



## Utilization of a low cost agro-residue for production of coagulant aids and their applications

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### ABSTRACT

Different samples of rice husk ash (RHA) and sodium silicate were prepared and characterized using FTIR, NPTIR and XRD. The selected sample of RHA was obtained by calcination of untreated rice husk (RH) in a semi-closed system at 650 °C. Four novel polyinorganic coagulants were also prepared, namely, poly aluminum chloride silicate, poly hydroxy aluminum sulphate silicate, poly ferric chloride silicate and poly ferric aluminum chloride silicate. Applications were carried out for the removal of some pollutants from ground, sewage and industrial waste waters. It was found that the maximum percentages removal of Fe<sup>2+</sup> and Mn<sup>2+</sup> ions in ground water reached 99 and 97%, respectively, the maximum percentage removal of, Pb<sup>2+</sup> ion in industrial waste water reached 97%. In addition, the maximum percentages removal of COD, BOD and TSS in sewage waste water reached 90, 92, and 93%, respectively.

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### 1. 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 tons of rice is produced each year, giving an average of 20% of the rice as husk, i.e. an annual total production of about 120 million tons per annum. In Egypt, the annual rice production is about 5,700,000 tons, which produces 1,000,000 tons of rice husk equivalent to 200,000 tons of rice husk ash. In the majority of rice producing countries, the husk produced from the processing of rice is either burnt or dumped as waste [1].

Rice husk is a by-product from rice mill that has been 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 [2].

There are several methods for the extraction of silica from biomass. Many authors [3–6] 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 acid solution for 1 h followed by burning in the atmosphere at 650–700 °C for 4 h [4]. By means of this method, the extracted silica was found in the form of amorphous structure which is the most reactive form for silylation reaction [4].

Sodium silicate, the precursor for silica production, is currently manufactured by smelting quartz sand with sodium carbonate at 1300 °C [7]. This conventional technology requires high energy costs, produce considerable air pollution, impurity of the product and need to maintenance of the oven due to attack of base. This could be avoided by processing rice husk silica, instead of sand, by ambient temperature methods. Rice husk ash is produced commercially by husk combustion and contains over 60% silica and is an economically viable raw material for the production of silicates, silica gel, zeolite and silica [8]. 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 [9].

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 1930s to strengthen flocs and reduce the potential of deterioration. When activated silica is added to water, it produces a stable solution that has a negative surface charge. The

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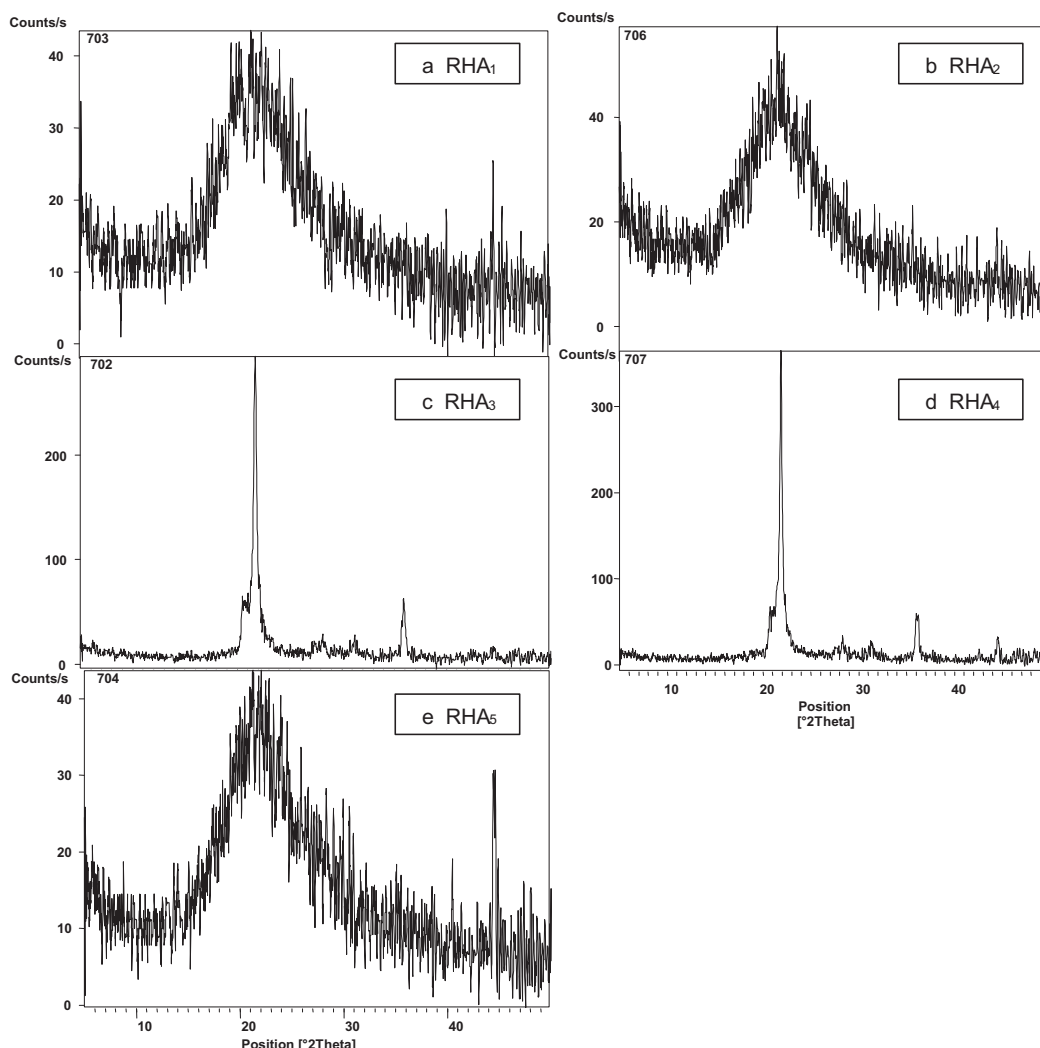


