
Low-cost Rice Husk Ash and Silica for Chromium Ion Sorption from Aqueous System: Characterisation and Kinetics

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Abstract: Several materials have been developed and used to remove Chromate (VI) from industrial wastewater before discharge into the environment because of its toxicity and lethality. In this study, low-cost adsorbents (rice husk ash (RHA) and silica (RHS)) were prepared from rice husks purchased locally from a rice mill industry and characterised. While the crystallinity and mineralogy of the adsorbents were analysed using powdered XRD crystallography, analysis of the physico-chemical properties was performed using standard procedures. Elemental analysis (CHN) was done using Perkin Elmer CHN elemental analyser and FTIR Spectrometer was used to determine the functional groups on the surface of the adsorbents at room temperature. The prepared samples were used as adsorbents for the removal of chromate (VI) ion in a batch sorption process with reaction conditions *vis-a-viz* adsorbent dosage = 0.5 g, adsorbate volume = 500 ml, adsorbate solution concentrations: 10-200 mg/l, time = 4 h, temperature = ambient temperature. The residual Cr (VI) concentration in the solution was analyzed spectrophotometrically at $\lambda = 540$ nm following the 1,5-diphenylcarbazide procedure. Results obtained for the characterisation of the adsorbents were similar and comparable with what obtained in literatures. Physico - chemical analysis revealed a high ash content of 89% and silica content of 95.83%. XRD analysis for the rice husk ash samples reflected the presence of cristobalite (SiO₂) in amorphous form and a characteristics broad peak at 2θ angle = 26.5°. FTIR analysis revealed the presence of silanol groups (Si-OH), silicic acid (Si-O-Si-OH) in the ash and Si-O-Si and Si-O in the silica. The results of effect of time-concentration experiments of chromium ion sorption by the adsorbents revealed that Cr (VI) ion sorption was both time and initial solution concentration dependent with over 80% removal achieved within the first 30 min of contact for both adsorbents as the initial chromate concentration was increased. Kinetic modeling of the process showed up for pseudo second order, hinting on chemisorption as the mechanism of interaction.

Keywords: Characterisation, Chromium, Cristobalite, Kinetics, Rice Husk, Ash, Silica

1. Introduction

Chromate (VI) amelioration in industrial wastewater before discharge into the environment has become mandatory due to its lethality. The extensive use of chromate compounds in mining operations, electronic device manufacturing, power generation, tannery, metal plating and production of stainless steel has been reported to generate process water containing up to 10-100 mg/L of chromate [1]; much higher than limit of 0.1 mg/L stipulated for industrial wastewater, thus requiring specialized or advance treatment for its removal. Chromium exhibits +3, +6 and 0 oxidation states in environmental matrix.

Hexavalent chromium is very mobile in the environment, speciated as dichromate, hydrogen chromate and chromate and a confirmed carcinogen and mutagen. Technological options of removal include chemical precipitation, membrane filtration, electrolysis and ion exchange. Conventionally, Cr⁶⁺ is removed by chemical reduction to the Cr³⁺ which is of lesser toxicity, and subsequent precipitation with a precipitant e.g. NaOH. The aforementioned technologies while able to effectively meet the standards, are hampered by various factors such as consumption of chemical agents, huge cost, generation of large amount of sludge requiring disposal and ineffective for the removal of low concentration of pollutants. Adsorptive method

The amount of chromium removed by the RHA and RHS samples (mg/g) was calculated using the equations:

$$\text{Amount of Cr (VI) sorbed per mg of adsorbent} = \frac{c_0 - c_e}{w} \times v \quad (3)$$

$$\text{Percentage Cr (VI) removal} = \frac{c_0 - c_e}{c_0} \times 100 \quad (4)$$

Where c_0 is the initial concentration of adsorbate (mg/L), c_e is the equilibrium concentration of adsorbate (mg/L), v is the volume of the solution (ml) and w is the mass of the adsorbent (g).

