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A LOW COST CONVERSION METHOD OF AGRO-RESIDUE TO COAGULANT AID

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ABSTRACT

Rice is one of the major crops grown throughout the world, it covers 1% of the earth's surface and is a primary source of food for billions of people Globally, approximately 600 million tons of rice paddy is produced each year. On average 20% of the rice paddy is husk, giving an annual total production of 120 million tons. In Egypt, the annual rice production is about 5,700,000 tons, equivalent to 200,000 tons of rice husk ash .After the separation of the rice from the paddy, one - third of the mass remains as a waste material ..Many workers have tried to use this agricultural waste to produce useful materials such as silica, zeolite, silica gel silicon carbide, activated carbon and sodium silicate notation coagulant aid. Rice husk ash is one of the most silica rich raw materials containing about 90-98% silica (this quantity depends on the soil type, plant variety and climatic conditions, geological factor, type of ground, near of harvest, sample preparation and analysis method..etc.The chemical process discussed below not only provides a solution for waste disposal but also recovers a valuable silica product, together with certain useful associate recoveries The activated silica or sodium silicate is one of the four basic types of coagulants aids beside pH adjusters, clay and polymers which increase a stability of coagulant and can unite with the positively charged aluminum or with iron flocs, resulting in a larger, denser lamellar floc that settles faster and enhances enmeshment.

The objectives of this study were to :produce rice husk ash (RHA) from rice husk, produce sodium silicate, and characterizations of new materials obtained by FTIR, XRD, and SEM. Under the study condition it was found that selected sample (optimum condition),of RHA which is designated as RHA_5 obtained by calcination of untreated RH at 650 ° C in semi closed system. FTIR shows signals at 1098 and 800 cm^{-1} for Si-O and O-Si-O respectively; XRD shows a sharp signal (amorphous silica) at $2\theta = 22^\circ$ and SEM examination indicate that rectangular particles should be distinguished. whereas RHA_5 used in manufacturing of sodium silicate which is designated as Ssi_5 and identified by XRD with its characteristic peak at 2θ about 28°, FTIR shows signals at (1443,994) for Si-O-Si, NFTIR shows signal at 7326 for overtone OH stretching Si-OH.

KEY WORDS : Rice, Rice husk Ash, Active silica and Sodium silicate

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INTRODUCTION

Rice is one of the major crops grown throughout the world .After the separation of the rice from the paddy, one - third of the mass remains as a waste material . Many workers have tried to use this agricultural waste to produce useful materials such as silica, silicon carbide, activated carbon, sodium silicate, silica gel, and zeolite [1].

Rice covers 1% of the earth's surface and is a primary source of food for billions of people. Globally, approximately 600 million tonnes of rice paddy is produced each year. On average 20% of the rice paddy is husk, giving an annual total production of 120 million tonnes. In Egypt, the annual rice production is about 5,700,000 tons, equivalent to 200,000 tons of rice husk ash, in the majority of rice producing countries much of the husk produced from the processing of rice is either burnt or dumped as waste [2].

Rice husk is a by-product from rice mill that was used as an energy source in many industries such as biomass power plant and rice mill. Burning rice husk generates rice husk ash (RHA) which is rich in silica and can be an economically valuable raw material for production of natural silica [3].

There are several methods for the extraction of silica from biomass. Many authors,[4-7] have suggested that acid preliminary treatment before thermal treatment is a reasonable method for natural silica extraction. The high purity of silica and low mineral impurity are retrieved by boiling in hydrochloric solution for 1 h followed by burning in the atmosphere at 650-700 °C for 4 h[5]. By means of this method, the extracted silica is found in a form of amorphous structure which is the most reactive form for silylation reaction[5].

Rice husk is unusually high in ash compared to other biomass fuels – close to 20%. The ash is 92 to 95% silica (SiO_2), highly porous and lightweight, with a very high external surface area. Its absorbent and insulating properties are useful to many industrial applications, and the ash has been the subject of many research studies [2].

Rice husk ash has many applications due to it's various properties. It is an excellent insulator, so has applications in industrial processes such as steel foundries, and in the manufacture of insulation for houses and refractory bricks. It is an active pozzolan and has several applications in the cement and concrete industry. It is also highly absorbent, and is used to absorb oil on hard surfaces and potentially to filter arsenic from water [2].