Fig. 1. (a–e) XRD patterns of RHA samples.

activated silica can unite with the positively charged aluminum or with iron flocs, resulting in a larger and denser floc that settles faster and enhances enmeshment.

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 for the dispersion of iron particles in distribution systems. Addition of silicate-based inhibitors has also been found to reduce iron corrosion rate. Finally, silicates are reported to decrease the oxidation rate of  $Fe^{2+}$  because ferrous iron diffusion through the silicate film is slower than through iron oxide scale [10].

This study deals with the preparation of polyinorganic coagulants from sodium silicate RHA based as well as the characterization of the materials obtained by FTIR and XRD in addition to their application as coagulant aids.

## 2. Materials and methods

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

Five samples of rice husk ash (RHA) were prepared: RHA<sub>1</sub> and RHA<sub>2</sub> were prepared by burning of rice husk (RH) for 2 h at 850° and 650 °C, respectively, after treatment with 10% hydrochloric acid for

1 h in a reflux at 100 °C; RHA<sub>3</sub> and RHA<sub>4</sub> were prepared by burning of RH for 2 h at 850° and 650 °C, respectively, and then washed with distilled water and; RHA<sub>5</sub> was prepared by burning of RH for 2 h at 650 °C without further treatment.

The same protocol was used for the preparation of the three solution of sodium silicate:  $SiO_2/NaOH = 1/2$ ,  $T = 100\text{ °C}$  and  $t = 1\text{ h}$ . The solutions of sodium silicate are designated as SSi<sub>2</sub>, SSi<sub>4</sub> and SSi<sub>5</sub> according to the type of RHA which are RHA<sub>2</sub>, RHA<sub>4</sub> and RHA<sub>5</sub>, respectively.

RHA samples and dry sodium silicate were characterized by elemental analysis using ionic chromatography, (DIONEX 500), X-Ray Diffraction (Cu-K $\alpha$ pw 3050/60–2006), and Fourier Transform Infra Red (FTIR) and Near Fourier Transform Infra Red (NFTIR) Jasco FT/IR 460 plus spectrometer in the 400–4000  $cm^{-1}$  of FTIR and 4000–7500  $cm^{-1}$  of NFTIR wave number range.

Sodium silicate (SSi<sub>5</sub>) was chosen as a precursor for the preparation of poly silicic acid solution (PSi), by dilution of sodium silicate containing 15%  $SiO_2$  with distilled water to a concentration of 0.25 M  $SiO_2$ . The diluted solution was reacted with 0.25 M HCl with magnetic stirring; the pH of the final solution reached about 2 and  $SiO_2$  concentration of 0.125 M. Four new poly inorganic coagulants were also prepared; these are: poly aluminum chloride silicate (PACSi), poly hydroxy aluminum sulphate silicate (PAHSSi), poly ferric chloride silicate (PFeClSi) and poly ferric aluminum chloride

