

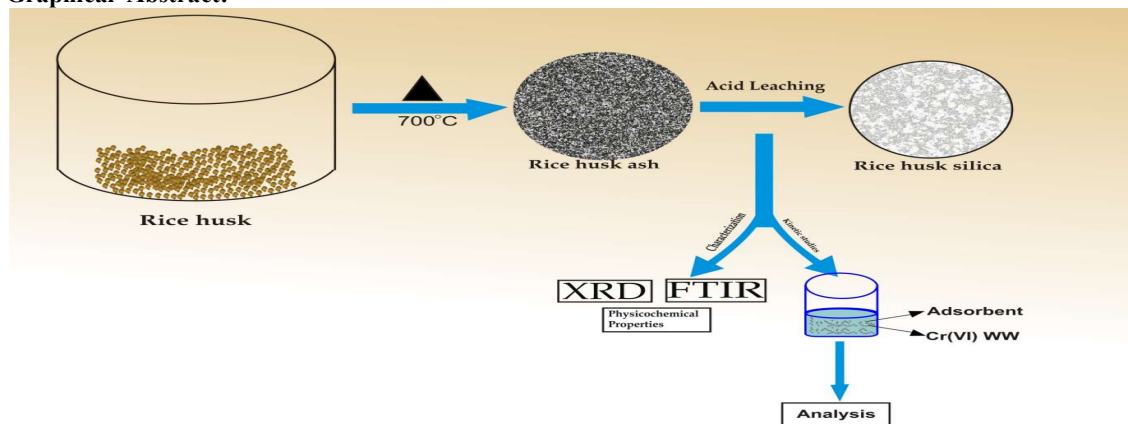
Biosorptive Removal of Hexavalent Chromium by Rice Husk Ash and Silica from Aqueous Solution

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Abstract

Hexavalent chromium ion removal by adsorption using rice husk ash and silica prepared from rice husks obtained locally from rice mill as biosorbents was evaluated as low cost wastewater treatment in this study. Batch equilibrium isotherm experiments were performed as well as effect of dosage and initial chromate solution pH to determine the potentials of the sorbent to remove hexavalent chromate ion from synthetic fed wastewater. Equilibrium isotherm experimental data isotherms were tested with isotherm models (Langmuir, Freundlich and Tempkin models), being best represented by the Langmuir model. Optimum conditions were: dosage = 0.5 g / 200 ml at room temperature and $\text{pH}_0 > 6$. The equilibrium between adsorbate in the solution and on the adsorbent surface was practically achieved in 2 h. The monolayer sorption capacity was 67.45 mg/g for rice husk silica and 55.98 mg/g for rice husk ash. Estimation of energy of the sorption process revealed chemisorption as the prevailing means of interaction between the adsorbents and adsorbates moieties. The abundance and affordable (cheap) cost of rice husks justifies its use as a precursor in the preparation of rice husk ash and silica as effective adsorbents for chromium removal from industrial effluents.

Graphical Abstract:



Keywords: Hexavalent chromium, Biosorption, Isotherm, Rice husk ash, Rice husk silica

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Introduction

Biosorptive treatment of wastewater involves the use of biological materials via a metabolically - mediated physicochemical pathways to accumulate and sorb the inherent pollutants. This technique is an environmental cleanup practice used by Scientists and Water Engineers to provide an economical alternative for removing toxic wastes including heavy metals, pesticides and other organic compounds which can be toxic to wildlife and humans in small concentration from industrial effluents. Biosorption technique can be simply defined as the passive binding (uptake) of pollutants by dead or living biomass (Gupta and Rostagi, 1999). The use of dead biomass as biogenic materials or biosorbent has proven to provide some advantages over the live biomass; absence of nutrient needs for growth, higher sorption capacity, simple operation, low operational cost and ease of regeneration of biomass. Use of living biomass may lead to their death or toxicity after pollutant accumulation, growth of living biomass may become impaired and increased cost incurred as a result of continuous supply of nutrients to the biomass (Ofomaja et al., 2010). Hence, the use of dead biomass is economical. These biosorbents can effectively sequester metal ions in the solution and decrease the concentration from the ppm to ppb level efficiently.