RHA is a general term describing all types of ash produced from burning rice husks. In practice, the type of ash varies considerably according to the burning technique. Two forms predominate in combustion and gasification. The silica in the ash undergoes structural transformations depending on the temperature regime it undergoes during combustion. At 550°C – 800°C amorphous silica is formed and at greater temperatures, crystalline silica is formed [2].

Sodium silicate, the precursor for silica production, is currently manufactured by smelting quartz sand with sodium carbonate at 1300°C [8-9] This conventional technology requires high energy costs , produce considerable air pollution, impure of the product and need to maintenance of oven due to attack of base that could be avoided by processing rice hull silica, instead of sand, by ambient temperature methods. Rice hull ash is produced commercially by hull combustion and contains over 60% silica and can be an economically viable raw material for the production of silicates, silica gel,zeolite and silica [10-11].

The presence of silica in rice husk (RH) has been known since 1938.[12] Rice husks produce a high ash content, varying from 13 to 29 wt.% depending on the variety, climate, and geographic location. The ash is largely composed of silica (87-97%) with small amounts of inorganic salts [13] Due to its high silica content RH has become a source for preparation of a number of silicon compounds such as silicon carbide[14-15] ,silicon nitride [16] ,sialon, zeolite[17], silica ash obtained by calcining RH is also used in the cement industry. RH silica has fine particle size and high reactivity and has been used in the production of activated silica, sodium silicate, potassium silicate and solar grade silicon [18]. Though the ash of RH is rich in silica, the raw RH contains mainly organic matter (≈85 %)composed of cellulose, lignin, d-xylose, small quantities of methyl glucuronic acid and d-galactose, and small quantities of proteins and vitamins, inorganic compounds [19]. The elemental analysis of the organic matter as calculated by Sharma et al. is 51 wt.% carbon, 7 wt.% hydrogen and 42 wt.% oxygen[19].

The four basic types of coagulants aids are pH adjusters, activated silica, clay and polymers. Activated silica has been used as a flocculants since the 1930's to strengthen flocs and reduce the potential of deterioration [20] When activated silica is added to water, it produces a stable solution that has a negative surface charge. The activated silica can unite with the positively charged aluminum or with iron flocs, resulting in a larger, denser floc that settles faster and enhances enmeshment.

The addition of activated silica is especially useful for treating highly colored, low-turbidity waters cause it adds weight to the floc., It is usually produced on-site by reacting sodium silicate with an acid to form a gel [21].When using activated silica, the resultant floc is larger, denser, more chemically stable, and settles faster than iron and aluminum flocs[20] .

Silicate compounds were first used as a coagulation aid because of their ability to adsorb onto particles and decrease surface charge. These properties were soon applied to sequestration (dispersion) of iron particles in distribution systems[22-26]. Addition of silicate-based inhibitors has also been found to reduce iron corrosion rate[27]. Finally, silicates are reported to decrease the oxidation of Fe^{+2} because ferrous iron diffusion through the silicate film is slower than through iron oxide scale [28].

The objectives of this study were to :

Produce rice husk ash (RHA) from rice husk, produce sodium silicate, and characterizations of new materials obtained by FTIR, XRD, and SEM.

2.Materials and Experimental procedure

2.1 Materials

All reagents used are of commercial grade except sodium hydroxide is an analytical grade product. Deionized water was used to make all solutions

2.2 Experimental procedure

The experimental part is divided into two main sections:

The first section concerned with the preparation and characterization of five samples of rice husk ash (RHA) $RHA_1$and RHA_2 were prepared by burning of RH for

2 hrs in muffle furnace at 850°C, 650°C, respectively, after treatment with hydrochloric acid 10% for 1 hr in reflux at 100°C. RHA_3 and RHA_4 were prepared by burning of RH for 2 hrs of in muffle furnace at 850°C,650°C ,respectively, after washing with distilled water . (RHA_5) was prepared by burning of RH for 2 hrs in muffle furnace at 650°C .

The second section concerned with the preparation of sodium silicate. RHA samples were reacted with sodium hydroxide with a molar ratio SiO_2/ NaOH of 1:2 in reflux at 100°C for 1 hr or until no silica residue to select optimal condition. The solution of sodium silicate are designated as SSi_2, SSi_4 and $SSsi_5$ according to the type of RHA of RHA_2, RHA_4' and RHA_5, respectively .