silicate (PAIFeClSi). The preparation was done by the slight neutralization of inorganic coagulants (0.25 M  $\text{AlCl}_3$ , 0.125 M  $\text{Al}_2(\text{SO}_4)_3$ , 0.25 M  $\text{FeCl}_3$ , with 0.25 M sodium carbonate at 60 °C with rapid mixing to obtain ( $\gamma=2$ ,  $B=67\%$  and  $r_1=0.1$ ), ( $\gamma=1.5$ ,  $B=50\%$  and  $r_1=0.1$ ), ( $\gamma=2$ ,  $B=67\%$  and  $r_2=0.2$ ) and ( $\gamma=2$ ,  $B=67\%$ ,  $r_1=0.1$  and  $r_2=0.2$ ), respectively; where  $\gamma$  is the molar ratio of  $[\text{OH}]/[\text{Al}]$ ,  $B$  represents the basicity,  $r_1$  is the molar ratio of aluminum to silicon and  $r_2$  is the molar ratio of iron to silicon.

The samples of new poly inorganic coagulants were used to remove some pollutants from ground water such as iron, manganese, arsenic, lead, fluoride and nitrate ions in addition to turbidity and colour using representative samples obtained from a certain well. They were also applied for the removal of lead from industrial waste water. The third application is concerned with the removal of BOD, COD and TSS from sewage waste water to obtain the water quality for re-use in agricultural drip irrigation systems, where, the treatment depends on precipitation, coagulation and adsorption techniques by poly inorganic coagulants (PIC). Each sample was mixed with 5–10 ppm of PIC and agitated for 1 min rapid mixing (300 rpm), followed by slow mixing for five minutes and (30 rpm) and 20 min standing time. The concentrations of pollutants were measured in ore samples and in the filtrate using AAS and ASTM methods [11].

### 3. Results and discussion

#### 3.1. Characterization of rice husk ash samples

The data listed in Table 1 represent the results of the chemical analysis of the prepared five samples of rice husk ash (RHA) together with data obtained previously [12]. Table 1 shows that the ash produced from burning of rice husk contains a great amount of silica and small amounts of other elements which are considered as impurities. The most common trace elements in RHA are sodium, potassium, calcium, magnesium, iron, titanium and manganese [12]. Differences in composition may occur due to geographical factors, type of ground, and time of harvest and sample preparation. For RHA<sub>1</sub> sample burnt at 850 °C after treatment with acid, the content of silica reached 99.2%, as for RHA<sub>2</sub> sample, burnt at 650 °C after treatment with acid, the content of silica reached 98.5%. In RHA<sub>3</sub> samples, burnt at 850 °C and washed only with distilled water, the content of silica reached 90% and metal oxides were detected, Table 1. In RHA<sub>4</sub> samples, burnt at 650 °C and washed only with distilled water, the content of silica reached 89% and the content of metal oxides were less than 7% due to the partial dissolution of these oxides in distilled water. In RHA<sub>5</sub> sample, burnt at 650 °C without any treatment, the content of silica reached 87.5% and the metal oxide content reached 8%.

Fig. 1a and b show the X-ray diffractograms of the RHA<sub>1</sub> and RHA<sub>2</sub>, it indicate that the amorphous silica peak appeared around  $2\theta$  of 22° as a result of calcination of rice husk at 850 and 650 °C, respectively, after treatment with 10% HCl. This may be due to the formation of silicon tetrachloride by chlorination technique. Fig. 1c and d describe the X-ray diffractograms of the RHA<sub>3</sub> and RHA<sub>4</sub>, it show a sharp peak around  $2\theta$  of 22° for crystalline silica which resulted from calcination of rice husk at 850 and 650 °C, respectively. Fig. 1e shows the X-ray diffractogram of the RHA<sub>5</sub> which indicate a broad band  $2\theta$  around 22° due to amorphous silica resulted from calcination of rice husk at 650 °C. RHA<sub>2</sub> and RHA<sub>5</sub> silicates are active towards the synthesis of sodium silicate. The results obtained indicate that increase of the precalcination temperature increases the crystallinity of untreated rice husks. Also acid treatment decreases the degree of crystallinity of the precalcined rice husks [12].

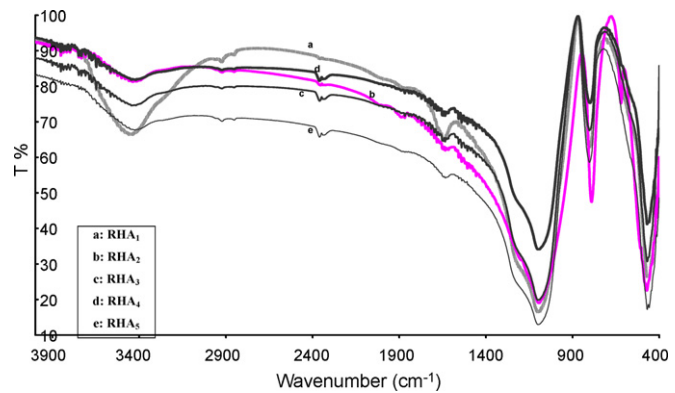


Fig. 2. FTIR spectra of RHA samples.

