

Comparative Study of the Adsorption of Cu (II) and Cr (VI) Ions from Aqueous Solution Using Raw *Annona squamosa*

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Abstract: In this study the adsorption of heavy metal Cu (II) and Cr (VI) ions using raw carbon from *Annona squamosa* (RAS) was carried out [1]. The use of cheap eco friendly adsorbents prepared from freely and abundantly available *Annona squamosa* (RAS) seed have been investigated by batch methods. The effects of pH, concentration, adsorption capacity have been investigated. Adsorption capacity of *Annona squamosa* (RAS) was showed highest value around pH=5 for Cu (II) ions and pH=2 for Cr (VI) ions. The applicability of the linear form Langmuir model to RAS was proved by the high correlation coefficients $R^2=0.9994$ for Cu (II) ion adsorption and low $R^2=0.9817$ value for Cr (VI) ions. The results of this investigation show that raw carbon was prepared from *Annona Squamosa* seed (RAS) was higher adsorption capacity for removal of Cu (II) ions than Cr (VI) ions from aqueous solutions. The equilibrium adsorption is achieved in 1hr 20 min for Cu (II) and 1hr 30 min for Cr (VI). The isotherms like Langmuir and (D- R) were well fitted for adsorption of Cr (VI) ions and Langmuir, Elovich, Freundlich and Dubinin – Radushkevich (D-R) were well fitted for adsorption of Cu (II) ions. Monolayer adsorption behavior was explained using Langmuir-type isotherm for adsorption of Cu (II) and Cr (VI) ions. The kinetic study of Cu (II) and Cr (VI) ions and were explained using Pseudo-first-order, Pseudo-second-order, Elovich and Intraparticle diffusion equations.[2]

Keywords: *Annona squamosa*, Adsorption, Desorption, Kinetics, Adsorption isotherm

1. Introduction

The contamination of natural and Industrial water by heavy metals is recognized as a major environmental concern due to the impact and persistence of these pollutants. People have paid attention to it which will make us sick such as cancer or even make us to die. Among the heavy metals arsenic, copper, cadmium, lead, mercury, nickel and zinc are severely affected the environment. It will established that the presence of heavy metals in the environment even moderate concentration is responsible for producing a variety illness related with risk of dermal damage and respiratory diseases[3]. Chromium compounds are widely used in industries such as leather tanning, electroplating manufacture of dye, paint and paper. Chromium exists in the aqueous mainly in Cr (III) and Cr (VI) oxidation states. The hexavalent form has been most hazardous due to its carcinogenic properties. Cr (VI) causes skin irradiation resulting in the ulcer formation. Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu based agri-chemicals [4]. Continued inhalation of Copper containing sprays is linked with an increase in lung cancer among workers. Copper sulphate is used widely as an algicide in ponds and even in water supply reservoirs.

Hence removal of Cu (II) ions and Cr (VI) ions from waste water assumes importance. The conventional method for heavy metal removal from waste water includes oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. [5] Among all adsorption is highly effective and economical. Though the raw *Annona Squamosa* (RAS) carbon is a well-known

adsorbent for the removal of heavy metals from waste water, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence several research workers used different low-cost adsorbent such as coconut coir pith, sawdust, sludge ash banana pith, activated phosphate rock vermiculite and monotrillonite. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of Chromium and Copper metal ions from aqueous solution

The objective of the present study is to evaluate the capacity of *Annona squamosa* as adsorbent (RAS) using the adsorption process. Several isotherms and kinetic models were used to evaluate the adsorbents. Condition parameters such as contact time pH, initial concentrations and adsorbent concentration were considered [6].

2. Materials and Methods

2.1. Materials

To able to carry out the experiment, Mortar Pestle, DEEP VERSION model EI pH meter. (model MSW 275) at 150 rpm, weighing balance, Electric oven, UV visible spectrophotometer, and desiccators are required. Other apparatus used were test tubes, watch glasses, polythene bags, crucible, measuring cylinders, spatula, conical flask, and plastic containers. Reactions were carried out using standard method [7].

2.2 Methods

2.2.1 Sample collection

Samples of *Annona squamosa* plant was used for fencing purpose. The fruit was rich in protein and after using this fruit, the seed is used as good adsorbent by activating it in different methods. The seed was collected from house in Andrapradesh.

