

Extraction of highly pure silica from local rice straw and activation of the left carbon for chromium (VI) adsorption

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ABSTRACT

The main objectives of the present work is develop an efficient procedure for treating the rice straw (RS) to separate silica and activating the carbon left behind for Cr(VI) adsorption from its aqueous solutions. This has been possible by first digesting the RS with NaOH solution to dissolve the silica content followed by an acidification step to obtain silica gel which was dried at 110 C° and calcined at 750 C°. The determined optimum factors thereof have resulted in 85.5% silica leaching efficiency and a product purity of 99.8%. The separated silica has been specified through relevant chemical as well as via XRD and FTIR analyses. The residue left behind after silica extraction was then heat-treated for its activation before being applied for Cr (VI) adsorption. The relevant adsorption factors have included the effects of pH and the time as well as the effect of the initial Cr (VI) concentration. Using the optimum values of the latter, the prepared activated carbon was applied for chromium management from a titania waste solution assaying 650 ppm Cr species and it was possible to realize an adsorption efficiency exceeding 98%.

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KEYWORDS

Rice straw;
Activated carbon;
Chromium;
Silica;
Titania waste.

INTRODUCTION

Rice is a staple food of over half the world's population and is the 2nd largest cereal crop but produces large amount of crop residues^[1]. The world's annual rice residue output (straw and rice hull) is estimated to be around 600 million tons while in Egypt it is around 6 million tons. In the rice producing countries, much of its residues are either burnt, a matter which causes severe air pollution in addition to the loss of valuable resources^[2]. Therefore, it is quite urgent to undertake proper researches on utilize the rice residues. The rice residue is mainly composed of cellulose, hemi-cellulose, lignin and silica and can thus be considered as an

important silicon source. The silica in the rice straw, rice husk and rice husk ash attains around 10, 20 and 55% respectively and would vary with the variety, climate and location of the rice growth^[3]. Silica is used in several industries including electronics, ceramic and polymers, etc^[4]. Many studies have thus been applied for silica leaching from the rice residues including controlled combustion in air or oxygen flow at 600-650 C°^[5-6] as well as alkali digestion using NaOH^[7] or Na₂CO₃^[8].

On the other hand, activated carbon is used in medicinal purposes, capacitors, pollutant removal and catalysis. Metallurgically, active carbon can indeed be produced from agricultural by-products^[9-10]. Therefore, many studies have thus been achieved for preparation

of activated carbon from biomass^[11-14]. As a matter of fact, there are two basic processes employed to manufacture activated carbon and are referred as chemical activation^[15-20] and physical activation^[21-22]. Chemical activation depends on the action of inorganic chemicals on the raw material to dehydrate the organic constituents during carbonization while the physical is achieved by oxidizing the carbonaceous matter with air at low temperatures or steam application or else by using CO₂ at high temperatures (800-1200 C°). The basic difference between the two procedures is that while the chemical occurs in one step, the physical employs two steps (carbonization and activation). On the other hand, the temperatures used in physical activation range from 800 to 1200 C° while in chemical, the temperature range from 350 to 800 C°^[15, 23-24].

Choice of Cr (VI) in this work to study its removal is based on the fact that its compounds are extensively used in several industries; a matter which produces hazardous effluents^[25]. Chromium (VI) is highly toxic and carcinogenic and hence its removal represents a necessary environmental challenge. In general, chromium conc., in industrial wastes ranges from 0.5 to 270 mg/l increases to 20-170 g/l in plating wastes^[26] while its tolerance limit into potable water is only 0.05 mg/l^[27]. In order to comply with this limit, it is essential to treat Cr (VI) effluents to reduce its conc., to the acceptable levels. The commonly used procedures for this aim include chemical precipitation, ion exchange, reverse osmosis and solvent extraction^[28-30]. However, apart from being economically expensive, these techniques are disadvantageous where it suffers from incomplete metal removal in addition to generation of toxic sludges. Efficient and environment friendly methods are thus greatly needed and in this context activated carbon is broadly applied as adsorbent where it is considered as a simple, relatively low-cost and effective for wastewater treatment^[21, 31-32]. On the other hand, some works have presented an excellent review of activated carbon for removing Cr (VI) ions from wastes^[33-35]. The present work aims to develop a method for treating the rice straw to separate the silica content and activating the carbon left behind for Cr (VI) adsorption from its aqueous solutions.