Fig. 2a–e and Table 2 show the results of FTIR spectra together with data obtained previously [13,14] for the five RHA samples under investigation.

#### 3.2. Characterization of sodium silicate $\text{SSi}_5$

The data listed in Table 3 describe the results of the chemical analysis of the three sodium silicate samples. The solutions of sodium silicate are designated as  $\text{SSi}_2$ ,  $\text{SSi}_4$  and  $\text{SSi}_5$  for RHA<sub>2</sub>, RHA<sub>4</sub> and RHA<sub>5</sub>, respectively; the ratio of sodium oxide to silica was of the order of 1:2.2 as confirmed with the recommended procedure.

The FTIR spectrum shown in Fig. 3 displayed the characteristic broad bands of sodium silicate for, silanol OH groups and adsorbed water, Si–O–Si and Al–O–Si located at 2923–3390, 994–1443 and 464–877  $\text{cm}^{-1}$ , respectively [13–15]. NFTIR spectrum shown in Fig. 4 displays the characteristic bands of sodium silicate for, overtone OH– stretch Si–OH, overtone OH– stretching, (OH– stretching(2) crystal water,  $\text{H}_2\text{O}$  combination), and  $\text{H}_2\text{O}$  bending located at 7327, 6971–6611, 5338–5204 and 4451  $\text{cm}^{-1}$ , respectively [14]. Fig. 5 shows the X-ray diffraction pattern of sodium silicate ( $\text{SSi}_5$ ) powder, obtained by grinding after drying at 105 °C for 2 h, which indicates a broad band appeared around  $2\theta$  equal to 28.

#### 3.3. Determination of equilibrium time

Determination of equilibrium time of silica consumption is shown in Fig. 6 which shows that the three lowest cost RHA samples (RHA<sub>2</sub>, RHA<sub>4</sub> and RHA<sub>5</sub>). Evidently the relatively high degree of crystallinity of RHA<sub>4</sub> leads to low conversion values of RHA<sub>4</sub> to sodium silicate as compared to the amorphous character of RHA<sub>2</sub> and RHA<sub>5</sub>, which lead to relatively high conversion values at the

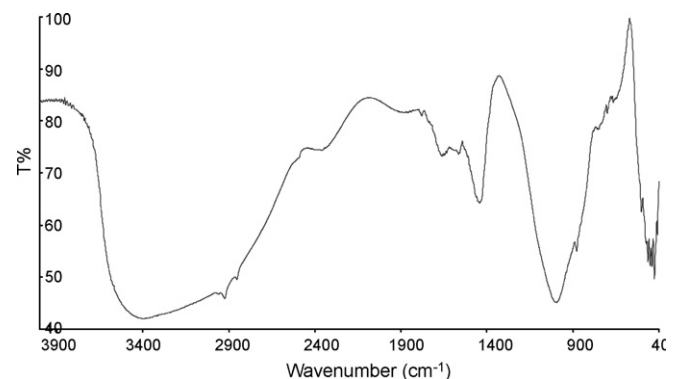


Fig. 3. FTIR spectrum of  $\text{SSi}_5$ .

**Table 1**  
Chemical composition of the five RHA samples prepared as compared with a reference.

| Parameter (%)                  | RHA <sub>1</sub> | RHA <sub>2</sub> | RHA <sub>3</sub> | RHA <sub>4</sub> | RHA <sub>5</sub> | Reference [10] |
|--------------------------------|------------------|------------------|------------------|------------------|------------------|----------------|
| SiO <sub>2</sub>               | 99.2             | 98.5             | 90               | 89               | 87.5             | 62.5–97.6      |
| Fe <sub>2</sub> O <sub>3</sub> | –                | –                | 2.0              | 2.0              | 2.0              | 0.01–2.78      |
| MnO                            | –                | –                | 0.043            | 0.043            | 0.043            | 0.01–1.96      |
| Al <sub>2</sub> O <sub>3</sub> | –                | –                | 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 <sub>2</sub> O              | –                | –                | 1.0              | 1.0              | 1.45             | 0.01–1.58      |
| K <sub>2</sub> O               | –                | –                | 1.55             | 1.55             | 2.1              | 0.1–2.54       |
| P <sub>2</sub> O <sub>5</sub>  | –                | –                | 0.057            | 0.057            | 0.057            | 0.01–2.69      |
| Residue                        | ≈0.8             | ≈1.5             | ≈3.0             | ≈4.0             | ≈4.5             | –              |