Abundant natural materials like microorganisms (microbial, bacterial, fungal), plant-derived (algal biomass, lignocellulosic materials), biopolymers (e.g. chitosan), and industrial by-products, have been suggested as potential biosorbents for heavy metal removal due to the presence of metal-binding functional groups. The mechanisms of interaction between the cell wall of the biomass and the pollutant could be physical and / or chemical. The process involves binding of ions onto the functional groups present on the surface of the biosorbent in aqueous solutions by means of various interactions: complexation, ion exchange, precipitation etc, rather than

oxidation through aerobic or anaerobic metabolism (Gupta et al., 2010). Biosorption is influenced by various process parameters such as pH, temperature, initial concentration of the metal ions, biosorbent dose and speed of agitation. Rice milling generates a by-product known as husk which is about 22% of the rice paddy. Rice husk accounts for about one-fifth of the annual gross rice production. The rice husk is traditionally considered as a waste material and as such is generally disposed of by dumping, burning or used as a low-grade fuel. During controlled firing and proper conditions, ¼ (w/w) of the husk is usually converted to rice husk ash made up of about 90 % amorphous silica of a very high purity. Advantages such as low cost, abundance, availability and possibility of regeneration and reuse have greatly favoured the application of rice husk in the removal of pollutants including heavy metals in aqueous solution in recent times (Viere et al., 2010; Gibb et al., 2009)

Presence of chromium in the environment is due to its extensive use in a variety of industrial applications: mining operations, leather tanning, steel production units, power generation, cement industries, mining, metal plating and so on (Gupta and Rostagi, 1999). Chromium occurs in several different oxidation states that range between -2 and +6, with the +3 and +6 states being the stable forms in the natural environments. Chromium (VI) is highly mobile in the environment and very toxic. Cr (VI) can easily penetrate the cell wall; chronic exposure can lead to mutagenesis and carcinogenesis (Gibb et al., 2010). The highest level of Cr (VI) ions permitted in a discharge into inland surface and potable water, are 0.1 and 0.05 mg/L, respectively (Mojdeh et al., 2009; EPA, 1990). Various physico-chemical methods have been studied and tested for detoxification and removal of chromium-laden waste waters in the recent years. Among these are phytoremediation, ion exchange, chemical reduction, solvent extraction, precipitation, liquid membrane, reverse osmosis, etc. However, they have high operating costs and problems in the disposal of the residual metal sludges (Mutongo et al., 2014). The economic recovery of chromium from wastewater is essential in minimising its environmental impact. This study is therefore aimed at hexavalent chromium removal from industrial effluent using rice husk ash and silica prepared from locally obtained rice husk wastes in a batch sorption study via equilibrium isotherm process. The effect of dosage and pH on the process shall be examined.

Experimental

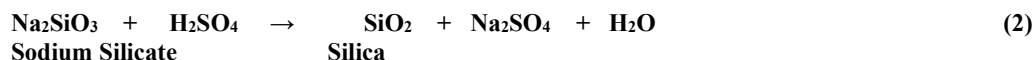
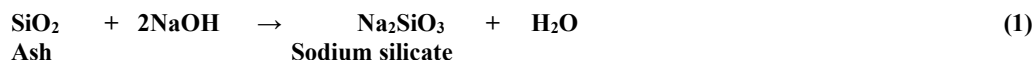
(a) Materials

i. Preparation of Rice Husk Ash (RHA)