The RHA and sodium silicate were characterized by X Ray Diffraction (XRD) Cu-Kαpw 3050/60-2006, Fourier Transform Infra Red (FTIR) (Jasco FT/ IR 460 plus, and Scanning Electron Microscope (SEM) JOEL JEM-100S.

3 .Results and discussion

3.1 The first section:

The data listed in table (1) describe the chemical properties of five samples of rice husk ash and comparison with a previous literature[31]. It can be evidenced that the ash produced from the rice husk burning contains a great amount of silica and small amounts of other elements considered as impurities. The most common trace elements in RHA are sodium, potassium, calcium, magnesium, iron, titanium , manganese and chloride[29]. Differences in composition may occur due to geographical factors, type of ground, year of harvest, sample preparation and analysis method , In RHA_1 the sample was burnt at 850 °C after treatment with acid (no metal oxide residue and the content of silica reach to 99.2 %) . In RHA_2 the sample was burnt at 650 °C after treatment with acid (no metal oxides residue and the content of silica reach to 98.5 %) and residue may be unconvertible metal oxide. In RHA_3 the sample burnt was at 850 °C with no treatment with acid (only washed with distilled water) in which the content of silica reach to 90 % and metal oxide appear as show in table(1). In RHA_4 where the sample burnt at 650 °C with no treatment with acid but only washed with distilled water (the content of silica reach to 89 % and metal oxides less than 7 % due to partial dissolution of these oxides in distilled water). In RHA_5 the sample was burnt at 650 °C with no acid treatment and no water washing, (the content of silica reach to 87.5 % and metal oxide reach to 8 %) .

Figs. (1-2) describe the X-ray diffractogram of the $RHA_1$and RHA_2 which indicate that the amorphous silica peak appeared around 2θ equal to 22° as a result of calcinations of rice husk at 850 and 650°C, respectively, after treatment with HCl 10% may be due to formation of silicon tetrachloride by chlorination technique[3,5,30]. Figs. (3&4) describe the X-ray diffractogram of the $RHA_3$and RHA_4 which indicates the crystalline silica sharp peak appeared around 2θ equal to 22° resulted from calcination of rice husk at 850 and 650°C, respectively, after washing with distilled water Fig. (5) describes the X-ray diffractogram of the RHA_5 indicates the amorphous silica peak appeared around 2θ equal to 22°resulted from calcination of rice husk at 650°C, with no washing, the RHA_2 and RHA_5 are active towards the synthesis of sodium silicate [31,32]. Another observation is the effect of precalcination temperature on increasing the crystallinity of untreated rice husks with HCl. It was verified that no acid treatment process also affects the increase of the degree of crystallinity of the precalcined rice husks. [30]

Figs.6 (a-e) describe the FTIR of the five RHA samples, FTIR spectrum of RHA_1 (fig.6a) displayed characteristic bands for Si-O ,and Si-O-Si , at 1101 and 803cm^{-1},respectively,[33-34]. FTIR spectrum of RHA_2 (fig. 6b) displayed characteristic bands for Si-O and Si-O-Si at 1092 and 791cm^{-}1,respectively,[33-34] .FTIR spectrum of RHA_3 (fig. 6c) displayed characteristic bands for Si-O, and Si-O-Si at 1100 and 803 cm^{-1},respectively,[33-34]. FTIR spectrum of RHA_4 (fig.6d) displayed characteristic bands for Si-O and Si-O-Si at 1100 and 802 cm^{-1} ,respectively,[33-34]. FTIR spectrum of RHA_5 (fig.6e) displayed characteristic bands for Si-O and (Si-O-Si) at 1098, 800 cm^{-1},respectively, [33-34].

The morphology of silica extracted from RHA of RHA_1 and RHA_2 are shown in Figs.7 and 8, respectively. Different shapes of silica particles; globular and rectangular shapes, were found in the extract. Even though the grinding of the extract was carried out before SEM measurement, the silica depositing along the skeleton of rice husk (rectangular structure) was remaining in the extract. While the fine silica particles were appeared in the globular shapes , the black parts in RHA_1 is less than that of RHA_2 due to the brightness which increases with the increase in temperature of calcination [35,36].