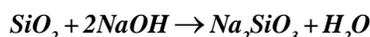
EXPERIMENTAL

Materials

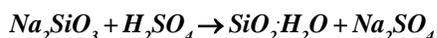
A rice straw (RS) sample as working raw material in the present work had been collected from *Kafr Saqr city, El-Sharkia, Egypt*. As will be later indicated, a representative portion of the collected RS sample was subjected to chemical analysis.

Extraction of silica from the rice straw

Before silica extraction from the rice straw, the adhering soil and dust have first to be properly removed by extensively washed with distilled water under vigorous stirring until the washing water turned clear. In a next step the mineral content has been removed using H₂SO₄ solution (10%) at L/S ratio 10/1 (v/w) with stirring for 2h. The obtained residue after filtration was repeatedly washed with water. To the washed residue NaOH solution was added and boiled for a proper digestion time with stirring to dissolve the contained silica *viz.*^[8].



The remaining residue after silica extraction was washed with warm water (60 C°) before filtration; the pH of the filtrate then adjusted to 7 with H₂SO₄ solution under stirring where a gelatinous silica precipitate is formed:



As a matter of fact, the silica gel started to precipitate when pH decreased to < 9 and the precipitate has been aged for 24 h. The gel was broken and stirred in water and the obtained slurry was then centrifuged followed by washing. The centrifuging step has actually been repeated for 4 times to obtain a clear gel which was then transferred into a glass dish for drying at 110 C°. The obtained product has then stored in a plastic bottle.

Preparation of activated carbon

The residual sludge left after silica extraction has been thoroughly washed with distilled water till attaining a neutral wash solution (pH 7) and was then dried at 110 C°. The dried product has thus been ready for the carbonization process where it was subjected to a proper sequence of three heating steps in a muffle furnace at 250, 500 and 600 C° for 2h at each temperature before cooling in a dessicator. The obtained acti-

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TABLE 1 : Chemical composition of the working rice straw sample

| Component | SiO ₂ | K ₂ O | CaO | Na ₂ O | MgO | P ₂ O ₅ | Al ₂ O ₃ | MnO ₂ | Fe ₂ O ₃ | TiO ₂ | L.O.W ^(a) (110 C°) | L.O.W ^(b) (600 C°) | C ^(c) |
|-----------|------------------|------------------|-----|-------------------|-----|-------------------------------|--------------------------------|------------------|--------------------------------|------------------|----------------------------------|----------------------------------|------------------|
| Wt (%) | 13.9 | 2.9 | 1.1 | 0.2 | 1.8 | 0.1 | 0.6 | 0.3 | 0.9 | 0.4 | 10.6 | 34.8 | 31.8 |

a) L.O.W (loss of weight after drying as moisture), b) L.O.W (loss of weight after ignition as combined water), c) Dark black residue after minerals and silica extraction and ignition at 600 C°

vated carbon ($\approx 30\%$ from the original straw weight) has then been stored in a plastic bottle.

Preparation of Cr (VI) synthetic solution

A stock solution of 1000 ppm Cr(VI) was prepared by dissolving 2.828 g of K₂Cr₂O₇ (Merck) in 1000 ml of 1% H₂SO₄ acid solution. The required concentrations have been prepared from the stock solution by proper dilution.

Experimental procedures

Optimization of silica extraction factors

The factors affecting silica separation from the working rice straw by alkali digestion with NaOH solution have systematically been studied to optimize their values. These included NaOH conc., digestion time and temperature as well as NaOH/straw impregnation ratio.

Optimization of Cr (VI) adsorption upon activated carbon

The chromium (VI) adsorption procedure upon the prepared activated carbon has been carried out by vigorously shaking properly weighed sample portions (0.25g) of the latter with aliquots of the synthetic Cr (VI) solution in plastic tubes (50 ml). The slurry was then filtered and the metal content in the filtrate was measured. The adsorption efficiency of Cr (VI) was determined by the difference in its conc., before and after the adsorption process.