© Adsorption Experiments

All sorption studies were done and carried out at 25°C. Adsorbate solution pH was corrected to 5.3 using 0.1M HNO₃ and NaOH for the entire reaction.

Effect of Initial Solution Concentration

This was done by contacting 0.5 g of the RHA and RHS samples with 500 ml of varying concentrations of the adsorbate (Cr⁶⁺) solution that ranged between 10-200 mg/L in a batch reactor. The system was agitated on a magnetic stirrer at a speed of 200 rpm. Solution samples were withdrawn with a syringe after 4 hr of contact filtered using 0.45 μm membrane filter centrifuged and the supernatant was analysed for residual Cr(VI) as previously described.

Effect of Time

The time-concentration profiles of the sorption of the adsorbate by the samples was studied to obtain the kinetic parameters by contacting 2 g of adsorbent sample to 1000 ml of adsorbate solution of varying initial concentrations (10-200 mg/L) in a batch reactor. The system was agitated on a magnetic stirrer at a speed of 200 rpm. Solution samples were withdrawn with a syringe at intervals between 0 and 4 hr of contact, filtered using 0.45 μm membrane filter, centrifuged and the supernatant was analysed for residual Cr(VI) as previously described.

3. Results and Discussion

3.1. Physical and Chemical Characterisations of RHA and RHS Samples

Results of the proximate analysis of RHA presented in Table 2 showed its high ash content thus indicating the highly inorganic nature of RHA with silica content of 95.83%. The values obtained for the physicochemical parameters for the RHS prepared in this study are similar and compare

favourably with what obtained in literatures [16, 17].

3.2. Instrumental Characterisation via FTIR and XRD Analysis of RHA and RHS Samples

In the FTIR spectral of the RHA (Figure 1), the peak between 2830 - 3720 cm⁻¹ and 3440 - 2900 cm⁻¹ were ascribed to the presence of OH and Si-OH groups on the RHA surface. The band at 3430 cm⁻¹ pertained to the silanol group and water adsorbed on the surface of RHA [18, 19]. The structure of the silanol groups are similar to that of silicic acid and are in form of silicon dioxide structure (Si-O-Si-OH) [16]. The weak broad peaks around 1600 cm⁻¹ corresponded to stretching of ketonic (C=O) and aldehydic (C-OH) groups. The presence of other organics groups were indicated at 2940 - 1300 cm⁻¹, for instance, the bands observed between 2920 - 2855cm⁻¹ and at 1423 cm⁻¹ corresponded to the presence of methyl groups and aromatic rings due to the presence of lignin, respectively [18]. The peak at 1100cm⁻¹ is ascribed to Si-O-Si and -C-O-H stretching and OH deformation while peaks at 793 cm⁻¹ and 469 cm⁻¹ suggest the presence of Si-H [17, 19]. FTIR analysis of the RHS presented in Figure 1 showed a little broad band between 3380 cm⁻¹ and 3240 cm⁻¹ is ascribed to the hydroxyl group of both the silanol groups and water molecules bonded to the silica surface of RHS. Characteristic peak detected at 1647 cm⁻¹ pertained to the bonding vibration of water molecule trapped in the SiO₂ matrix. Notable silica peaks were detected at 1014 cm⁻¹, 989 cm⁻¹ for (Si-O-Si) and 866 cm⁻¹ and 478 cm⁻¹ for (Si-O) groups, respectively.

Table 2. Physicochemical Properties of RHA Samples.

Parameters	Amount (%)
<i>Proximate Analysis</i>	
Ash content	89
Moisture	0.69
Volatile Matter	5.6
Fixed Carbon	6.2
<i>Inorganic Composition</i>	
SiO ₂	95.83
MgO	0.50
Fe ₂ O ₃	0.19
CaO	0.33
Al ₂ O ₃	0.39
<i>Elemental analysis (CHN)</i>	
Carbon	6.989
Hydrogen	0.073
Nitrogen and others	0.889

