels out after 65 °C. It indicates that in a given time period, the maximum leaching can be obtained at the temperature of 65 °C. Therefore, the washing temperature of 65 °C was chosen as the optimum temperature. An optimum temperature of 60 °C has been observed by previous study on rice husk washing conducted for three temperature levels and liquid to solid ratio of 80 for 3 h duration [21].

4.1.2 Effect of L/S ratio

Figure 4.3 represents the change of electrical conductivity with time (per gram of washed rice husk), in five minutes time span up to 90 minutes, for five different L/S ratios. The washing temperature was kept constant at 65°C.

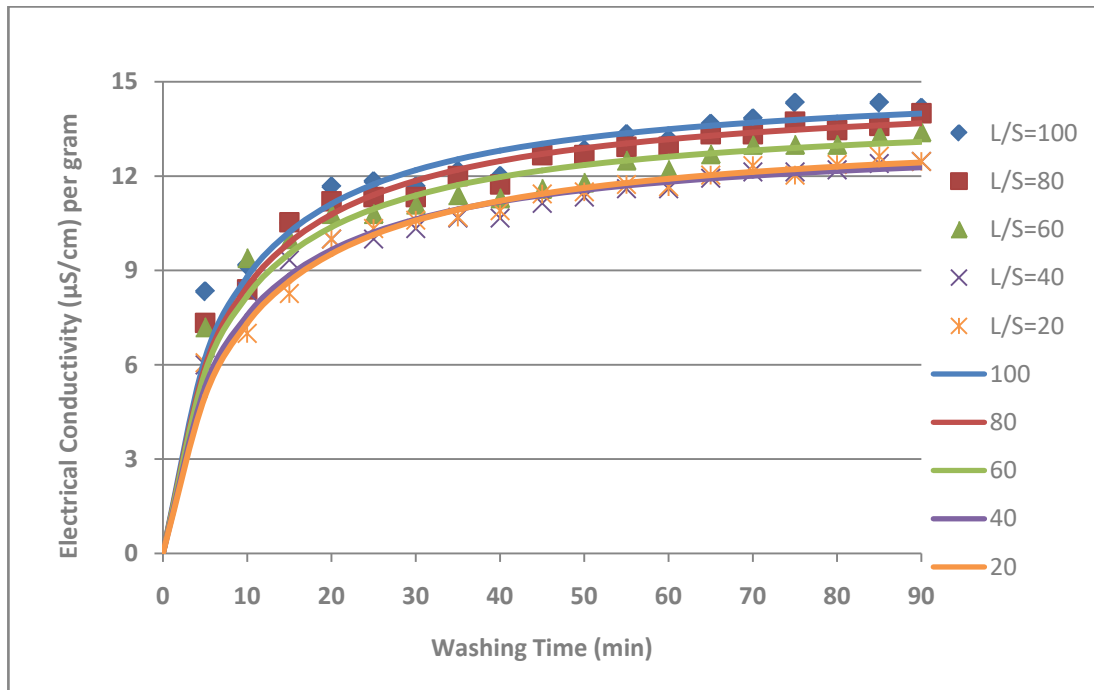


Figure 4. 3: Increment of Electrical conductivity per gram Vs Washing time for five L/S ratio.

According to the Figure 4.3, the electrical conductivity is increasing with L/S ratio and L/S ratio of 100 shows the highest conductivity values. Extraction of salt into de-ionized water is higher with decrease of solid content and increase of de-ionized water amount. The difference of the trends of electrical conductivity values are diminishing towards high L/S ratios.

The second order kinetic linearized equation was applied to all the L/S ratio cases as shown in the Figure 4.4. Table 4.3 summarizes the calculated kinetic parameters and corresponding R^2 values. It can be observed that the proposed second order kinetic model can successfully represent the ash leaching behavior with respect to different L/S ratios, since all the R^2 values are above 0.99. Further, for 90 minutes of washing time, the modeled leaching capacity was compared with the experimental leaching capacity in the Table 4.4 which also shows a good agreement.