Analytical procedures

Rice straw analysis

A representative sample portion of RS has first been subjected to chemical analysis. Thus, silica was spectrophotometrically determined using the molybdate procedure at 640 nm whereas Al, Ti and Mn were determined using Alizerine red, Tiron, potassium periodate at 475, 430 and 528 nm respectively. Iron, Ca and Mg have been determined titrimetrically against EDTA stan-

dard solution using sulfosalicylic acid, murexide and Eriochrome Black T indicators respectively while Na and K were determined using the flame photometer technique. On the other hand, both the moisture and combined water contents have been gravimetrically determined at 110 and 600 C° respectively. From the obtained results shown in TABLE (1) it was found that SiO₂ attains 13.9 % while the black residue left after both minerals removal and silica extraction followed by ignition at 600 C° would represent the carbon content.

Chromium control analysis

Chromium (VI) analysis in all the aqueous solutions obtained during the preformed adsorption experiments has spectrophotometrically been determined using 1,5 diphenyl-carbazide reagent at 540 nm^[36]. The obtained results have also been emphasized by UNICAM atomic absorption (969 model) at 357.9 nm.

RESULTS AND DISCUSSION

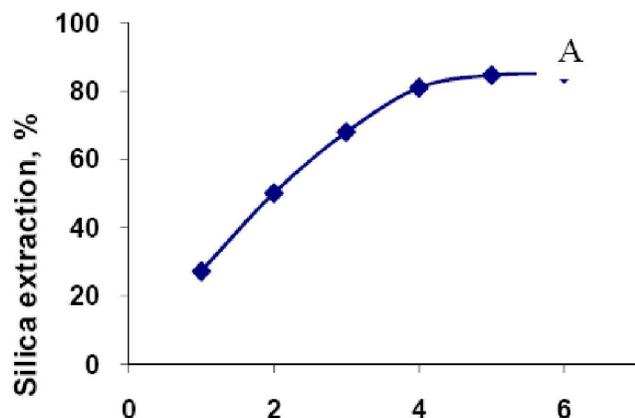
Effect of relevant factors of silica extraction

Effect of sodium hydroxide concentration

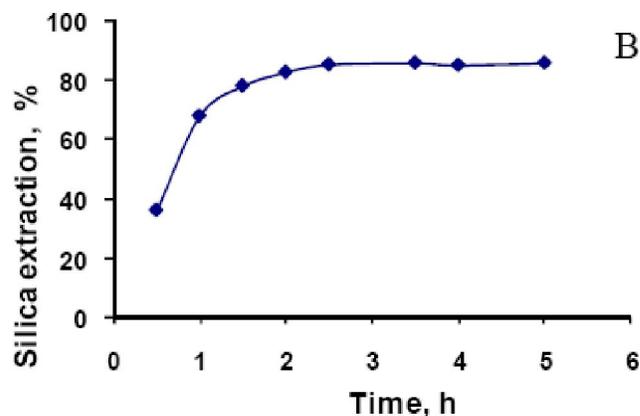
To study the effect of NaOH conc., several sample portions of the rice straw (10 g) were digested with variable NaOH solutions varying in conc., between 1 to 6% for 3 h in L/S ratio of 10/1 at 100 C°. From the obtained data represented in Figure (1-A), it is obvious that, as the NaOH conc., increased from 1 to 5% the silica extraction increased from 27.1 to 84.2% respectively. Further increasing the NaOH conc., to 6 % has however maintained the silica yield at almost the same level (85.2%). Thus, 5% would be considered as the optimum NaOH conc., for silica extraction from the working rice straw under the mentioned working conditions.