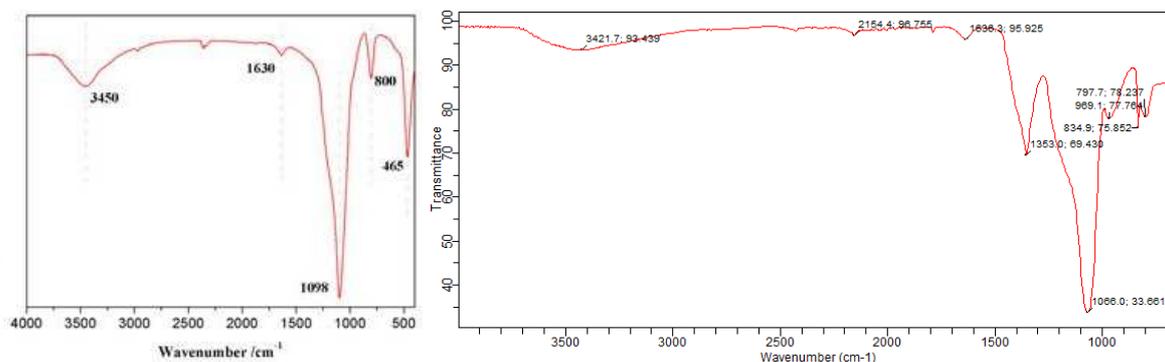


Figure 1. (a) FTIR Pattern of RHA, (b) FTIR Pattern of RHS.

The XRD spectra of the RHA and RHS are presented in Figure 2a and 2b, respectively. The spectrum of the RHA indicated a highly amorphous material with the broad peak spanning 2θ angle range of $18-30^\circ$ confirms an amorphous form of silica. RHA presented lower crystallinity than RHS. The spectrum of the RHS indicated a crystalline material with a sharp notable characteristic silica peak at $2\theta = 26.5^\circ$. This change in texture from amorphous to crystalline phase is attributed to the calcination of the material in temperature above 500°C [17, 19]. The value of the distance between the basal interlayer (d) was calculated using Bragg's law:

$$d = \frac{\lambda}{2\sin\theta} \quad (5)$$

d is the interlayer distance between planes of atoms; θ is diffraction angle; λ (1.542 \AA) is wave length. The incidence angles (2θ) of 22.75° and 26.50° for RHA and RHS, respectively gives basal interlayer distances (d) of 4.23 and 4.99 \AA , respectively. The d -spacing depends upon size and orientation of the charge balancing ion. The mineralogical classification of the RHS indicated the presence of cristobalite [20] and presence of cristobalite (SiO_2), Margaritasite and Macedonite for RHA.

3.3. Adsorption Experiments

Effect of Initial Chromate Solution Concentration (C_o)

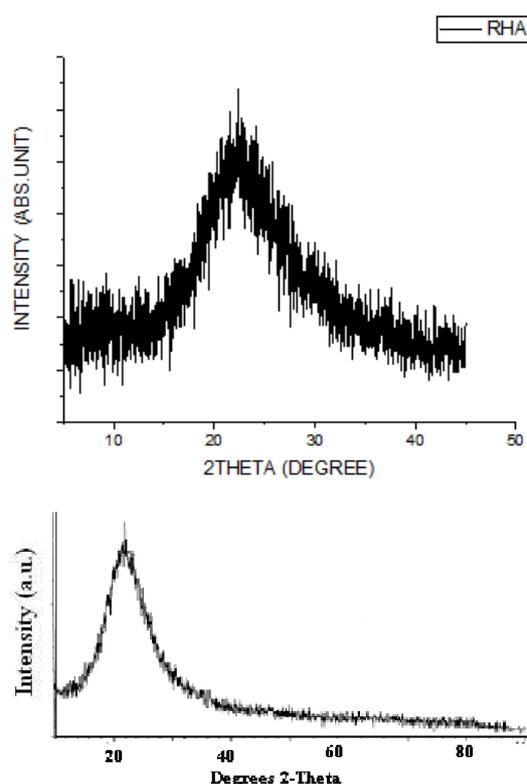


Figure 2. (a) XRD Diffractogram of RHA, (b) XRD Diffractogram of RHS.