Table 4. 3: Calculated kinetic parameters for different L/S ratios

L/S ratio	20	40	60	80	100
$k (cm \mu S^{-1} s^{-1})$	14.2×10^{-5}	16.5×10^{-5}	16.2×10^{-5}	15×10^{-5}	15.4×10^{-5}
$h (\mu S cm^{-1} s^{-1})$	0.026	0.029	0.032	0.033	0.035
$C_s (\mu S cm^{-1})$	13.62	13.32	14.14	14.81	15.11
R^2	0.998	0.997	0.995	0.997	0.995

Table 4. 4: Leaching capacity values at 90 minutes for different L/S ratios

L/S ratio	20	40	60	80	100
<i>Model</i> $C_{90} (\mu S cm^{-1})$	12.47	12.47	13.40	14	14.17
<i>Experimental</i> $C_{90} (\mu S cm^{-1})$	12.43	12.28	13.09	13.68	13.99

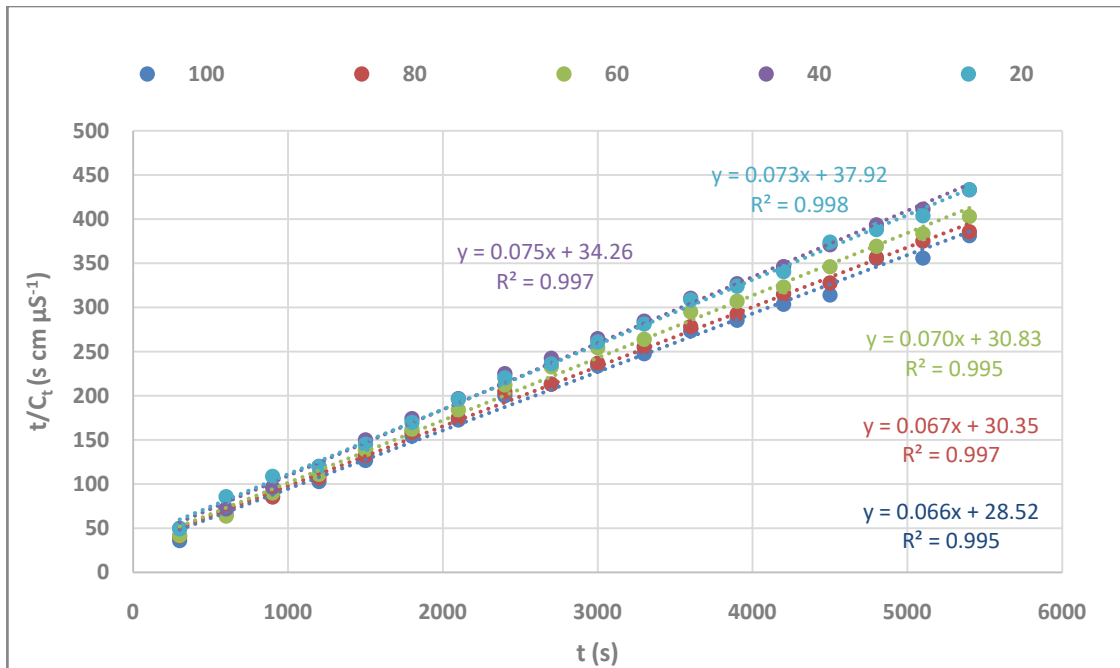


Figure 4. 4: t/C_t Vs time

As per the values in Table 4.3 the overall leaching rate constant k is increasing up to L/S ratio of 40 and decreasing thereafter. However, the initial leaching rate h is highest at L/S ratio of 100. The saturated leaching capacity is also increasing with the L/S ratio. It shows that in a given time period, the maximum leaching can be obtained at high L/S ratios and the difference is diminishing towards L/S ratio of 100. When increase the L/S ratio, it needs more water per unit mass of rice husk. In such a case, the cost of de-ionized water is high and the reactor capacity is also limited. Previous studies have used de-ionized or distilled water to the sample ratio in the range of 70-80 [21], [23]. Considering the above economic and scale factors as well as the previous studies, the maximum L/S ratio of 100 was chosen for the study considering the feasibility in industrial applications. Then L/S ratio of 100 which is having the highest initial leaching rate was chosen as the optimum L/S ratio.

4.2 Removal of Problematic Elements

4.2.1 Effect of temperature on elemental removal

Samples were analyzed for four different temperatures. L/S ratio was taken as 100 with constant washing time for 90 minutes. Significant removal was observed only with K, Si and Cl.