Effect of the digestion time

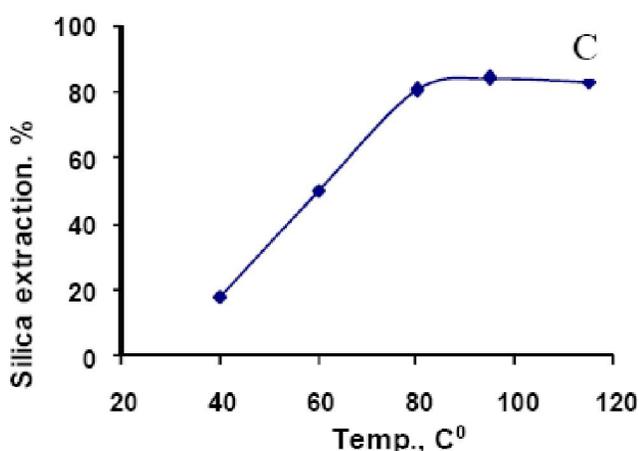
To optimize the effect of the digestion time on silica



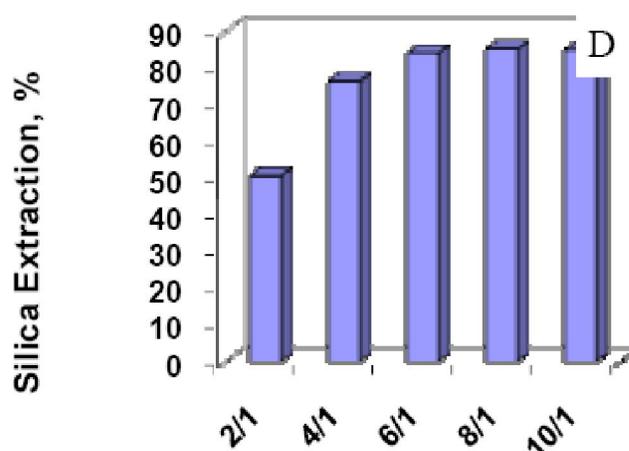
Effect of NaOH conc. on silica extraction from the working rice straw



Effect of the digestion time on silica extraction from the working rice straw



Effect of the digestion temperature on silica extraction from the working rice straw



Effect of NaOH/ straw ratio on silica extraction from the working rice straw

Figure 1 : Effect of relevant factors of silica extraction

extraction from rice straw, several experiments have been performed at different time periods varying from 0.5 to 5h while the other factors were fixed at NaOH conc., of 5%, a digestion temperature of 100 C° and an impregnation L/S ratio of 10/1. The results presented in Figure (1-B) indicated that the silica yield increased from 36.1 to 85.2% with increasing the reaction time from 0.5 to 2.5 h. However, no significant extraction increase was observed by extending the time behind 2.5 h, which was thus considered as the optimum time.

Effect of the digestion temperature

The effect of the digestion temperature upon silica extraction from rice straw using 5% NaOH was studied between 40 to 120 C°. The other experimental conditions were fixed at a digestion time of 2.5 h with an impregnation ratio (L/S) of 10/1. The corresponding

results in Figure (1-C) indicated that as the digestion temperature increased from 40 to 80 C°, the silica extraction efficiency increased from 18.1 up to 78.4% and was further increased to 84.5% at 100 C° while it remained almost constant thereafter (83.9 %) at 120 C°.

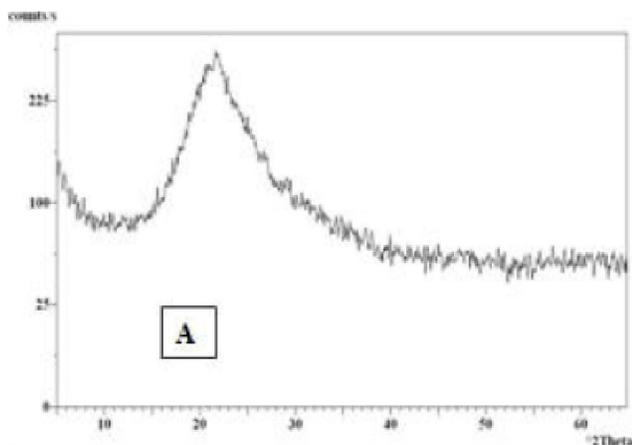
Effect of the NaOH/straw impregnation phase ratio