3.2 The Second Section

The data listed in table (2) describe the chemical properties of three samples of sodium silicate; The solution of sodium silicate are designated as SSi_2, SSi_4 and $SSsi_5$ according to the type of RHA of RHA_2, RHA_4' and RHA_5, respectively; the practical ratio between sodium oxide and silica is about 1 : 2.2 and it is confirmed with the recommended procedure.

The morphology of sodium silicate prepared from rice husk ash without washing is shown in Fig. 9, with different shapes of silica particles; globular and rectangular shapes were found .The FTIR spectrum shown in fig.10 displayed the characteristic bands of sodium silicate for, silanol OH groups and adsorbed water, Si-O-Si and Al-O-Si at broad band (2923-3390) cm^{-1}, (994-1443) cm^{-1} and (464-877) cm^{-1}respectively [33-34,37] . NFTIR spectrum shown in fig.11 displayed characteristic bands of sodium silicate for, overtone OH – stretch Si-OH, overtone OH-stretching, (OH-stretching(2) crystal water ,H_2O combination), and H_2O bending at 7327 cm^{-1} (6971- 6611) cm^{-1},(5338-5204)cm^{-1} and 4451 cm^{-1} 'respectively,[35] . Fig .12 shows the x-ray diffraction pattern of sodium silicate powder obtained by grinding after drying at 105 °C for 2 hrs which indicates a sharp peak appeared around 2θ equal to 28° (d spacing 3.24 A°)

[37], And abroad band around 2θ equal to 12.5°(d spacing 9.43A°) due to low content of adsorbed water in sodium silicate powder [37].

3.3 Effect of neutralization time

The time –silica consumption was presented in Fig (13) and comparison depending on the type of silica and treatment procedure the three lowest cost samples namely (RHA_2 ,RHA_4 and RHA_5) were selected. The time of neutralization is longer in RHA_4) where as the type of silica is crystalline silica according the XRD analysis) than that in RHA_2 and RHA_5 where the type of silica is amorphous silica according the XRD analysis may be due to metal oxide in RHA_5 enhances neutralization while the pretreatment of RHA_2 with acid increases activity of silica (amorphous silica) RHA_4. More than 50% of silica is consumed within half hour in RHA_5 ; but less than 50 % of silica in RHA_4need more than half hour to consuming. At one hour of neutralization a small quantity of silica residue 5 % is found in RHA_5 but remaining residues is about 20% still in RHA_4. After storage no exchange in silicate prepared in RHA_2 RHA_5 but some silica return to suspend in solution of RHA_4.

4. CONCLUSIONS

Within limits of the present study the following conclusions can be established :

1) Rice husk ash was a low cost alternative source of active silica and highly pure silica (~ 99 %.wt)
2) The activated silica or sodium silicate is one of the four basic types of coagulants aids beside pH adjusters, clay and polymers which increase a stability of coagulant and can unite with the positively charged aluminum or with iron flocs, resulting in a larger, denser lamellar floc that settles faster and enhances enmeshment .
3) It is possible to obtain a high silica content by applying simple technique and it is possible to transform agroresidue or industrial residue to useful materials , avoiding damage to the environment.
4) The most suitable procedures for synthesis of sodium silicate (co-agulant aid) were to be :
    - the reaction of sodium hydroxide with amorphous activated silica derived from RHA without treatment at 650 °C.
    - the reaction of sodium hydroxide with crystalline activated silica previously washed with distilled water at 650 °C
    - the reaction of sodium hydroxide with amorphous activated silica previously treated with HCl 10% at 650°C.

Table (1): Chemical analysis of the five RHA samples prepared as compared with a reference

Parameter (%)	RHA_1	RHA_2	RHA_3	RHA_4	RHA_5	Reference [32]
SiO_2	99.2	98.5	90	89	87.5	62.5-97.6
Fe_2O_3	-	-	2.0	2.0	2.0	0.01-2.78
MnO	-	-	0.043	0.043	0.043	0.01-1.96
AL_2O_3	-	-	1.0	1.0	1.0	0.01-1.01
MgO	-	-	0.7	0.7	0.7	0.01-1.96
CaO	-	-	0.65	0.65	0.65	0.1-1.31
Na_2O	-	-	1.0	1.0	1.45	0.01-1.58
K_2O	-	-	1.55	1.55	2.1	0.1-2.54
P_2O_5	-	-	0.057	0.057	0.057	0.01-2.69
Residue	≈ 0.8	≈ 1.5	≈ 3.0	≈ 4.0	≈ 4.5	-