The Rice Husk was collected from a nearby rice mill without any pretreatment except sieving to remove dirt and washed several times with deionized water to remove surface particles and dried in an open air. Rice husk ash was prepared from the dried rice husk by calcination in a muffle furnace (CARBOLITE, 5220) and acid leaching using nitric acid (Analar grade). Acid leaching of rice husk was done to remove soluble elemental impurities and increase the purity of silica content. 60 g of the rice husk was soaked in 120 ml of concentrated 37% hydrochloric acid and heated at 100°C for 30 min. Rice husk was filtered and rinsed for several times with distilled water until neutral pH and dried at 100 °C for 2 h. The rice husk ash was obtained by pyrolysis of the rice husk in a muffle furnace at 700 °C for 6 h in the form of a white-grey powder.

ii. Preparation of Rice Husk Silica

The chemicals and reagents used in the process were of analytical grade. RHA preparation carried out by the addition of 35 g of the rice husk ash powder into 250 ml of 1N NaOH, followed by vigorous stirring and allowed to stand for 12 h to produce sodium silicate. The sodium silicate solution was filtered to remove undissolved materials and then titrated drop-wise with 3M H₂SO₄ until a final pH 5 was obtained. The soft gel formed was aged for 4 days, filtered through suction filtration, washed with distilled water and dried in the oven at 110°C for 24 h and then calcined in the muffle furnace at 700°C for 5 h to produce rice husk silica. The acidic condition of pH 5 indicates approximately the complete precipitation of silica from sodium silicate by the following reaction:



ii. Methods

a. Preparation and analysis of adsorbate

Hexavalent chromium stock solution of known concentration (1000 mg/L) was prepared in a double distilled deionized water using potassium dichromate (K₂Cr₂O₇) salt. Varying concentrations (10-200 mg/L) was prepared from the stock as working solutions by serial dilution. The residual Cr (VI) concentration in the solution was determined spectrophotometrically at λ=540 nm using a UV – visible spectrophotometer (UV-1601, Shimadu) following the 1, 5 –diphenylcarbazide procedure.

b. Data analysis

The amount of chromium sorbed per unit mass of the adsorbent (mg/g) was calculated using the mass balance

equation:

$$q_e = \frac{c_o - c_e}{w} \times v \quad (1)$$

In which q_e is the amount of chromium sorbed (mg/g), c_o is the initial chromium concentration (mg/L), c_e is the equilibrium chromium concentration (mg/L), v is the volume of the solution (ml) and w is the mass of the adsorbent (g).

$$\text{Percentage metal ions removal} = \frac{c_o - c_e}{c_o} \times 100 \quad (2)$$

c. Determination of Point of Zero Charge

The point of zero charge of the adsorbents was determined by adopting the solid addition method via: 45 ml KNO₃ solutions of known strength were transferred into five (5) sets of 100 ml conical flasks. The pH_o values of the solutions were roughly adjusted using either 0.1M HNO₃ or NaOH to vary between pH=2 and pH=12. The total volume of the solution in each flask was then made up to 50 ml by adding the KNO₃ solution of the same strength. The pH_o of the solutions were accurately noted. 1g of the adsorbent was added to each flask and immediately securely capped. The mixture was then manually agitated and allowed to equilibrate for 48 h with intermittent manual after which the final pH_f was noted. The difference between the initial and final pH ($\Delta\text{pH} = \text{pH}_o - \text{pH}_f$) values was plotted against the pH_o. The point of intersection of the resulting curve on pH_o gave the point of zero charge.

d. Determination of Surface Area

The method designed for surface area of siliceous material by Sears, 1956 was adopted in this experiment. To a 100 ml dilute HCl (pH=3), 1.5 g of the sample was added, followed by 30 g of NaCl with continuous stirring and made up to 150 ml using distilled water. This was followed by titration of the solution against 0.1N NaOH. The amount of volume (V) of NaOH needed to raise the pH from 4 to 9 was then noted. The procedure was repeated and the average volume was taken for the calculation of the surface area. The surface area was calculated using the equation:

$$S = 32 V - 25 \quad (3)$$

with, S= Surface area (m²/g) and V= Average volume of NaOH Needed.

e. Batch 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.