**Table 2**  
Band components analysis of FTIR (cm<sup>-1</sup>) of rice husk ashes.

| RHA <sub>1</sub> | RHA <sub>2</sub> | RHA <sub>3</sub> | RHA <sub>4</sub> | RHA <sub>5</sub> | Assignment        |
|------------------|------------------|------------------|------------------|------------------|-------------------|
| 3458             | 3436             | 3445             | 3425             | 3420             | OH– stretching    |
| 1101             | 1092             | 1100             | 1100             | 1098             | Asymmetrical Si–O |
| 803              | 791              | 803              | 802              | 800              | Si–OH overlapping |
| 472              | 471              | 469              | 469              | 470              | Si–O–Si           |

**Table 3**  
Chemical composition of the three dry sodium silicate samples.

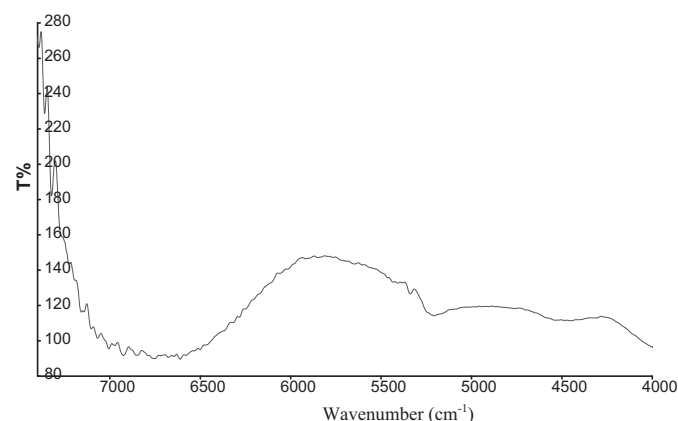
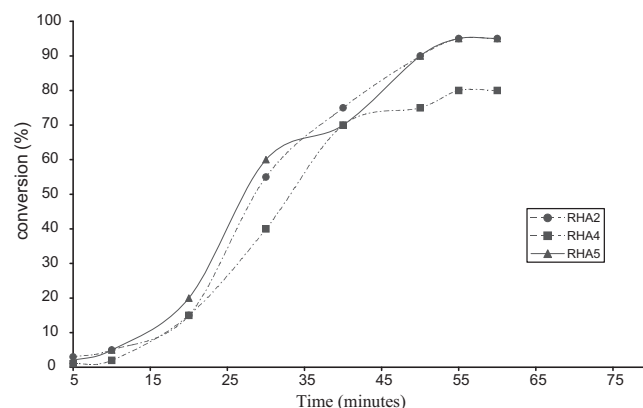
| Parameter (%)                  | Sodium silicate (SSi <sub>2</sub> ) | Sodium silicate (SSi <sub>4</sub> ) | Sodium silicate (SSi <sub>5</sub> ) |
|--------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| SiO <sub>2</sub>               | 69.5                                | 66                                  | 64.4                                |
| Na <sub>2</sub> O              | 29.5                                | 29.89                               | 29.94                               |
| MnO                            | –                                   | 0.027                               | 0.028                               |
| Al <sub>2</sub> O <sub>3</sub> | –                                   | 0.64                                | 0.65                                |
| MgO                            | –                                   | 0.3                                 | 0.45                                |
| CaO                            | –                                   | 0.35                                | 0.42                                |
| Fe <sub>2</sub> O <sub>3</sub> | –                                   | 1.15                                | 1.3                                 |
| K <sub>2</sub> O               | –                                   | 1.2                                 | 1.35                                |
| P <sub>2</sub> O <sub>5</sub>  | –                                   | 0.034                               | 0.036                               |
| Residue                        | ≈1.0                                | ≈0.4                                | ≈1.0                                |

same equilibrium time. At one hour a small quantity of silica residue (5%) is found in RHA<sub>5</sub> but the remaining residue is about 20% in RHA<sub>4</sub>. After storage, no precipitation of silica was found in the silicate solutions prepared from RHA<sub>2</sub> and RHA<sub>5</sub> but some silica appeared in the solution of RHA<sub>4</sub>.