Table (2) : Chemical analysis of the three dry sodium silicate samples

Parameter (%)	Sodium silicate (SSi_2)	Sodium silicate (SSi_4)	Sodium silicate (SSi_5)
SiO_2	69.5	66	64.4
Na_2O	29.5	29	29
MnO	-	0.027	0.028
AL_2O_3	-	0.64	0.65
MgO	-	0.3	0.45
CaO	-	0.35	0.42
Fe_2O_3	-	1.15	1.3
Na_2O	-	0.89	0.94
K_2O	-	1.2	1.35
P_2O_5	-	0.034	0.036
Residue	≈ 1.0	≈ 0.4	≈ 1.0

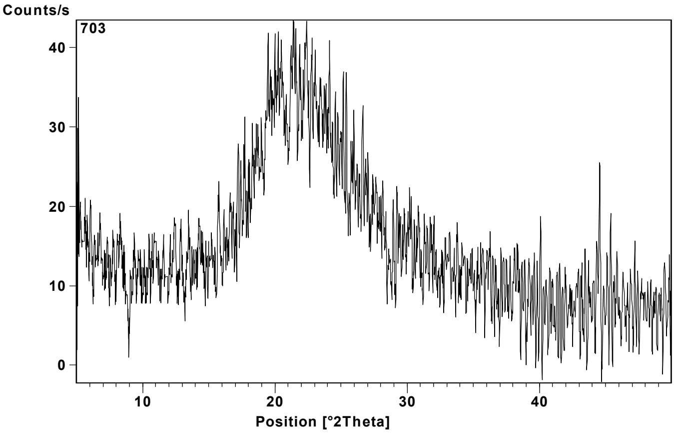


Fig.(1) : XRD pattern of RHA_1

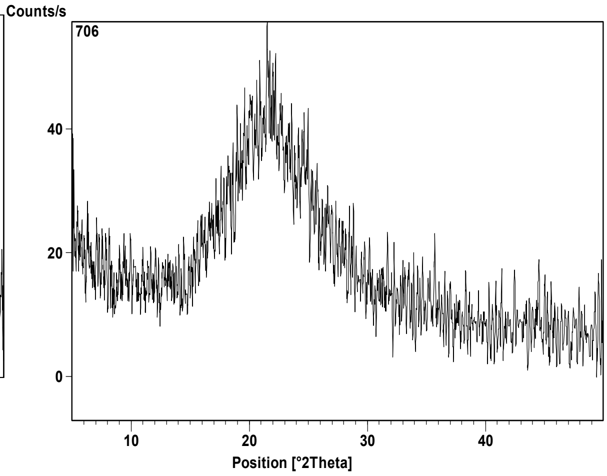


Fig.(2) : XRD pattern of RHA_2

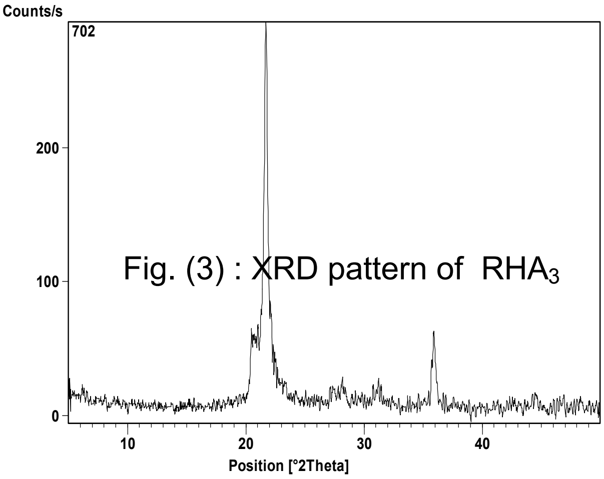


Fig. (3) : XRD pattern of RHA_3

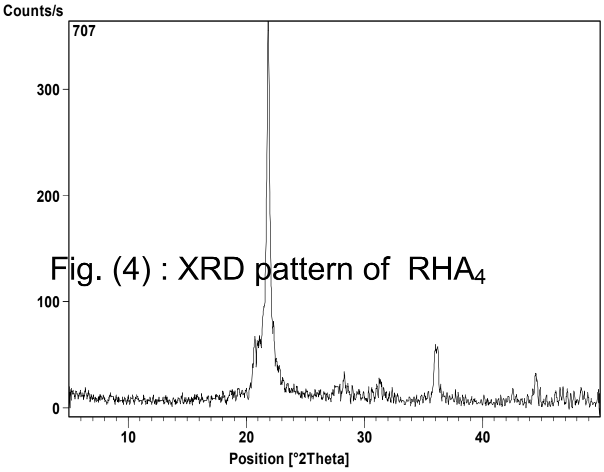


Fig. (4) : XRD pattern of RHA_4

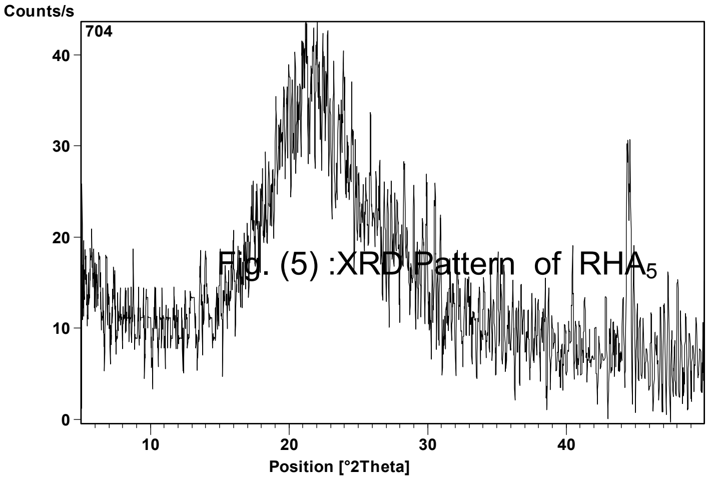
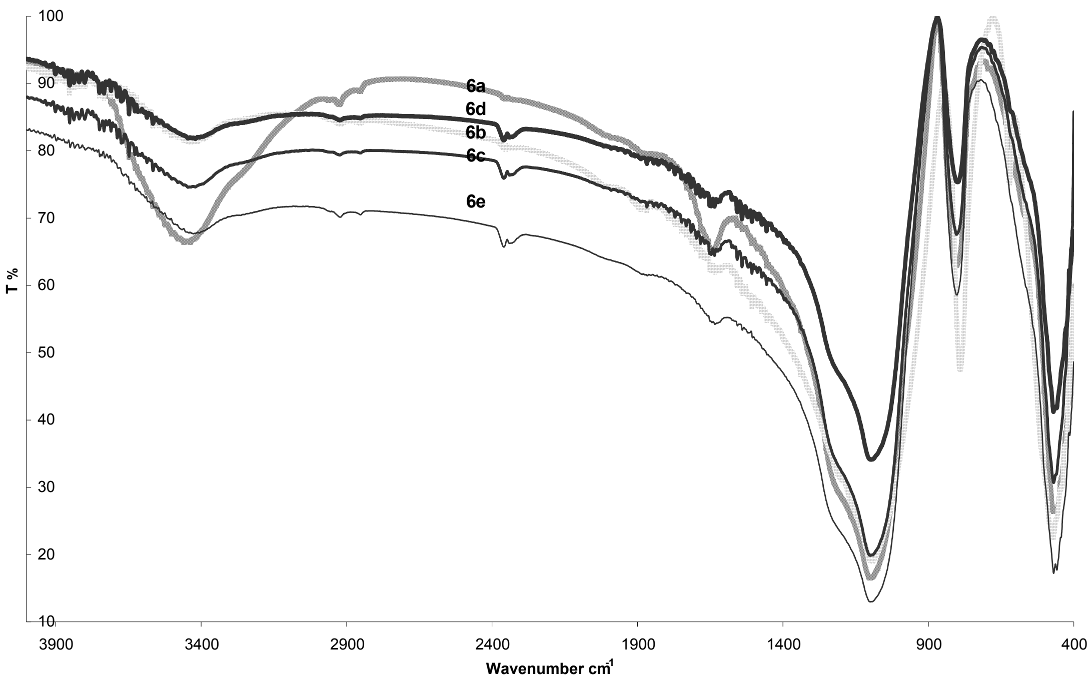