The result of effect of initial solution concentration on hexavalent chromium ion removal (%) by RHA and RHS

sample is shown in Table 3. It was observed that chromate removal from the aqueous system is dependent on and increases with initial solution concentration. That is, the amount of $\text{Cr}(\text{VI})$ ions sorbed per unit mass of the adsorbents increases with increase in initial adsorbate concentration. As the C_o was increased from $10 - 200 \text{ mg/L}$, the amount (%) of Cr^{6+} removed increased from 5% to 75% for RHA and 17% to 90% for RHS. The reason given for this observed trend is that the driving force needed to overcome resistance to the mass transfer of Cr ions between the aqueous and solid phases was increased by the increase in adsorbate initial solution concentration. Thus, as the C_o increases, it enhances interaction that led to the adsorption uptake of the chromate ions by the adsorbents. Consequently, an increase in the initial chromate concentration increased the amount of Cr^{6+} removed per gram of the RHS/RHA samples. At the initial concentration of 10 mg/L , the efficiency ranged between $3.67 - 5.15\%$ whereas at 200 mg/L initial chromate concentration, efficiency ranged between $32.56 - 74.87\%$ for RHA while it was $17.62 - 36.46\%$ for 10 mg/L and $39.10 - 90.91\%$ for RHS after 4 h of contact time.

Table 3. Percentage Chromate Removal by Adsorbents.

Concentration (mg/L)	10	50	100	200
% Removal by RHA	5	15	37	75
% Removal by RHS	17	38	75	90

Effect of Contact Time on sorption of $\text{Cr}(\text{VI})$

This was conducted between a time range of $0-4 \text{ h}$ by contacting 2 g of the adsorbent samples with 2 L of adsorbate solution of different concentrations ($10-200 \text{ mg/L}$) in a batch reactor. The results of the time-concentration profiles presented in Figure 3 and Figure 4 showed that chromate (VI) ions removal by RHA and RHS, respectively were clearly time dependent. The sorption rate of the adsorbate by the adsorbents was very rapid during the initial 15 min of contact, and thereafter slowed down. This was seen in the gradual approach of the state of equilibrium after the first 120 min period of the process. No appreciable adsorbate sorption was observed thereafter. Values up to 80% of the total chromate removed was obtained within the first 60 min of the process followed by an additional 20% removal after 90 min of contact time and then values less than 3% additional $\text{Cr}(\text{VI})$ removal occurred in the remaining 120 min of contact time. At the commencement of the process, there existed large number of vacant active sites on the adsorbent surface available for adsorption, these accounted for the initial rapid uptake of Cr observed at the inception of the sorption process. These active sites become saturated after the lapse of some time which results in the slowing down of the adsorbate removal during the later period of adsorption and eventual repulsion between the solute molecules on the solid surface and the bulk solution [21]. For the present study the equilibrium time of 120 min could be considered economically favourable for the sorption process.

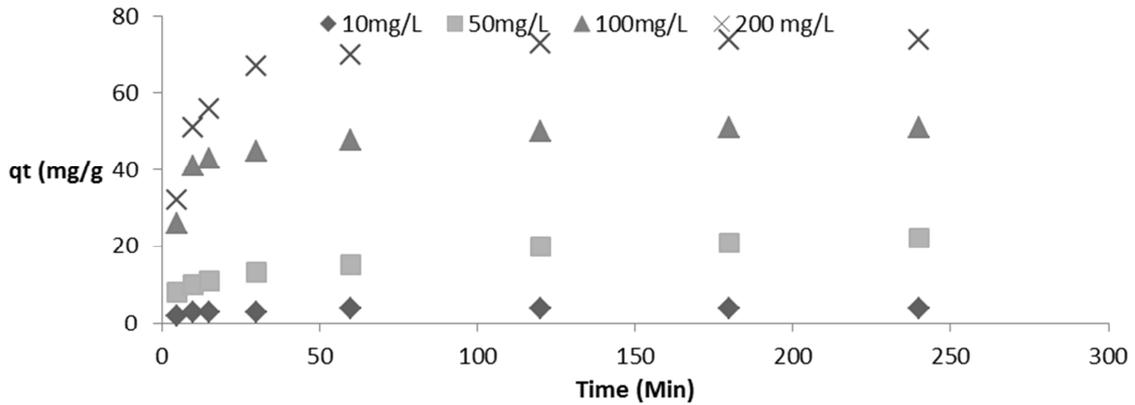


Figure 3. Effect of Contact Time on Cr Removal by RHA.