The NaOH/straw (ml/g) ratio upon silica extraction from the working rice straw using 5% NaOH solution at 100±5 C° for 2.5 h digestion time was investigated from 2/1 to 10/1. From the obtained results plotted in Figure (1-D), it was found that at the impregnation ratio of 2/1, the yield of silica attained 50.3% and increased to 83.8% as the ratio increased to 6/1. Further increase in the impregnation ratio did not result in a perceptible increase in the silica yield and therefore the

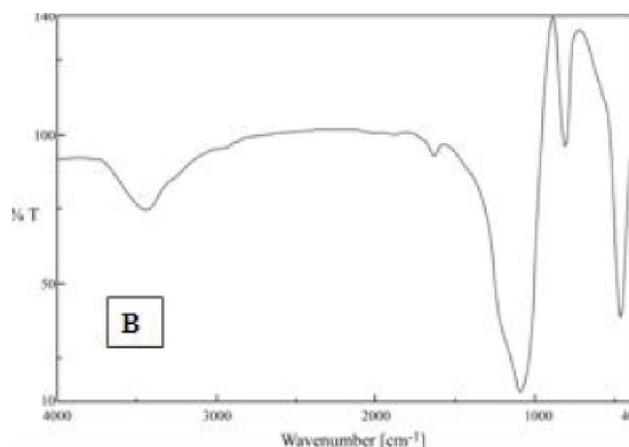
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TABLE 2 : Chemical composition of the silica product obtained from the working rice straw

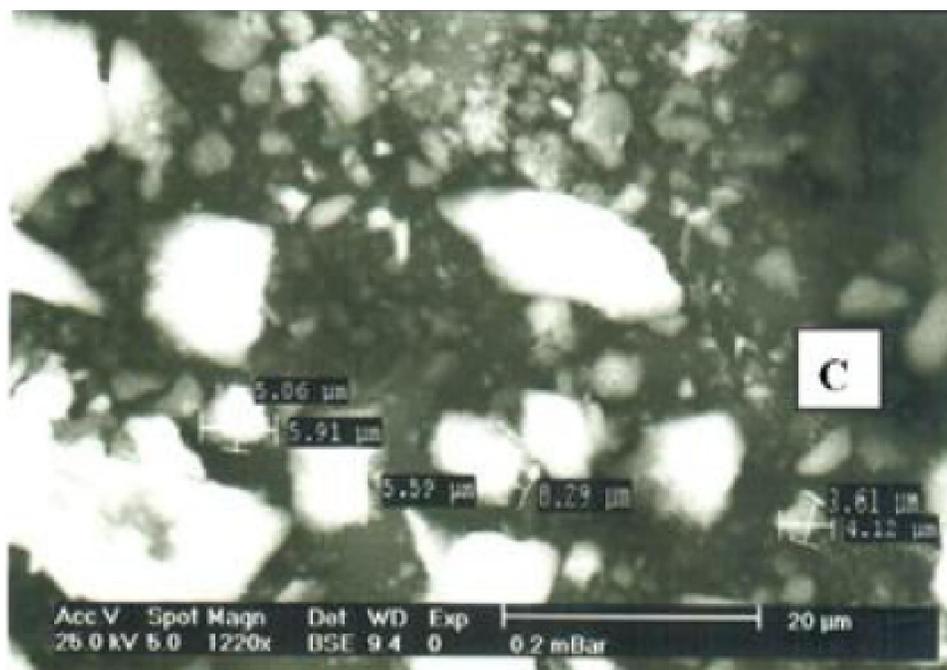
| Component | SiO ₂ | K ₂ O | CaO | Na ₂ O | MgO | Al ₂ O ₃ | MnO ₂ | Fe ₂ O ₃ | P ₂ O ₅ | TiO ₂ |
|-----------|------------------|------------------|-------|-------------------|-------|--------------------------------|------------------|--------------------------------|-------------------------------|------------------|
| Wt (%) | 99.8 | 0.006 | 0.003 | 0.076 | 0.005 | 0.00 | 0.003 | 0.001 | 0.00 | 0.001 |