Fig. (5) :XRD Pattern of RHA_5



Figs. (6a-e) : FTIR spectrums of a-RHA_1,b- RHA_2,c- RHA_3, d-RHA_4 and e- RHA_5

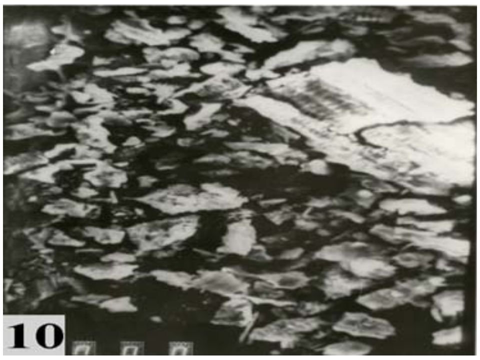


Fig (7) : SEM micrograph of RHA_2 (X 200)

Fig (8) : SEM micrograph of RHA_1 (X 200)

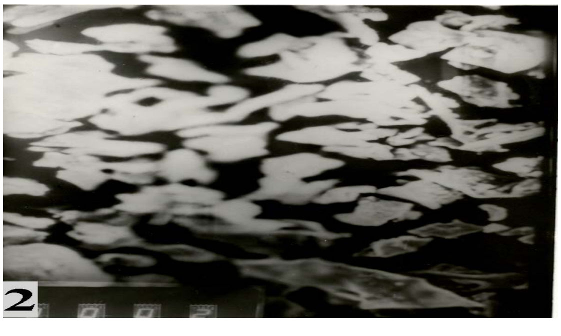


Fig (9) : SEM micrograph of SSi_5 (X 100)