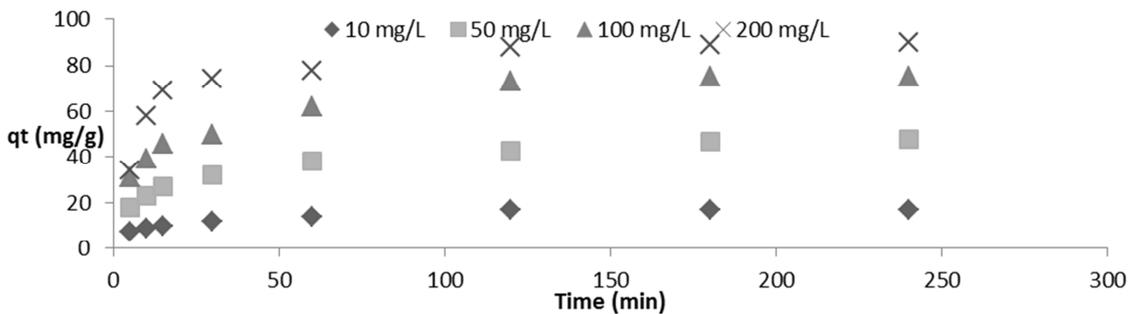


Figure 4. Effect of Contact Time on Cr Removal by RHS.

Kinetic Modeling of the Sorption Process

Kinetics of adsorption as a dynamic process is usually used to describe rate as well as mechanism of adsorbate uptake from the solution by the adsorbent. Data obtained from the kinetic studies of adsorbate uptake is used in selecting optimum operating conditions for the full scale batch process. Elucidation of the mechanism of Cr (VI) sorption by the RHA/RHS was studied with the aid of frequently used kinetic models. The data obtained from the time-concentration profile were fitted into the equations of the model: Lagergren pseudo-first order and pseudo-second order. The Lagergren pseudo first-order kinetic model is represented as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{6}$$

On integration gives the linear form expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{7}$$

Where q_e and q_t are the sorption capacity at equilibrium and time t respectively (mg/g). k_1 is the rate constant of pseudo –first order adsorption (min^{-1}). A plot of $\log (q_e - q_t)$ against t gave a linear relationship from where the pseudo - first order parameters (k_1 and q_e) were determined from the slope and intercept, respectively. The pseudo - first order parameters obtained from the plots for Cr (VI) sorption by RHA are presented in Table 4. The pseudo second order kinetic model considers the rate – limiting step as the

formation of a chemisorption bond as well as exchange or sharing of electrons between the sorbate and sorbent [22]. The non linear form is expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{8}$$

The linear form is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_{qe}} + \frac{1}{q_e} t \tag{9}$$

Where k is the overall rate constant of pseudo-second order sorption ((g/mg)/min). The plot of t/q_t against t gives a linear relationship, from which q_e and k could be determined from the slope and intercept, respectively. The pseudo - second order parameters obtained from the plots for CR (VI) sorption by RHS are presented in Table 5. Establishment of the better model amongst the two was carried out thus: i. From the results presented in Tables 4 and 5, it could be deduced that values of $q_{e \text{ calc}}$ obtained for the pseudo second order were closer in magnitude to the experimental data than what was obtained for the pseudo first order model ii. the values of R^2 obtained for the pseudo second order plot were very high, ($R^2 > 0.99$) compared to pseudo first order. Thus, it could be concluded that the pseudo second order model describes adequately the sorption process. This therefore implies that the mechanism of sorption of chromium (VI) on the adsorbents (RHA and RHS) was chemisorption.

