

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 (SiO_2) 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, Cr^{6+} is removed by chemical reduction to the Cr^{3+} 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

for Cr (VI) abstraction in waste streams has gained acceptance by researchers in recent times due to its simplicity of operations, economics, high efficiency and availability of many arrays of cheap environmental - friendly adsorbents [2]. Many agro-based adsorbents have been applied with success for the treatment of chromium contaminated wastewater.

Table 1. Some Biosorbents Used for Cr (VI) Removal.

Adsorbents	mg Cr (VI)/g	Reference
Potato peel	3.28	[3]
Sawdust	3.6	[4]
Rubber wood sawdust	44.1	[5]
Hazel nut shell	17.7	[6]
Groundnut husk	11.4	[7]
Aligator weed	82.57	[8]

Rice husk (RH) is an agricultural wastes obtained during rice milling, and composed of both mineral and organic materials including cellulose, lignin silica, alkalis and trace element. Traditionally, rice husk is considered a waste material and generally disposed off by dumping or burning, although some are used as a low-grade fuel. However, the amounts of rice husk available are so far in excess of any local use and have posed environmental problem. The unique physical and chemical properties of RH such as granular structure, chemical stability, high ash and silica content, has promoted its use in domestic and industrial application [9]. Rice husk has been applied (directly or as rice husk ash) as a resource in the industry as a value added material or in manufacture and synthesis of new materials [10]. Controlled burning of rice husk at moderate temperature followed by acid leaching treatment yields rice husk ash (RHA) of high silica content (> 92%) of very high purity [11, 12]. The high silica content in RHA has been employed for the production of silicon carbide, sodium silicate, zeolite and silica gel. Silica gels have been employed to remove heavy metals and organic pollutants from aqueous system [13-15]. Silica is a polymer of silicic acid made of inter-linked SiO_4 repeating units in tetrahedral arrangement. The active silica surface with large specific surface area and surface hydroxyl groups have been credited to its importance in adsorption and ion exchange processes. On the outer surface of the silica structure, there are free silanol groups, referred to as isolated silanol groups, and hydrogen bonded to adjoining silanol groups referred to as vicinal or germinal silanol group [16]. In this work, we report the preparation and characterization of rice husk ash and silica from rice husk as well as the kinetic of the adsorption of chromate VI ion from aqueous solutions by these materials in a batch reactor. Elucidation of mechanism of interaction was undertaken through kinetic modeling of the data obtained.

2. Materials and Methods

2.1. Materials

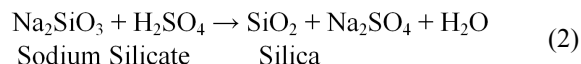
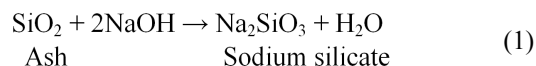
(a) Preparation of Rice Husk Ash (RHA)

Rice Husks (RH) was obtained from a nearby rice mill, sieved to remove very fine particles, washed with deionized

water and dried in an open air. Rice husk ash was prepared from the dried rice husk by acid leaching using nitric acid (Analar grade) followed by calcination in a muffle furnace (CARBOLITE, 5220). Acid leaching of the dried rice husks was done to remove soluble elemental impurities and to increase the purity of silica content. 50 g of the dried rice husks was soaked in 200 ml of 0.1M nitric acid solution and heated at 80°C for 15 min. Rice husk was filtered and rinsed several times with distilled water until neutral pH and dried at 100°C for 2 hr. The rice husk ash was obtained by pyrolysis of the acid leached rice husk in a muffle furnace at 700°C for 6 h in the form of a white- greyish powder.