i. Equilibrium Isotherm Studies

The isotherm studies were carried out by contacting 200 ml aqueous solution of known concentration of the adsorbate that ranged between 10 - 200 mg/l in a 250 ml borosilicate conical flask containing 0.4 g of the adsorbent. The flask was agitated at a constant rate of 200 rpm using a magnetic stirrer for a period of time after equilibrium is established. At the expiration of this period, the samples were withdrawn using a syringe, centrifuged at 5000 rpm for 5 min and then the supernatant liquid was analyzed for residual concentration of chromium using UV-visible. The amount sorbed per unit mass of the adsorbent (in mg/g) was calculated by using equation (1)

ii) Effect of adsorbent dosage.

The effect of the adsorbent dose on the sorption process was investigated at different adsorbent dosages of 0.2 - 1.0 g by contacting with 100 ml of known concentration of the adsorbate that ranged between 10-200 mg/l in a 250 ml borosilicate conical flask and agitated at a constant rate of 200 rpm using a magnetic stirrer. The contact time was kept at 2 h, since equilibrium was found to have been attained at 2 h contact time. Residual chromate concentration was determined as described above.

iii. Effect of initial adsorbate solution pH

The effect of pH_o on the sorption was studied by adjusting the initial adsorbate solution pH (pH_o) to range between pH=2 – 10 using 0.1 M HCl or NaOH and measured with a pH meter. For this experiment, the adsorbent loading was kept at 0.1g per 50 ml of known concentration of adsorbate solution and agitated at 200 rpm at ambient temperature. The contact time was kept at 2 h, since equilibrium was found to have been attained at 2 h contact time. Residual chromate concentration was determined as described above.

Results and Discussion

a. Equilibrium Isotherm Analysis

Equilibrium Isotherm analysis of a sorption process gives insight into the affinity of an adsorbent for an adsorbate. Adsorption equilibrium isotherm studies are described by sorption isotherm characterized by certain constants and parameters whose values express the surface properties and affinity of the adsorbents for the adsorbates [2]. Elucidation into the mechanism of adsorption process is obtained via the use of adsorption models. Design and optimization of an adsorption system is hinged on the data obtained from the equilibrium curves. The experimental data of the equilibrium isotherm studies of chromium ion sorption onto the two adsorbents used in this study (RHA and RHS) were fitted into three common equilibrium isotherm models namely, Freundlich, Langmuir and Tempkin equations.

The Freundlich isotherm model regarded as an empirical isotherm with no theoretical basis, hints that the adsorption occurs on a heterogeneous adsorbent surfaces and sites of varying affinities and binding strength. It assumes that the stronger sites are firstly occupied and can be applied to multilayer adsorption (Adelagun et al., 2014; Mohanty et al., 2009). The linearized form of Freundlich equation is:

$$\log q_e = \frac{1}{n} \log c_e + \log k_f \quad (4)$$

With n and k_f being Freundlich coefficients. For a favourable sorption, the value of n should lie between 1-10, while a high k_f value denotes a high affinity of the adsorbent for the adsorbate.

The Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical and homogeneous sites. The model assumes uniform energies of adsorption sites on the adsorbent surface and no transmigration of adsorbate in the plane of the surface (Nakbantote et al., 2007). The linearized form is presented as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m c_e} \quad (5)$$

With c_e and q_e being the concentration of chromium at equilibrium in the liquid (mg/L) and solid phase (mg/g), respectively, b (L/g) and q_m (mg/g) are the Langmuir equilibrium constant and the maximum adsorption capacity on a monolayer of the adsorbent active surface, respectively. The magnitude of b expresses the affinity between the adsorbent and adsorbate and is largely determined by the heat of sorption. An isotherm process is described to be favourable if the sorption capacity of the adsorbent increases with increase in initial concentration of the adsorbate (Weber and Chakravorti, 1974). A dimensionless constant known as equilibrium parameter (R_L) or separation factor is generally used to describe the nature of a Langmuir isotherm as either unfavourable ($R_L > 1$), linear ($R_L = 1$), Favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) and calculated as (eqn.6) with b as the Langmuir constant and c_o as the initial chromate concentration:

$$R_L = \frac{1}{1 + bc_o} \quad (6)$$

The Temkin isotherm model studies the interactions between adsorbent and adsorbate and the free energy of adsorption as a function of surface coverage. The linear form of the Temkin isotherm model equation is given as:

$$q_e = B_T \ln A + B_T \ln C_e \quad (7)$$

where B_T (J/mol) corresponds to Temkin isotherm constant, the heat of adsorption and A (l/g) is the equilibrium binding constant corresponding to the maximum binding energy. A high value of A and B_T indicates a strong bonding and fast sorption of the adsorbate on the adsorbent surface. The related isotherm parameters are presented in Table 1. The maximum sorption capacity (q_m) observed for both adsorbents were quite high in comparisons with some adsorbents reported in literatures for hexachromate ions removal (Mutongo et al., 2009, Dubey and Gopal 2007; Baral et al., 2006; Babu and Gupta, 2008; Karthikeyan et al., 2004; Crimono et al., 2000). The monolayer sorption capacity, q_m for RHS was higher (67.45 mg/g) than for RHA (55.98 mg/g). Probable reason for this difference could be attributed to the differences in their surface areas. The surface area of RHS as determined by Sear's method was 21.55 mg²/g while RHA was 15.72 mg²/g. The value of b (L/mg), the Langmuir constant indicates the heat of biosorption, is higher for RHS (0.065) than for RHA (0.043). The R_L values calculated using equation (6), showed favourable sorption process for all initial concentrations used. Calculated values of R_L values obtained showed favourable sorption of chromium ion onto the adsorbents. The R_L values decreased from 0.078 to 0.028 for RHA and 0.02 to 0.015 for RHS as the initial concentration was increased from 10 to 200 mg/L. These extremely low values of R_L are indications that the process is favourable. The Freundlich parameter n , an indication of the sorption intensity for the adsorbate by the adsorbent was high: RHS = 4.50, RHA = 3.20, an indication of strong intensity between adsorbents and adsorbate and strong bond formation. These two factors (n and R_L) thus suggest a favourable sorption process between the adsorbents and adsorbate. The high Freundlich constant k_f , suggests high affinity between Cr (VI) and the adsorbents RHS and RHA as shown in Table I. The values obtained for the Temkin parameters (B_T and A) showed high heat of sorption and binding energy.

Table I: Equilibrium Isotherm Models Parameters of Cr (VI) sorption on RHA and RHS

Isotherm Model	RHA			RHS		
	q_m	k_l	r^2	q_m	k_f	r^2
Langmuir	55.98	0.043	0.9711	67.45	0.065	0.9792
Freundlich	n	k_f	r^2	n	k_f	r^2
	3.2301	6.11	0.9025	4.5097	10.382	0.8968
Tempkin	B_T	A	r^2	B_T	A	r^2
	100.34	267.4	0.825	196.22	463.8	0.7999

The assessment of the suitability of the isotherm models to describe the process was examined by the evaluation of their linear coefficient of determination (R^2). Values of R^2 obtained from the isotherm models presented in Table I indicated that the highest correlation coefficient was obtained with the Langmuir isotherm model with $R^2 > 0.90$ among the models studied. Further assessment was done by comparing the theoretical plots obtained from each isotherm to the experimental data of chromium sorption onto the adsorbents. This was assessed

by the plot of q_e (amount of chromium biosorbed per unit mass of the adsorbent (mg/g)) against c_e (concentration of chromium remaining in solution (mg/l)) as shown in Figure I and Figure II. The Langmuir isotherm model showed the best description of the sorption process among the isotherm models; it displayed the highest conformity to the experimental values as very little variance was displayed between its predicted and experimental values. The Temkin isotherm model showed the poorest as displayed in the high variance between its theoretical q_e values and the experimental q_e values. Thus, it can be concluded that biosorption onto RHA and RHS biosorbents is monolayer coverage of the biosorbent surface by chromium ion.