2.2.2 Preparation of Adsorbent

The 5kg dried *Annona Squamosa* seed is soaked with distilled water and dried. Then the dried seed was powdered well and preserved in desiccators for further use [8].

2.2.3 Preparation of Copper and Chromium solution and analysis

Analytical grade chemical reagents were used to prepare stock solutions. 1000 mg/L of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1g of $\text{K}_2\text{Cr}_2\text{O}_7$ were prepared as stock solutions [9]. The solutions were used for further experimental studies. The pH values were adjusted with 0.1M HCL or 0.1M NaOH. Analytical grade reagents were used throughout this study. The Cu (II) ion and Cr (VI) ions content in the adsorption solutions was determined by UV visible spectrophotometer [10].

3. Desorption

Desorption helps to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal. After adsorption experiments the Cu (II) and Cr VI) were

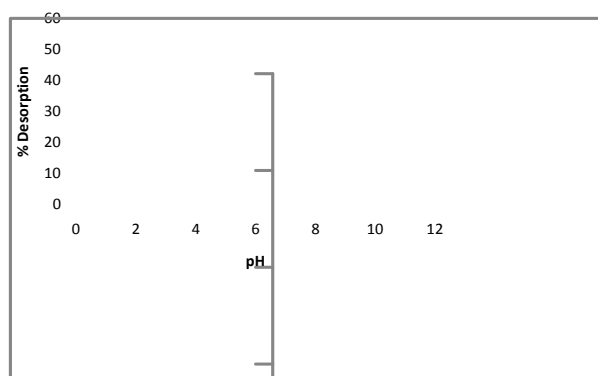


Figure 1: Desorption of Cr (VI) onto RAS

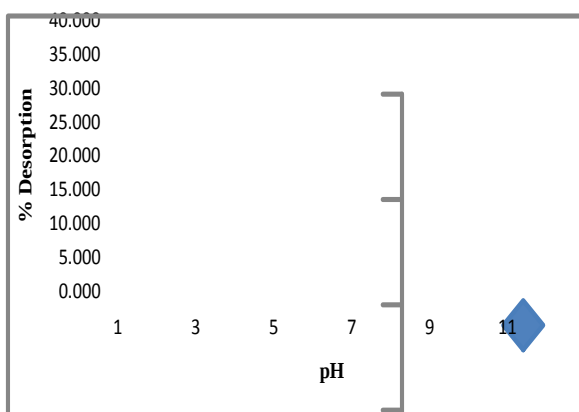


Figure 2: Desorption of Cu (II) onto RAS

separated out by filtration using Whatman filter paper No. 42 and the filtrate was discarded. The Cu (II) and Cr (VI) loaded RAS was given a gentle wash with double-distilled water to remove the non-adsorbed Cu (II) Cr (VI) if present. The metal loaded samples were agitated with different concentrations of HCl and NaOH solutions (0.5 – 2.0N) for 120 min. The maximum desorption were obtained for Cr (VI) at pH 6 and for Cu(II) at pH 3. [11].

4. Results and Discussion

4.1. Characterization

4.1.1 Scanning electron microscope

Scanning electron microscope (SEM) of *Annona squamosa* after and before adsorption clearly indicates that adsorbents had an irregular and porous surface, which indicated high surface areas. Thus, there was substantial adsorption on the biotic material (crushed *Annona squamosa* seed) (Fig.3a) before loading Cu(II) and Cr(VI), (Fig b and c) were Cu(II) and Cr(VI) after loading gets adsorbed onto RAS . In aqueous medium, RAS get swelled and their surface area increases to adsorb quite good quantity of Copper and Chromium [12].