(b) Preparation of Rice Husk Silica (RHS)

The chemicals and reagents used in the process were of analytical grade. Preparation of the rice husk silica was carried out thus: 35g of rice husk ash was mixed with 250 ml of 1N sodium hydroxide aqueous solution. The mixture was refluxed for 3 h at 110°C, filtered and stored in a refrigerator as sodium silicate. 50 ml of sodium silicate solution was poured into 15 ml distilled water at a time and stirred. This was followed by drop wise titration with 3M H_2SO_4 until a final pH 5 under stirring speed to form rice husk silica. The acidic condition of pH 5 indicates approximately the complete precipitation of silica from sodium silicate by the following reaction:



© Characterisation of adsorbents

The physico-chemical characterisation and proximate analysis of the samples (RHA and RHS) was carried out by following approved procedures. Elemental analysis (CHN) was done using Perkin Elmer CHN elemental analyser. FTIR Spectrometer (IR PRESTIGE 21, SHIMADZU) was used to determine the functional groups on the surface of RHA and RHS. Pellet pressed technique was used for this purpose at the spectral range of 4000–400 cm^{-1} with resolution of 4 cm^{-1} . The adsorbents crystallinity and mineralogy was assessed using powdered XRD crystallography (XRD D8, ADVANCE BRUKER), using copper as the target, with Ni as the filter media and K radiation maintained at 1.54Å. Diffraction patterns of the samples were recorded in the range of 10–90° at a scanning rate of 2°/min and step size of 0.01.

2.2. Methods

(a) Preparation and analysis of adsorbate

A stock solution of hexavalent chromium (1000 mg/L) was prepared in a double distilled deionized water using potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Working solutions of varying concentrations (10-200 mg/L) were obtained by serial dilution of the stock solution. The residual Cr (VI) concentration in the supernatant was determined using a UV – visible spectrophotometer (UV-1601, Shimadu) at $\lambda_{\text{max}} = 540 \text{ nm}$, following the 1, 5 – diphenylcarbazide procedure.

(b) Data analysis

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

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

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

Where c_o 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 - 2855 cm⁻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 1100 cm⁻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

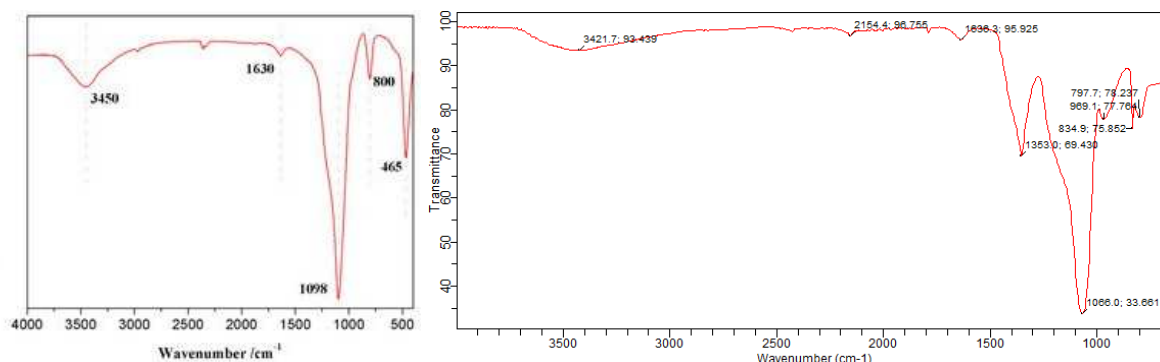


Figure 1. (a) FTIR Pattern of RHA, (b) FTIR Pattern of RHS.

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), Magaritasite and Macedonite for RHA.

3.3. Adsorption Experiments

Effect of Initial Chromate Solution Concentration (C_o)