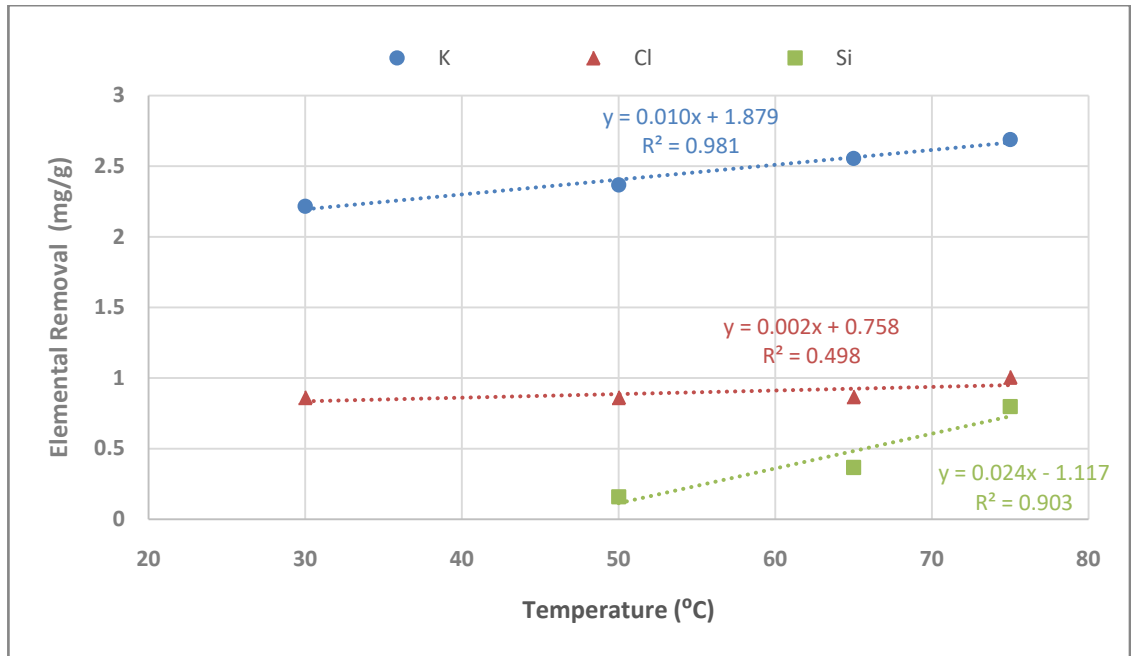


Figure 4. 5: Elemental Removal Vs Temperature

According to the Figure 3.5, leaching concentrations of elements linearly increase with temperature. Si shows the highest leaching dependency on the temperature and does not leach at room temperature at all. Water solubility of Si appreciably increases with temperature. Leaching of K also depends on the temperature, whereas very weak dependency can be observed for Cl. Similar results have been observed by previous study on rice husk washing conducted for three temperature levels and liquid to solid ratio of 80 for 3 h duration [21]. Therefore, if the primary requirement of washing treatment is to remove Cl, washing at room temperature is recommended and for other elemental removal higher temperature may be required.

Table 4. 5: Removal percentages with different temperature

Temperature	% removal of K	% removal of Cl
30 ⁰ C	73.114	80.130
50 ⁰ C	78.057	80.130
65 ⁰ C	84.257	80.744
75 ⁰ C	88.682	93.488

In a previous study of rice husk washing at the temperature range of 30-90⁰C; 85% to >90% of K and 68% - 85% of Cl have been removed [21]. The removal percentages obtained in the present study are also within a similar range.

4.2.2 Effect of L/S ratio on elemental removal

According to the literature survey K, Cl, Si, Na, Mg, Ca, Al, Fe &Ti were analyzed for five different L/S ratio samples. The washing temperature was kept constant at 65⁰C with constant washing time for 90 minutes. Again, significant removal was observed only with K, Si and Cl.