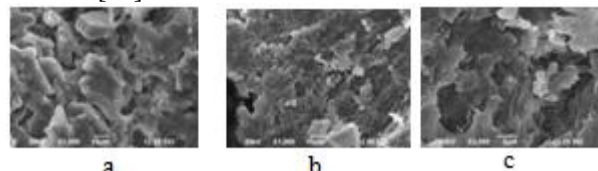


Figure 3: a. SEM image of RAS, b. RAS with Cu (II) c. RAS with Cr (VI)

4.1.2 Point of zero charge

The determination of the point of zero charge (pH_{zpc}) was done to investigate the surface charge and acid and basic characters of the adsorbent. For the determination of pH_{zpc}, 0.2g of the sample suspension was prepared in 50mL of NaNO_3 . Aliquots of suspension were adjusted to various pH values with dil. NaOH and HNO_3 . The suspensions were shaken for 2 hrs at 150 rpm. The final pH values were measured. [13]. The graph was plotted between initial and final pH and the point of Zero charge was determined. Figure 4 indicates that zero point charge for RAS is found to be 4.3. From this result zero point charge (pH_{zpc} 4.3 for (RAS)) is below the solution pH (pH = 5) hence negative charge density on the surface of RAS increased, so it is favours the adsorption of metal ions.[14]

4.1.3 Acidity and basicity of adsorbent (Boehm titration)

Acidity and basicity were estimated by mixing 0.2 g of RAS with 20 ml of 0.05 M NaOH, in a closed flask separately and agitating for 48 h at room temperature. Filtered and 5 ml of the filtrate was pipette out and titrated with 0.05 M HCl. This titration shows the number of acidic, basic, phenol, carboxyl sites. For RAS, the number of acidic sites present was found to be 1.756 m.mol/g, the number of basic sites was found to be 2.14 m.mol/g.[15]

4.1.4 Iodine value of the adsorbent

The iodine numbers of commercial adsorbents vary from 300 to 1,200 mg/g. Because the iodine molecule is relatively small, iodine number can be correlated with ability to absorb low-molecular-weight substances and provides a measure of surface area or capacity available to small molecules. The higher the iodine value, the higher will be the adsorption ability of the adsorbents. The iodine value of RAS was found to be 798.23 mg/g [16].

Table 1: Physico-chemical Characteristics of RAS

S.No	Parameters	RAS
1.	Yield (%)	60.3
2	Moisture content (%)	7.821
3	Ash content (%)	9.854
4	pH	6
5	Zero point charge (pHzpc)	4.3
6.	Iodine Value (mg/g)	798.23

5. Batch Adsorption Studies

5.1 Effect of pH on Cu (II) ions and Cr (VI) ions adsorption onto (RAS)

The results of the pH effect in the adsorption process were analyzed. The effect of pH changes due to the adsorbent type, its behavior in the solution and the type of ions in adsorbed. In this study, the optimum pH value for the Cu (II) ions and Cr (VI) were determined as pH=5 and pH=2. So further experiments were carried on by using this selected value [17].

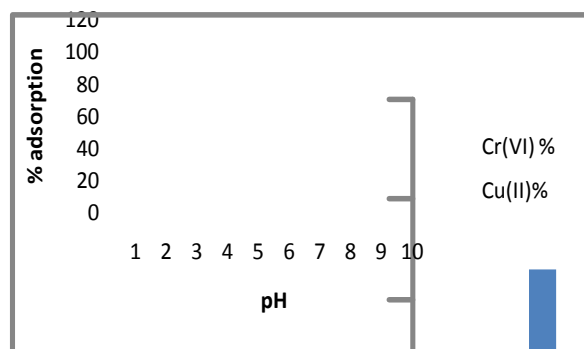


Figure 4: Effect of system pH on the adsorption of Cu (II) ions and Cr (VI) ions onto adsorbent (RAS)

5.2. Effect of adsorption dose on the adsorption of Cu (II) ions and Cr (VI) ions onto Adsorbent (RAS)

To observe the effect of adsorbent dose on metal adsorption different amounts of adsorbent 0.2g, 0.4g, 0.6g, 0.8g, and 1g were added into initial concentration of 50 mg/L solution. The mixtures were shaken in 250 mL stopperd flask at 25°C at pH=5 for Cu (II) and pH=2 for Cr (VI) until equilibrium time was reached. Separate mass of RAS was taken into 5

beakers containing 50mL of metal solution of initial concentration of 20mg/L. the solutions were agitated at a fixed stirring speed of 150 rpm for a predetermined contact time of 1 hr 20 min and fixed pH value 5 for Cu(II) ions and 1 hr 30 min and pH value 2 for Cr (VI) ions .The final concentration of solutions were determined by UV visible Spectrophotometer and the percentage removal of Cu (II) and Cr (VI) ions were determined .