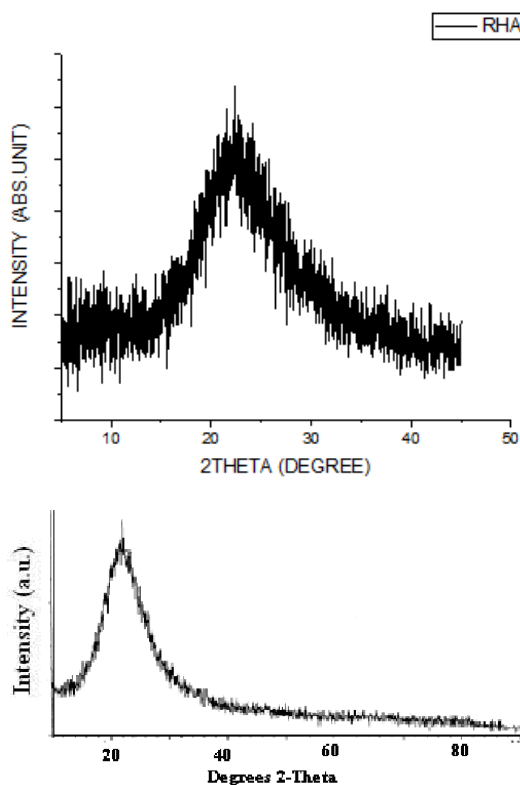


Figure 2. (a) XRD Diffractogram of RHA, (b) XRD Diffractogram of RHS.

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.

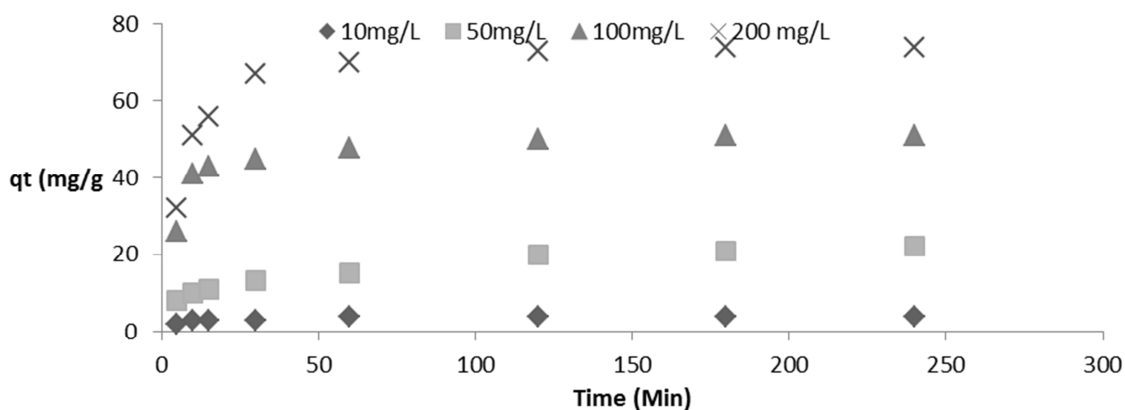


Figure 3. Effect of Contact Time on Cr Removal by RHA.

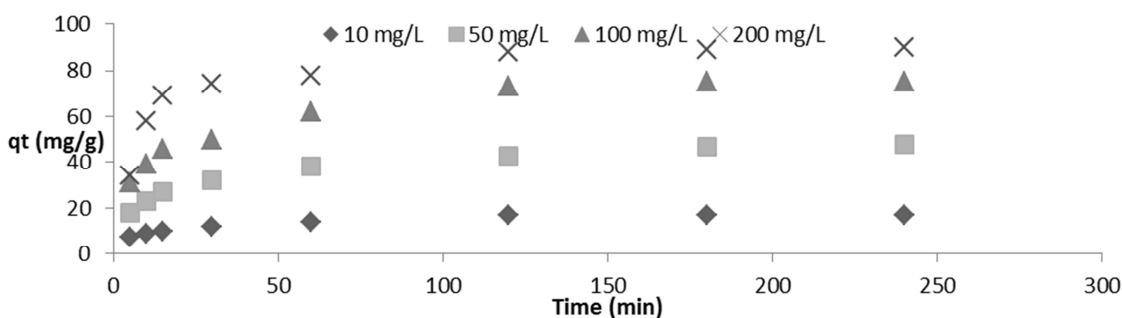


Figure 4. Effect of Contact Time on Cr Removal by RHS.

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:

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

On integration gives the linear form expressed as:

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

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:

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

The linear form is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_{qe}} + \frac{1}{q_e} t \quad (9)$$

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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