### 3.4. Application

The data listed in Table 4 represent the variations of physico-chemical properties of ground water before and after treatment using four samples of poly inorganic coagulants based on silica. It was found that, the maximum removals of iron is 97% using PACSi, manganese is 25% using PACSi, colour is 70% using PAHSSi and tur-

bidity is 74% using PAIFeClSi. The data listed in Table 5 represent the variations of physicochemical properties of alkaline ground water as affected by inorganic polymers. It was found that, the maximum removals of iron, manganese and fluoride reached 99%, 97%, 99% in case of PAIFeClSi, respectively. The objective of such experiments of ground water to study the influence of alkaline media in iron and manganese removals while pH still within range, finally the residual carbonate appear in final solution, and electrical conductivity is above permissible limits due to solubility of some materials during treatment without influence in quality of water. The data obtained for the polluted alkaline ground water samples by the four coagulants are show in Table 6. It was found that the maximum removals of colour, turbidity, Iron, manganese, arsenic, lead, reached 67%,

**Fig. 4.** NFTIR spectrum of SSi<sub>5</sub>.**Fig. 5.** XRD Pattern of SSi<sub>5</sub>.

**Table 4**  
Variations of physicochemical parameters of ground water samples by influence of poly inorganic co-agulants based on silica.

| Coagulants parameters                | Before treatment | After treatment |        |         |           | Permissible limits |
|--------------------------------------|------------------|-----------------|--------|---------|-----------|--------------------|
|                                      |                  | PACSi           | PAHSSi | PFeClSi | PAIFeClSi |                    |
| Colour (pt-co)                       | 35               | 12              | 11     | 28      | 12        | <20                |
| TDS (mg/l)                           | 552              | 625             | 566    | 662     | 638       | <1200              |
| Turbidity (NTU)                      | 8.9              | 2.5             | 2.3    | 2.5     | 2.3       | <5                 |
| EC ( $\mu\Omega/cm$ )                | 861              | 1005            | 904    | 1066    | 1028      | <1200              |
| pH                                   | 7.40             | 7.59            | 7.13   | 7.11    | 7.39      | 6.5–9.2            |
| Cl <sup>-</sup> (mg/l)               | 62               | 117             | 60     | 157     | 120       | <500               |
| SO <sub>4</sub> <sup>2-</sup> (mg/l) | 59               | 65              | 149    | 70      | 70        | <400               |
| Na <sup>+</sup> (mg/l)               | 36               | 70              | 51     | 80      | 72        | <200               |
| K <sup>+</sup> (mg/l)                | 4                | 4.0             | 4.0    | 4.0     | 4         | <10                |
| Ca <sup>2+</sup> (mg/l)              | 90               | 82              | 82     | 81      | 42        | <200               |
| Mg <sup>2+</sup> (mg/l)              | 31               | 30.0            | 30.0   | 29.4    | 30        | <150               |
| Fe <sup>2+</sup> (mg/l)              | 1.946            | 0.059           | 0.185  | 0.701   | 0.284     | <1.0               |
| Mn <sup>2+</sup> (mg/l)              | 2.1              | 1.64            | 1.67   | 1.95    | 1.95      | <0.5               |
| Al <sup>3+</sup> (mg/l)              | 0.114            | 0.137           | 0.158  | 0.114   | 0.182     | <0.2               |

**Table 5**  
Variations of physicochemical parameters of alkaline ground water samples by influence of poly inorganic coagulants based on silica.

| Coagulant parameters                 | Before treatment | After treatment |        |         |           | Permissible limits |
|--------------------------------------|------------------|-----------------|--------|---------|-----------|--------------------|
|                                      |                  | PACSi           | PAHSSi | PFeClSi | PAIFeClSi |                    |
| Colour (pt-co)                       | 13               | 5               | 5      | 6       | 6         | <20                |
| TDS (mg/l)                           | 507              | 716             | 779    | 797     | 726       | <1200              |
| Turbidity (NTU)                      | 2.1              | 1.3             | 1.3    | 1.4     | 2.0       | <5                 |
| EC ( $\mu\Omega/cm$ )                | 788              | 1118            | 1206   | 1247    | 1133      | <1200              |
| pH                                   | 7.37             | 8.26            | 8.08   | 8.19    | 8.26      | 6.5–9.2            |
| Cl <sup>-</sup> (mg/l)               | 47               | 110             | 48     | 151     | 107       | <500               |
| SO <sub>4</sub> <sup>2-</sup> (mg/l) | 48               | 60              | 151    | 63      | 64        | <400               |
| CO <sub>3</sub> <sup>2-</sup> (mg/l) | 0                | 30              | 20     | 35      | 45        | –                  |
| Na <sup>+</sup> (mg/l)               | 33.0             | 176             | 144    | 187     | 185       | <200               |
| K <sup>+</sup> (mg/l)                | 4.0              | 3.0             | 3.0    | 4.0     | 3.0       | <10                |
| Ca <sup>2+</sup> (mg/l)              | 86.0             | 38              | 78     | 52      | 26.0      | <200               |
| Mg <sup>2+</sup> (mg/l)              | 32.6             | 30.0            | 32.6   | 31.2    | 34.8      | <150               |
| Fe <sup>2+</sup> (mg/l)              | 2.5              | 0.1             | 0.05   | 0.09    | 0.008     | <1.0               |
| Mn <sup>2+</sup> (mg/l)              | 1.5              | 0.083           | 0.608  | 0.163   | 0.044     | <0.5               |
| Al <sup>3+</sup> (mg/l)              | 0.1              | 0.116           | 0.130  | 0.025   | 0.142     | <0.2               |
| F <sup>-</sup> (mg/l)                | 1.0              | 0.87            | 0.93   | 0.13    | 0.01      | <0.8               |