Table 4. Kinetics Models Parameters of Chromium (VI) sorption on RHA.

Pseudo First Order Model

co (mg/L)	q _{e exp.} (mg/g)	q _{e1 cal.} (mg/g)	K ₁ (gmg ⁻¹ min ⁻¹)	R ²
10	6.121	2.329	0.0154	0.874
50	25.970	7.710	0.0306	0.777
100	50.667	10.552	0.0289	0.894
200	78.63	14.389	0.0175	0.634

Second Order Model

co (mg/L)	q _{e exp.} (mg/g)	q _{e2 cal.} (mg/g)	K ₂ (gmg ⁻¹ min ⁻¹)	R ²
10	6.121	5.45	0.126	0.992
50	25.970	29.99	0.199	1.000
100	50.667	49.25	0.314	0.997
200	78.63	73.77	0.200	0.999

Table 5. Kinetics Models Parameters of Chromium (VI) sorption on RHS.

Pseudo First Order Model

co (mg/L)	q _{e exp.} (mg/g)	q _{e1 cal.} (mg/g)	K ₁ (gmg ⁻¹ min ⁻¹)	R ²
10	7.221	1.101	0.0154	0.671
50	34.700	8.716	0.0306	0.707
100	66.661	11.152	0.0289	0.888
200	108.23	34.119	0.0175	0.634

Second Order Model

co (mg/L)	q _{e exp.} (mg/g)	q _{e2 cal.} (mg/g)	K ₂ (gmg ⁻¹ min ⁻¹)	R ²
10	7.221	7.45	0.249	0.999
50	34.700	31.69	0.432	1.000
100	66.661	66.85	0.351	0.997
200	108.203	103.43	0.447	1.000

Estimation of Sorption Performance

A parameter k_2q_e (min⁻¹) defined as the second order rate index was used to define the kinetic performance as described by Wu et al., [23].

At the half-life of the sorption process,

$$q_t = 0.5q_e \quad (10)$$

and

$$t_{0.5} = \frac{1}{k_2q_e} \quad (11)$$

Using equation (11), results obtained presented in Table 6 showed that increase in the initial concentrations of chromate ion in solution led to a reduction in the values of the half-life of the sorption process. This indicates therefore increase in initial adsorbate concentration brings about a lowering of the time needed to reduce it to half its initial amount.

Table 6. Sorption performance of RHA for Cr (VI) removal.

Parameters	10 mg/l	50 mg/l	100 mg/l	200 mg/l
k_2q_e (min ⁻¹)	2.218	7.33	6.080	25.13
$t_{0.5}$	0.854	0.667	0.426	0.247

Table 7. Sorption performance of RHS for Cr (VI) removal.

Parameters	10 mg/l	50 mg/l	100 mg/l	200 mg/l
k_2q_e (min ⁻¹)	5.510	14.072	36.08	50.13
$t_{0.5}$	0.254	0.167	0.066	0.034

4. Conclusion

Based on the findings in this work, it is justifiable that both RHA and RHS can be used for the abstraction of Cr (VI) ions from contaminated effluents. The following deductions were drawn:

XRD analysis revealed the presence of cristobalite (SiO₂), Magaritasite and Macedonite in RHA and cristobalite in RHS, respectively.

FTIR analysis revealed that functional groups such as –

OH, -C-OH, C=O, Si-O-Si and Si-H are present on the RHA and RHS surfaces.

Kinetics study showed that sorption is favourably influenced by increase in initial adsorbate concentration and time.

Kinetic modeling followed the pseudo second order rate expression, a hint on chemisorption as mechanism of interaction.

The equilibrium time of 120 min is favourable economically for hexavalent chromate adsorption by RHS

and RHA from aqueous system.

The adsorption rate of RHS is higher than that of RHA.

Both RHS and RHA are effective adsorbents for the removal of Cr (VI) from aqueous solution.

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