The XRD pattern of the prepared silica product from the working rice straw



The FT-IR spectrum of the obtained silica product from the working rice straw



The SEM of the obtained silica product from the working rice straw

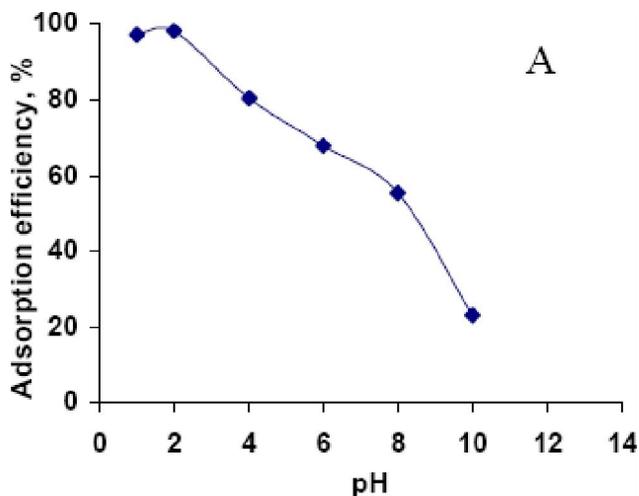
Figure 2 : XRD (A), FT-IR (B) and SEM (C) of the prepared silica product from the rice straw using NaOH

ratio of 6/1 was chosen as the optimum value.

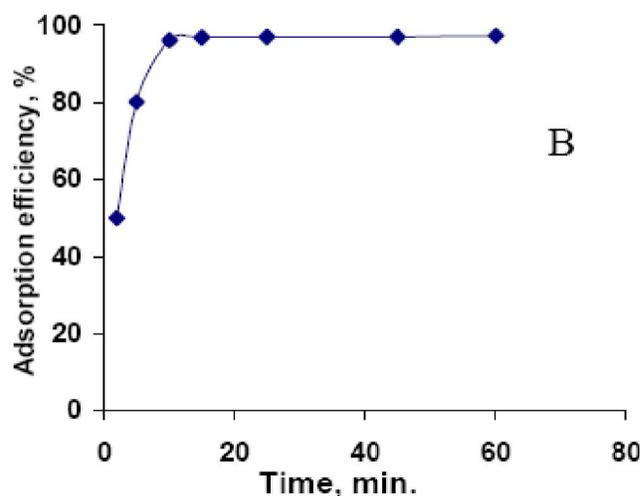
Results of the silica product analysis

The composition of the obtained silica powder was determined by wet chemical analysis after being heated for 2h at 750 C°. The results shown in TABLE 2 indicate that the metal oxides including those of Ca, K, Mn, Na, Fe, Ti and Mg in the rice straw have almost

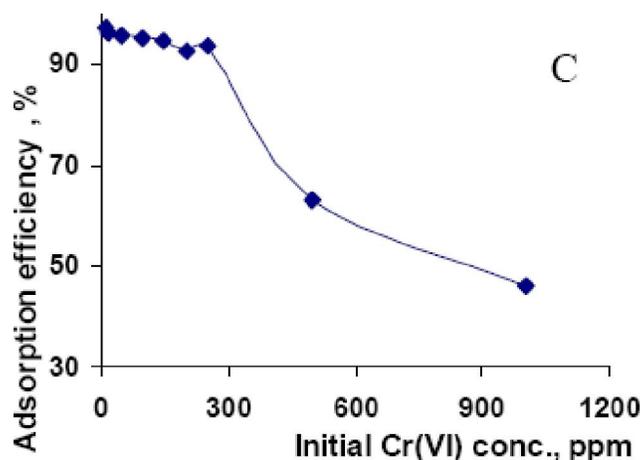
been removed using H₂SO₄ acid in the final product in a manner that the silica content attained up to about 99.8%. In addition, the prepared silica powder has also been characterized by X-ray Diffraction (XRD) as well as by Fourier Transform Infra Red Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). The X-ray diffraction pattern of the product has shown (Figure(2-A) a broad peak between 16° and 38° and is



Effect of pH on Cr (VI) adsorption from its aqueous solution upon the activated carbon prepared from the working rice straw



Effect of the contact time on Cr (VI) adsorption from its aqueous solution at pH 2 upon the activated carbon prepared from the working rice straw