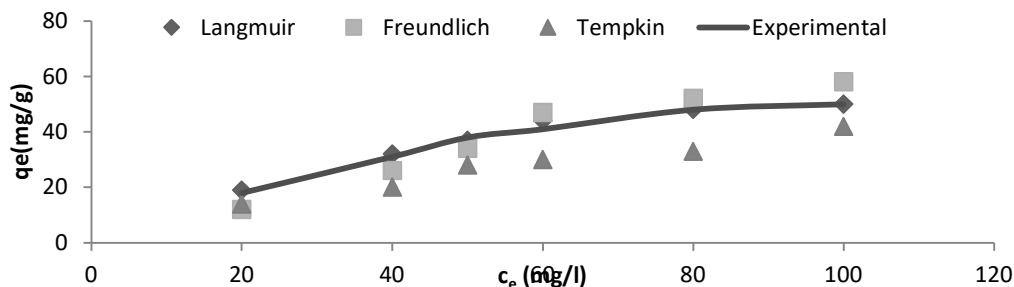


Figure I: Plots of Equilibrium Isotherms for Cr (VI) Removal by RHA

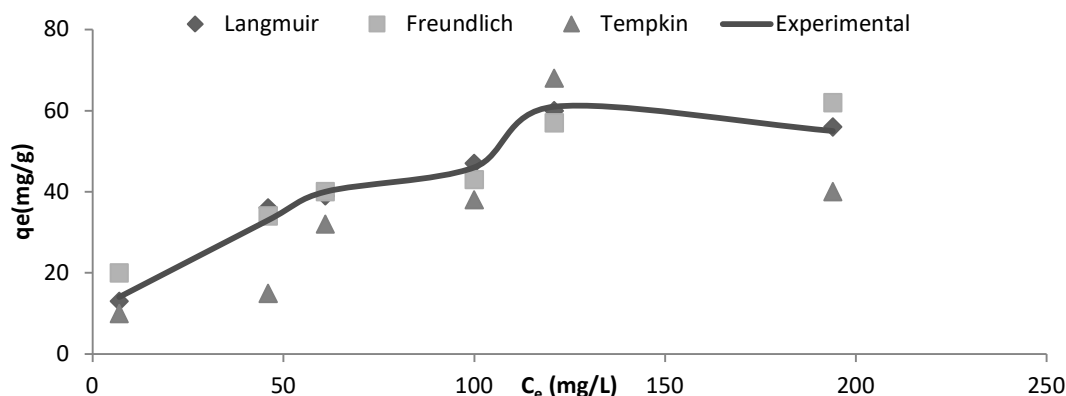


Figure II: Plots of Equilibrium Isotherms for Cr (VI) Removal by RHS

b. Effect of Adsorbent Dosage

The effect of adsorbent dosage on the sorption of Cr (VI) ions onto the adsorbents (RHA and RHS) was assessed via isotherm experiment at varied dosages of the adsorbent (0.1- 1.0 g) and the result obtained is presented in Figure II. The results showed that the amount (%) of Cr (VI) removed from the system increases with adsorbent dosage increment. As the adsorbent dosage increases there is a corresponding increase in the number of active sites available for adsorption of the adsorbate per unit volume of solution, which leads to an increase in the removal efficiency. There was increase in percentage removal from 0.4% to 39% for RHA and 18% to 58% for RHS as the dosage was increased from 0.1 g to 0.5 g but it became negligible at a higher adsorbent dose (> 6 g) as a result of setting in of equilibrium and then saturation of the adsorbent surface with the adsorbate ions which makes removal efficiency to become almost constant. Furthermore, it could be observed that RHS was more effective than RHA as observed by the amount (%) removal achieved which is as a result of its higher surface area as determined by the Sears method (see Table II). The high RHS surface provides more active sites (areas) for the chromium ions to interact with. Hence, increase in percentage removal.