**Table 6**  
Variations of physicochemical parameters of alkaline ground water samples polluted with arsenic, and lead by influence of poly inorganic co-agulants based on silica.

| Coagulant parameters                 | Before treatment | After treatment |        |         |           | Permissible limits |
|--------------------------------------|------------------|-----------------|--------|---------|-----------|--------------------|
|                                      |                  | PACSi           | PAHSSi | PFeClSi | PAIFeClSi |                    |
| Colour (pt-co)                       | 13               | 8               | 7      | 5       | 6         | <20                |
| TDS (mg/l)                           | 559              | 780             | 705    | 822     | 682       | <1200              |
| Turbidity (NTU)                      | 8.7              | 1.9             | 1.8    | 1.2     | 1.4       | <5                 |
| EC ( $\mu\Omega/cm$ )                | 887              | 1204            | 1130   | 1278    | 1089      | <1200              |
| pH                                   | 7.45             | 8.33            | 7.58   | 7.67    | 8.07      | 6.5–9.2            |
| Cl <sup>-</sup> (mg/l)               | 65               | 118             | 67     | 145     | 115       | <500               |
| SO <sub>4</sub> <sup>2-</sup> (mg/l) | 84               | 124             | 168    | 120     | 92        | <400               |
| CO <sub>3</sub> <sup>2-</sup> (mg/l) | 0                | 45              | 0      | 10      | 10        | –                  |
| Na <sup>+</sup> (mg/l)               | 48               | 128             | 113    | 148     | 135       | <200               |
| K <sup>+</sup> (mg/l)                | 4.0              | 3.0             | 3.0    | 3.0     | 3         | <10                |
| Ca <sup>2+</sup> (mg/l)              | 86               | 80              | 80     | 80      | 54        | <200               |
| Mg <sup>2+</sup> (mg/l)              | 28.1             | 28.8            | 28.8   | 30.0    | 27.6      | <150               |
| Fe <sup>2+</sup> (mg/l)              | 2.1              | 0.063           | 0.044  | 0.049   | 0.097     | <1.0               |
| Mn <sup>2+</sup> (mg/l)              | 1.243            | 0.890           | 1.190  | 1.245   | 0.532     | <0.5               |
| Al <sup>3+</sup> (mg/l)              | 0.113            | 0.207           | 0.256  | 0.057   | 0.076     | <0.2               |
| Pb <sup>2+</sup> (mg/l)              | 13.559           | 1.613           | 1.860  | 0.319   | 1.533     | <0.05              |
| As <sup>2+</sup> (mg/l)              | 1.221            | 0.257           | 0.128  | 0.096   | 0.032     | 0.05               |

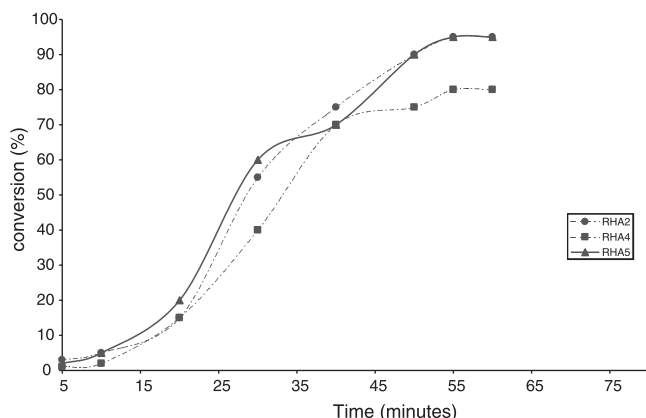
**Table 7**  
Effect of poly inorganic polymers based on silica of sewage waste water.