Effect of the initial Cr (VI) conc. on its adsorption from its aqueous solution at pH 2 upon the activated carbon prepared from the working rice straw

Figure 3 : Factors affecting Cr (VI) adsorption upon the prepared activated carbon

centered at 22° thus indicating a typical pattern for amorphous silica^[24]. Furthermore, the absence of peaks of possible impurities such as sodium sulfate or alkaline earth metals affirmed the high purity of the prepared product. On the other hand, from the obtained FT-IR spectrum shown in Figure (2-B), the absorption bands in the range of $3540-3430$ and 1643 cm^{-1} are actually due to H-O-H stretching and bending modes of the adsorbed water respectively. In the meantime, the sharp peaks at 1091 , 775 , and 465 cm^{-1} are assigned to the asymmetric, symmetric and the bending modes of SiO_2 respectively^[37]. Finally the silica product has also been subjected to SEM analysis to demonstrate its a morphological characteristic (Figure 2-C).

Factors affecting Cr (VI) adsorption upon the prepared activated carbon

Effect of pH

The effect of pH upon Cr (VI) adsorption using 0.25g the prepared activated carbon from a synthetic solution (25 ml) assaying 50 ppm was studied at different pH values ranging from 1 to 10. As illustrated in Figure (3-A), it was ascertained that, the optimum pH is 2 at which the adsorption efficiency of Cr (VI) attained up to 98.1% . As the pH was increased, the chromium removal has progressively been decreased until 21.1% at 10. Aliabadi et al., (2006)^[38] have found that, during chromium removal using sawdust and pine leaves the metal exhibited different complex species accord-

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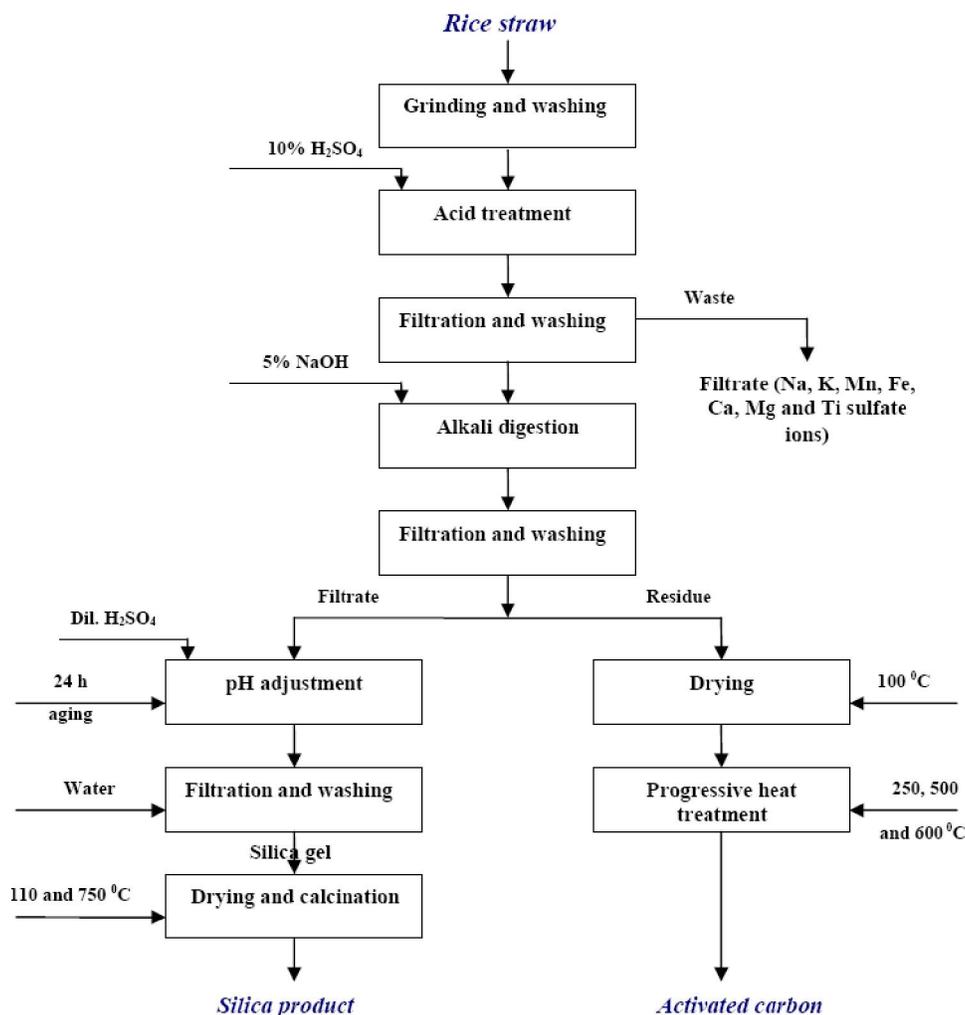