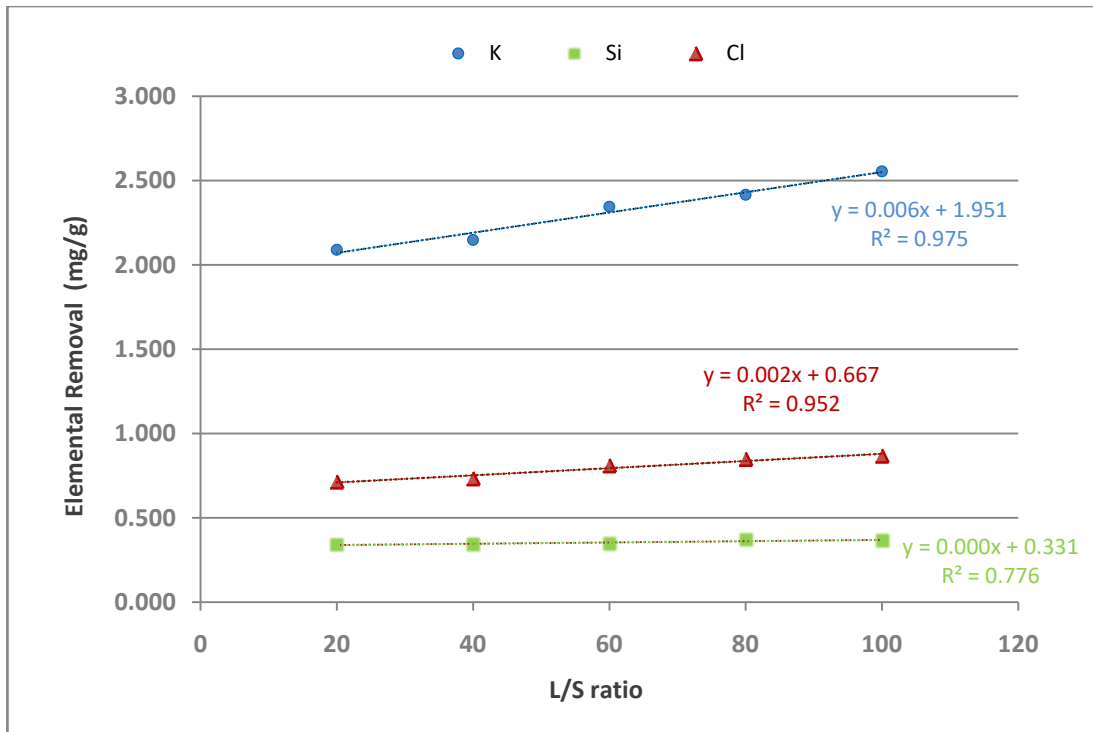


Figure 4. 6: Elemental Removal Vs L/S ratio

Figure 4.6 shows that the leaching concentrations of three elements linearly increase with increment of L/S ratio. However, compared to Figure 4.5, leaching dependency of elements on L/S ratio is far less than on temperature. Virtually Si has no dependency and Cl shows a very weak dependency. Only K shows appreciable dependency and hence increase of L/S ratio is desired only if the primary requirement of the washing treatment is to remove K.

Table 4. 6: Removal percentages with different L/S ratio

L/S ratio	% removal of K	% removal of Cl
100	84.268	80.727
80	79.683	78.933
60	77.360	75.345
40	70.844	68.170
20	68.918	66.376

4.3 Leaching Kinetics of K and Cl at Optimum Operating Conditions

Since K removal is depending on both washing temperature and L/S ratio, it is desirable to operate at high temperature and high L/S ratio. Therefore, the optimum parameters identified from the conductivity measurements were used for the kinetic study.

At 65⁰C washing temperature and L/S ratio of 100, the concentration values of K, Cl and Si calculated for different time intervals starts from 5 minutes span for 60 minutes. Si starts to leach after 30 minutes and its initial concentration values are not significant.