Table II: Surface area and pH_{pzc} of RHS and RHA.

Rice Husks	Surface Area (m^2/g)	pH_{pzc}
RHA	211	8.9
RHS	260	4.6

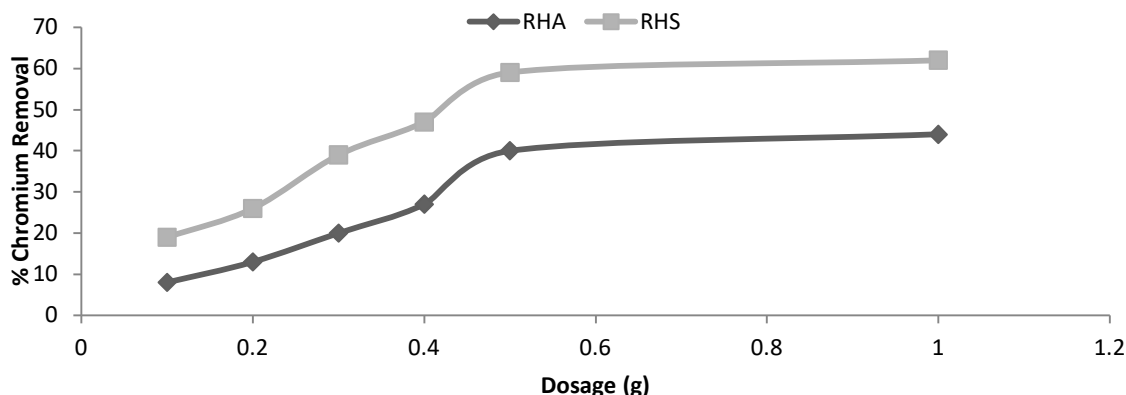


Figure II: Plots of Effect of Adsorbent Dosage on Cr (VI) Removal by RHS and RHA

c. Effect of Initial Solution pH.

The influence of the initial chromate solution pH (pH_0) studied at a pH range of 2-11 on the extent of its adsorption by the adsorbents is shown in Figure III. The results obtained showed that the amount of chromium ion removed increased per gram of the adsorbents as the pH_0 was increased. At solution $pH > 6$, biosorption of Cr (VI) was higher compared to $pH < 4$. Hexavalent chromate removal from solution increased from 3% at pH of 2 to 39% at pH of 11 for RHA, and from 9% at pH 2 to 47% at pH11 for RHA. The efficiency of a sorption process is basically affected by pH due to its influence on both the adsorbate and adsorbent moieties: it affects the degree of ionization and speciation of the adsorbate and the surface charge of the adsorbents (Zarrabi et al., 2014).

To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{PZC}) of the adsorbent. The pH value at which the surface charge is zero is called the point of zero charge (pH_{Pzc}). When the $pH < pH_{Pzc}$ the surface of the adsorbent is positive and is favoured for adsorption of anions while at $pH > pH_{Pzc}$, the surface is positive and cations adsorption is favoured. In the present study, the pH_{Pzc} obtained for the adsorbents was found to be 8.9 and 4.6 for RHA and RHS respectively. As the initial pH of the adsorbate increases, the surface of the adsorbent become negatively charged, which favours electrostatic interaction with the cationic chromium ions in solution. This explains why biosorption of the chromium ions increased with increase in initial solution pH and the amount removed (%) in alkaline environments was higher than in the acidic environment.