Figure 4 : Schematic flow-sheet of the proposed silica extraction and activated carbon preparation from the working rice straw

ing to the solution pH. In the acidic medium, the species $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ and HCrO_4^- exist and which in the alkaline medium would be converted to CrO_4^{2-} . Based on the obtained results we can decide that, the activated carbon adsorbed the chromium species chemically.

Effect of the contact time

The effect of the contact time on Cr (VI) adsorption from solution (25 ml) assaying 50 ppm at pH 2 using 0.25 g activated carbon was studied through various time periods ranging from 2 up to 60 min. From the results in Figure (3-B), it was found that as the contact time increased from 2 to 10 min, the adsorption efficiency of Cr (VI) increased from 52 to 94.1% respectively. Extending the contact time to 15 min has resulted in increasing the Cr (VI) adsorption efficiency

to 98.2%. So 15 min equilibration time was used for all further studies.

Effect of initial chromium ion concentration

The effect of initial Cr (VI) conc., upon its removal using the activated carbon prepared from the working rice straw was investigated in the range from 10 to 500 ppm in 25 ml solution at pH 2 using 0.25 g activated carbon. The mixture was shaken for 15 min. The results in Figure (3-C) revealed that the adsorption efficiency of Cr (VI) was decreased by increasing its conc., where it reached its maximum value of 96% at conc., values below 250 ppm Cr (VI) and was then seriously decreased to 62.1% as the chromium assay increased from 250 to 500 ppm. From the obtained results of the relevant factors affecting Cr (VI) adsorption from its solutions assaying 250 ppm upon 0.25 g prepared acti-

vated carbon, it can be concluded that the optimum values thereof include a pH of 2, a contact time of 15 min at 25C°. Under these conditions, an adsorption efficiency exceeding 98 % could be attained.

Case study

To investigate the applicability of the studied procedure for waste management of Cr (VI) removal from its aqueous solution, a titania waste solution was used. The latter represents the waste produced after acid digestion of ilmenite using H₂SO₄ acid for the preparation of white TiO₂ pigment. Analysis of the provided waste was found to assay 650 ppm Cr (VI) species. The proposed method was successively applied for Cr (VI) adsorption with adsorption efficiency 98.2%.

Summing up, the obtained results for silica extraction and activated carbon preparation from a local rice straw have been formulated in an overall proposed flow-sheet Figure 4.

CONCLUSION

The present work presents an efficient procedure for proper treating the rice straw to separate a pure silica product and activating the carbon left behind. To realize these objectives, the rice straw after removal of its mineral content with 10% H₂SO₄ was subjected to alkali digestion with 5% NaOH solution at an impregnation L/S ratio of 6/1 at 100 C° for 2.5 h to dissolve its silica content. This was followed by an acidification step where a bright silica gel was obtained at pH 7 which was centrifuged, dried and calcined at 750 C° to obtain a pure silica product. The purity and specification of the latter were determined by chemical, XRD, FT-IR and SEM analyses. The residue left behind after silica extraction was then progressively heat-treated for its activation at 250,500 and 600 C° before being applied for Cr (VI) adsorption from a synthetic solution. The obtained optimum conditions of the latter procedure have then been applied for a case study using the prepared activated carbon for Cr removal from a titania waste solution produced during ilmenite processing for TiO₂ pigment preparation using H₂SO₄. The suggested procedure has resulted under the working conditions in more than 98% adsorption efficiency.

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