Fig (10) : FTIR spectrum of SSi_5

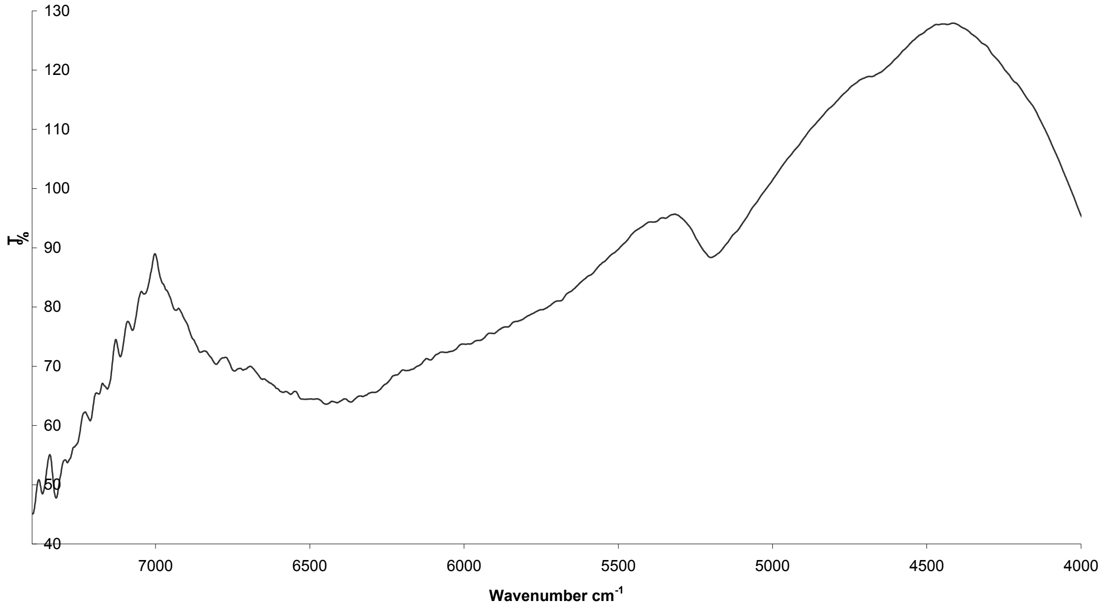


Fig (11) : NFTIR spectrum of SSi_5

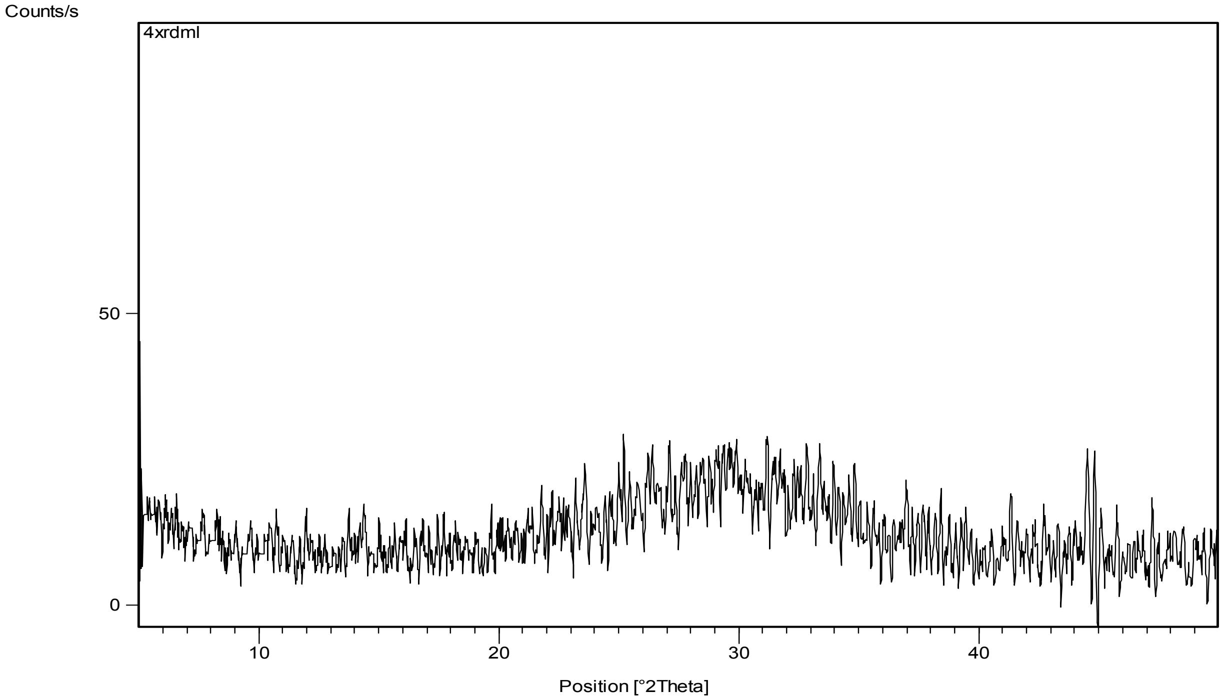


Fig (12) : XRD Pattern of Ssi$_5$

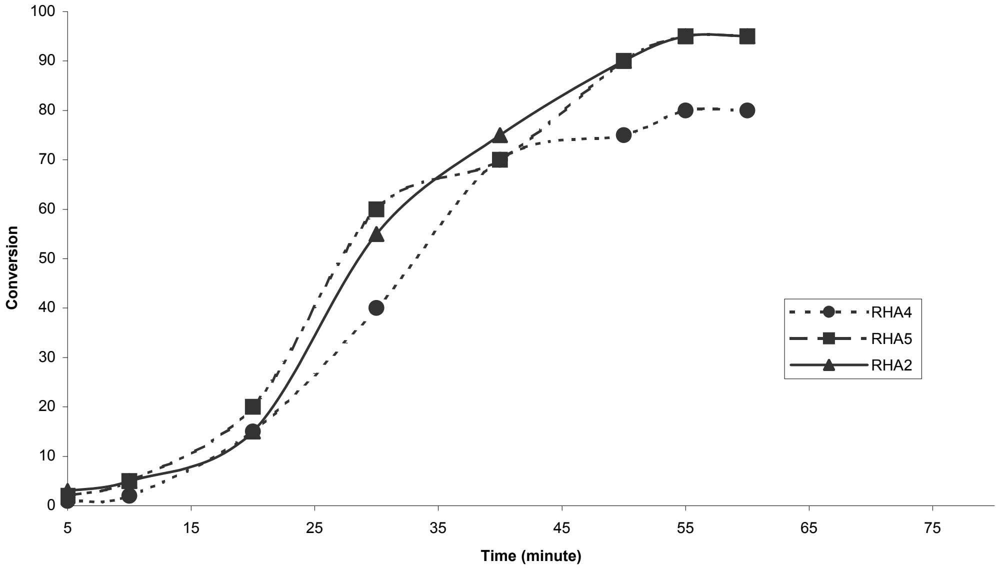


Fig (13) : RHA$_2$, RHA$_4$ and RHA$_5$ conversion (%) versus time of neutralization

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