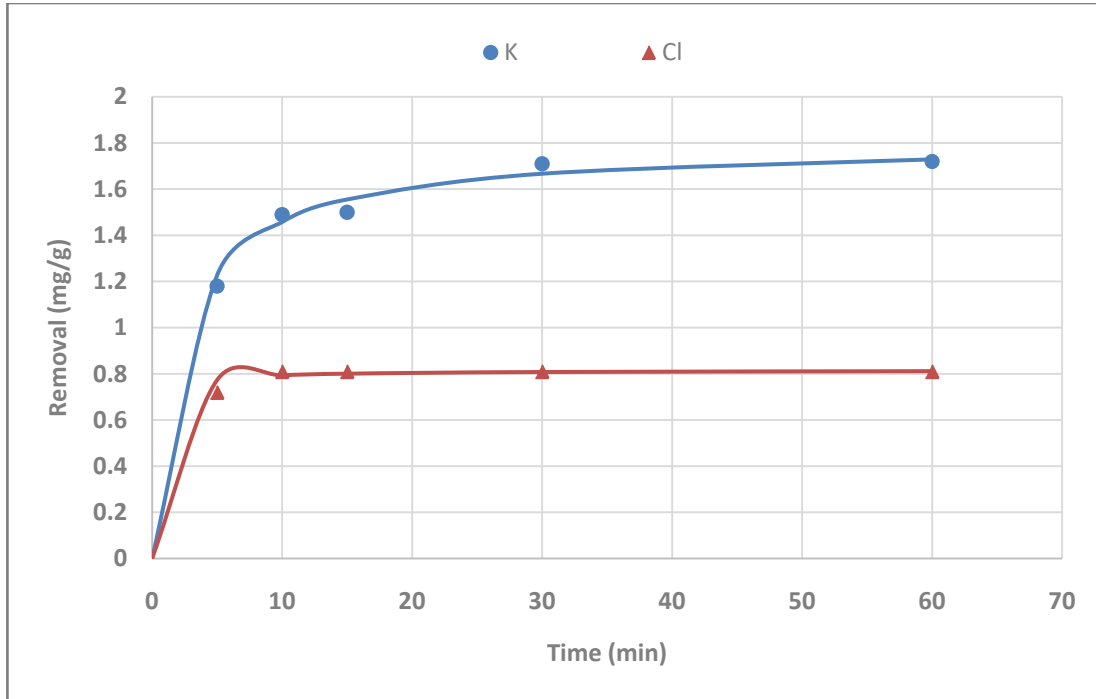


Figure 4. 7: Removal Vs Time

Hence the second order kinetic linearized equation applied for higher extractable elements such as K and Cl. The second order kinetic linearized equation was applied to all the time interval cases as shown in the Figure 4.8. Table 4.5 summarizes the calculated kinetic parameters and corresponding R^2 values. It can be observed that the proposed second order kinetic model can successfully represent the ash leaching behavior of K and Cl with respect to different time intervals. Further, within 10 minutes leaching time, 97% of leachable Cl and 81% leachable K is removed.

Table 4. 7: Calculated kinetic parameters for K and Cl

	K	Cl
$k (g\ mg^{-1}\ s^{-1})$	0.004	0.075
$C_s (mg/g)$	1.796	0.815
$h (mg\ g^{-1}\ s^{-1})$	0.013	0.05
R^2	0.999	1

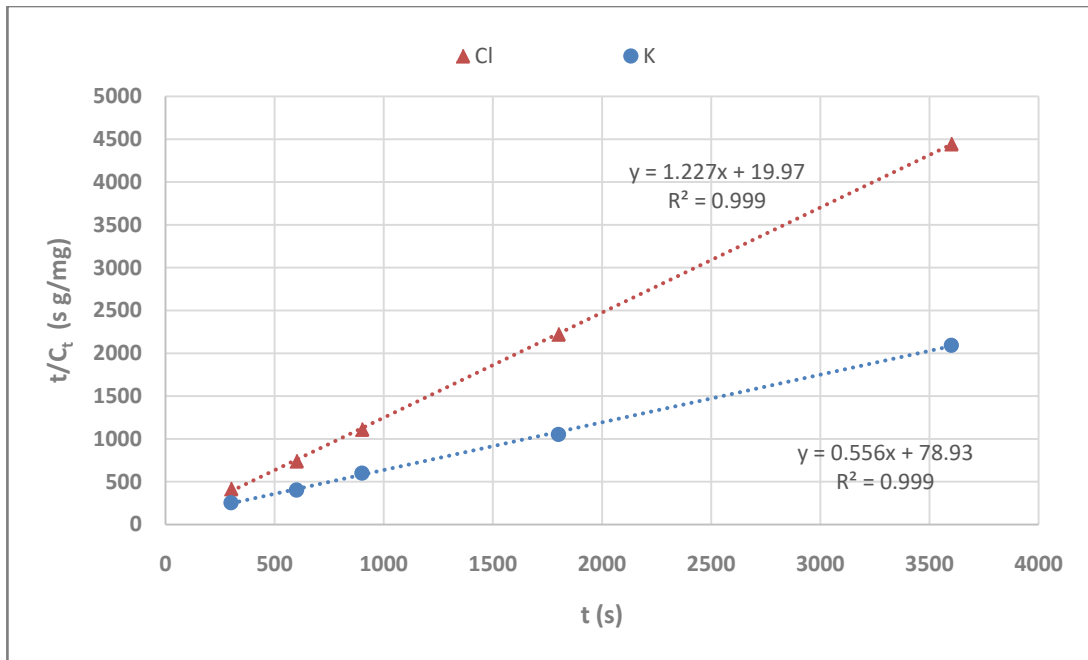


Figure 4. 8: t/C_t Vs time

According to the Table 4.5, the overall leaching rate constant k and the initial leaching rate h are higher in Cl. This indicates that Cl has high solubility in water.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