| Coagulant parameters | Before treatment | After treatment |        |         |           | Permissible limits |
|----------------------|------------------|-----------------|--------|---------|-----------|--------------------|
|                      |                  | PACSi           | PAHSSi | PFeClSi | PAIFeClSi |                    |
| TDS (mg/l)           | 1500             | 1683            | 1700   | 1870    | 1599      | <2000              |
| TSS (mg/l)           | 550              | 40              | 47     | 40      | 39        | <50                |
| pH                   | 7.4              | 7.35            | 7.35   | 7.6     | 7.77      | 6.0–9.0            |
| COD (mg/l)           | 300              | 44.5            | 55.0   | 58.2    | 30.8      | <80                |
| BOD (mg/l)           | 200              | 25.1            | 40.0   | 35      | 16.5      | <50                |

**Table 8**

Effect of poly inorganic polymers based on silica on industrial waste water.

| Coagulant parameters    | Before treatment | After treatment |        |         |           | Permissible limits |
|-------------------------|------------------|-----------------|--------|---------|-----------|--------------------|
|                         |                  | PACSi           | PAHSSi | PFeClSi | PAIFeClSi |                    |
| pH                      | 3.5              | 8.97            | 8.68   | 7.05    | 8.65      | 6.0–9.0            |
| Pb <sup>2+</sup> (mg/l) | 50.0             | 0.078           | 1.438  | 0.01    | 1.411     | <0.05              |

**Fig. 6.** RHA<sub>2</sub>, RHA<sub>4</sub> and RHA<sub>5</sub> conversion (%) versus equilibrium time.

86%, 99%, 57%, 97% and 98%, in case of PAIFeClSi, respectively. In all cases the residual aluminum was less than the permissible limits (0.2 mg/l). Many researchers used adsorbent materials for removal of some pollutants [16–20]. Concentration of sulphate and chloride ions increased by using poly inorganic coagulants, whereas the concentration of sodium increased due to the use of sodium carbonate to raise pH value. Table 6 also shows that the total dissolved solids and the electrical conductivity increased due to the spiking of new materials in solution, whereas no considerable variation was observed in the concentration of calcium, magnesium and potassium. Table 7 deals with the treatment of sewage waste water by poly inorganic polymers impregnated with silica which showed that, the maximum removal of BOD, COD and TSS reached 92%, 90% and 93% with PAIFeClSi; respectively. As for the total dissolved solids it increased due to the formation new spiked ions. No variations of pH occurred and all the values after treatment are within permissible limits according to Egyptian law 44/2000. From Table 8 the treatment of wastewater by poly inorganic polymers showed that, the removals of lead reached 97% for all samples of poly inorganic coagulants impregnated with silica, the industrial wastewater type is lead acid battery factory and the waste water was taken from paste manufacture section and no interfering materials because of the paste of lead acid battery consist of mainly lead oxide ion and the water must be soft water.

Finally, the comparison between the conventional coagulant and novel coagulants was carried out in my thesis and the dose was reduced to 0.2 of conventional coagulants dose and the efficiency of novel coagulants are more than three folders of conventional coagulants [21].

#### 4. Conclusions

Within the limits of the present study, the following conclusions are derived.

Rice husk ash represents a low cost alternative source of active silica with highly pure silica content (~99% wt). The activated silica or sodium silicate is one of the four basic types of coagulants aids beside pH adjusters, clay and polymers which increase the stability of coagulant and can unite with the positively charged aluminum

or with iron flocs, resulting in a larger and denser lamellar floc that settles faster and enhances enmeshment. It is possible to obtain high silica content by applying a simple technique to transform agro-residue or industrial residue to useful materials, thus avoiding damage to the environment.

The most suitable procedures for synthesis of sodium silicate (co-agulants aid) are found to be: (i) The reaction of sodium hydroxide with amorphous activated silica derived from RHA at 650 °C without treatment, (ii) the reaction of sodium hydroxide with crystalline activated silica previously washed with distilled water at 650 °C, (iii) the reaction of sodium hydroxide with amorphous activated silica previously treated with HCl 10% at 650 °C. The copolymer of iron and aluminum impregnated with silica is the most favorable coagulant in treatment of all types of waste, drinking, industrial and sewage waters. It was found that the maximum percentages removal of Fe<sup>2+</sup> and Mn<sup>2+</sup> ions in ground water reached 99% and 97%, respectively, using PAIFeClSi the maximum percentage removal of Pb<sup>2+</sup> ion in industrial waste water reached 97% using PFeClSi. In addition, the maximum percentages removal of COD, BOD and TSS in sewage waste water reached 90%, 92%, and 93%, respectively, using PAIFeClSi.

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