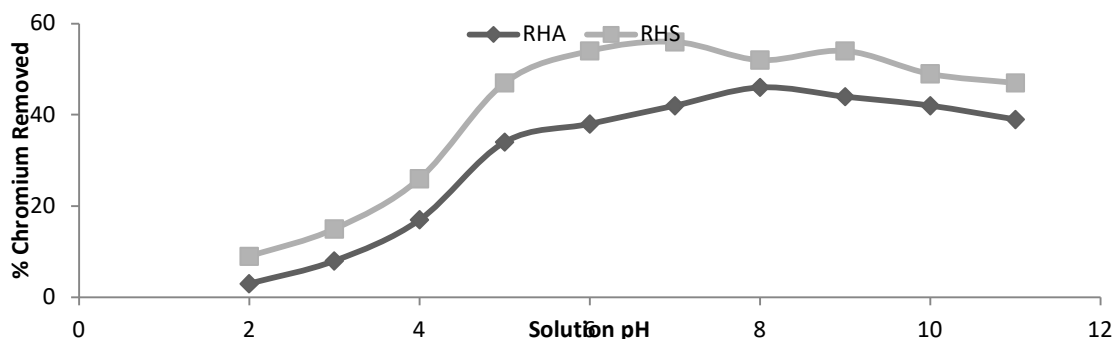


Figure III: Plots of Effect of Initial Solution pH on Cr (VI) Removal by RHS and RHA

Estimation of Energy of Sorption

Experimental sorption data obtained from the equilibrium isotherm studies was fitted into the Dubinin – Radushkevich (DR) equation (8) to estimate the energy of the sorption process of Cr (VI) onto the adsorbents (RHS and IRS). The DR linear isotherm equation is expressed as:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \tag{8}$$

Where, q_m (mol/g) is DR saturation capacity and K_{DR} is the DR constant related to adsorption energy (mol^2/kJ^2). ε (Polanyi potential) is calculated as:

$$\varepsilon = RT \left(1 + \frac{1}{ce} \right) \tag{9}$$

The DR parameters q_m and k , calculated from the intercept and slope of the plots of $\ln q_e$ against E^2 were 66.0724 mol/g and $0.00012 \text{ mol}^2/\text{kJ}^2$ for RHS and 51.7815 mol/g and $0.000008 \text{ mol}^2/\text{kJ}^2$ for RHA, respectively. Elucidation of the energy of sorption process is evaluated by determining the mean free energy of adsorption (E_{DR}). E_{DR} (J/mol) is the free energy change per molecule of the adsorbate when transferred from infinity in solution to the surface of the active sites of the adsorbent (Slivijic et al., 2009). E_{DR} is calculated as follows:

$$E_{DR} = \frac{1}{\sqrt{2K_{DR}}} \quad (10)$$

According to Pils and Laird 2007, the magnitude of E_{DR} determines and classifies the type of adsorption as chemisorption or physisorption. A physisorption process has the value of E_{DR} ranging between 1-16 kJ/mol, while adsorption processes with E_{DR} magnitude greater than 16 kJ/mol is termed chemisorption. The E_{DR} obtained for the sorption of Cr (VI) onto RHS was 290.22 kJ/mol and 119.09 kJ/mol for RHA, respectively. The values of E_{DR} obtained for sorption process in this study is greater than 16 kJ/mol, an indication that the mechanism of interaction between the adsorbent and the adsorbate is chemisorption. This is an indication of chemisorption as the prevailing mode of interaction between the sorbate Cr (VI) and adsorbents as confirmed from the kinetic of sorption studies (reported elsewhere) in which pseudo second order kinetic model prevailed.

Conclusion

The present study shows that the RHS and RHA are effective adsorbents for the removal of Cr (VI) from aqueous solution. Higher percentage of the adsorbate removal by RHA and RHS were possible provided that the initial chromate solution concentration (c_0) was low. Optimum conditions for Cr removal were found to be $\text{pH}_0 > 6$, adsorbent dosage = 0.5 g/ 200 ml of solution of solution for Cr concentration up to 500 mg/L. The equilibrium between adsorbate in the solution and on the adsorbent surface was practically achieved in 2 h. The Langmuir models suits the experimental data better than other models considered with maximum adsorption capacities of RHA and RHS been found to be 55.98 mg/g and 67.45 mg/g respectively. The abundance and affordable (cheap) cost of rice husks justifies its use as a precursor in the preparation of rice husk ash and silica as effective adsorbents for chromium removal from industrial effluents.

Conflict of Interest

The authors wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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