- In this study, three washing parameters; washing temperature in the range of 30⁰C to 75⁰C, water/biomass ratio in the range of 20 to 100 and washing time up to 90 minutes were studied and the optimum washing conditions were found at a temperature of 65⁰C, water/biomass ratio of 100 and 10 minutes washing time. Further, the second order kinetic model successfully represents the leaching behavior of K and Cl.
- Washing temperature has significant effect on Si removal, a considerable effect on K removal and a very weak effect of Cl removal whereas water/biomass ratio has an appreciable effect on K removal, a very weak effect on Cl removal whereas almost no effect of Si removal.
- At the selected temperature and water to biomass ratio, about 84% of K and 81% of Cl can be removed from rice husk and therefore water washing is an effective technique for removal of K and Cl. Within 10 minutes leaching time, 97% of leachable Cl and 81% of leachable K is removed. Rice husk contains high amount of Si, however the water washing could not facilitate significant removal of silicon from rice husk.
- The obtained optimum parameters can be used to design a rice husk washing pretreatment facility for industrial applications. The use of de-ionized water may be not economical for industrial use and therefore, use of city water supply may be required. The moisture content of washed rice husk is high. Therefore, several methods such as blending the rice husk with wood, air drying or drying using hot stack gas (flue gas) can be recommended to remove moisture content before used in combustion applications. Further, the leachate contains high amount of potassium ions and chloride ions can be used for irrigation purposes.

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Appendix A

Electrical conductivity per gram of husk sample

Washing temperature: 65 °C

		L/S ratio				
		100	80	60	40	20
Time(min)	5	8.33	7.33	7.20	6.00	6.07
	10	9.17	8.40	9.40	8.33	7.00
	15	10.50	10.53	10.00	9.33	8.27
	20	11.67	11.20	10.80	10.00	10.00
	25	11.83	11.33	10.80	10.00	10.33
	30	11.67	11.33	11.10	10.33	10.60
	35	12.17	12.00	11.40	10.67	10.70
	40	12.00	11.73	11.30	10.67	10.90
	45	12.67	12.67	11.60	11.13	11.43
	50	12.83	12.67	11.80	11.33	11.50
	55	13.33	12.93	12.50	11.60	11.73
	60	13.17	12.93	12.20	11.60	11.67
	65	13.67	13.33	12.70	11.93	12.03
	70	13.83	13.33	13.00	12.13	12.33
	75	14.33	13.73	13.00	12.13	12.03
	80	13.50	13.47	13.00	12.20	12.37
85	14.33	13.60	13.30	12.40	12.63	
90	14.17	14.00	13.40	12.47	12.47	

Appendix B

Electrical conductivity per gram of husk sample

L/S ratio: 100

		Temperature (°C)			
		30	50	65	75
Time(min)	5	3	6.17	8.33	8.33
	10	4	7.50	9.17	9.33
	15	4.17	9.00	10.50	9.17
	20	4.17	9.50	11.67	10.83
	25	6.33	9.83	11.83	10.83
	30	6.33	10.50	11.67	11.67
	35	6.83	10.50	12.17	12.17
	40	7.17	10.50	12.00	12.17
	45	7.17	10.83	12.67	12.67
	50	7.50	11.17	12.83	12.67
	55	7.83	11.33	13.33	12.67
	60	8.00	11.33	13.17	12.50
	65	8.00	11.33	13.67	13.67
	70	7.83	11.83	13.83	13.50
	75	8.33	11.50	14.33	14.17
	80	7.83	10.83	13.50	14.50
	85	7.83	11.83	14.33	15.67
90	8.17	11.83	14.17	14.17	

Appendix C

Washing temperature: 65 °C; Washing time: 90 minutes

Elemental removal (mg/g) at different L/S ratios

L/S ratio	Na	K	Ca	Mg	Ti	Si	Al	Fe	Cl
100	0.019	2.555	0.032	0.012	0.00010	0.366	0.005	0.008	0.868
80	0.018	2.416	0.040	0.015	0.00000	0.371	0.003	0.007	0.849
60	0.015	2.346	0.038	0.015	0.00009	0.347	0.004	0.010	0.810
40	0.011	2.148	0.031	0.015	0.00008	0.343	0.002	0.007	0.733
20	0.010	2.090	0.033	0.023	0.00016	0.342	0.004	0.013	0.714