5.3. Effect of contact time on the adsorption of Cu (II) ions and Cr (VI) ions onto Adsorbent (RAS)

The effect of dosage and contact time on the removal of Cu(II) and Cr (VI) ions increase of adsorbent dosage from 0.2g to 1g the removal of Cu (II) and Cr (VI) ions were observed at the beginning of the contact time. Following the rapid removal, the removal rate decreased, and an apparent equilibrium was reached after 1 hr 20 min hours for Cu (II) and 1hr 30 min for Cr (VI) ions depending upon on the adsorbent dosage [18]. The high removal rate at the start of the contact time was due to the large amount of surface area available for adsorption of the Cu (II) and Cr (VI) ions. At this stage, the adsorption mainly occurred on the surface of the adsorbent. After the rapid uptake, the capacity of the adsorbent became exhausted and the adsorption would be replaced by the transportation of Cu (II) and Cr (VI) ions from the external sites to the internal sites of the adsorbent particles. Therefore the uptake late began to drop down [19].

5.4. Effect of Initial metal ion concentration of the adsorption of Cu (II) ions and Cr (VI) ions onto Adsorbent (RAS)

The effect of initial metal ion concentration provides an important to evaluate the adsorption process and adsorption capacity. The results shows the effect of initial Cu(II) and Cr(VI) concentration (50 – 250mgL⁻¹) with time is shown in Fig.3 From the results adsorption of Cu (II) and Cr (VI) increases very rapidly upto 85 min . Following the rapid removal, the removal rate decreased, and an apparent equilibrium was reached after 1 hr 30 min and 1hr 20 min depending the uptake of Cu (II) and Cr (VI) ions onto RAS with increase in the Cu (II) and Cr (VI) ions concentration from 50 to 200 mg g⁻¹the percentage removal decreased. The decrease in percentage can be explained that all absorbent had a limited number of active sites, which would have become saturated above a certain concentration may be due to the higher adsorption rate and utilization of all the available sites for the adsorption at higher adsorption rate and all available sites for the adsorption at higher concentration [20].

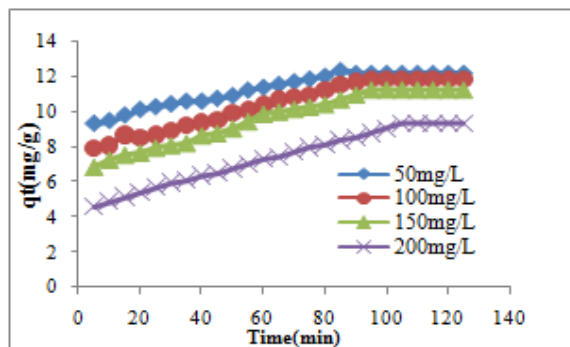


Figure 5: Effect of contact time of the adsorption of Cr (VI) onto RAS

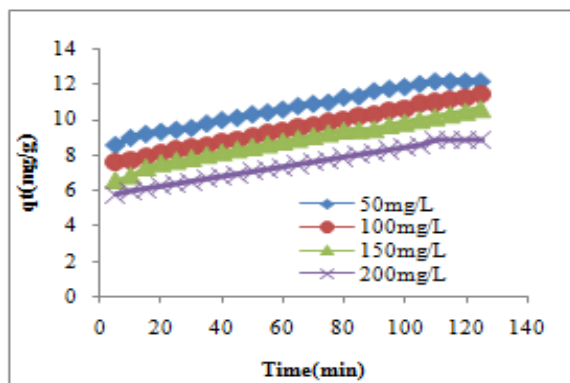


Figure 6: Effect of contact time of the adsorption of Cu (II) onto RAS

6. Adsorption isotherm investigation

6.1. Langmuir isotherm:

Table .2 indicates that Langmuir model has perfectly application of copper and chromium sorption with a regression coefficient, R^2 equal to Cu (II) (0.9994.mg/g) and Cr (VI) (0.9817 mg/g), respectively. The Langmuir non-linear equation is commonly expressed as followed:

$$q_e = (Q_m K_a C_e) / (1 + K_a C_e) \quad (1)$$

In equation (1) q_e and C_e were the (q_e) amount of Cr (VI) and Cu (II) ions adsorbed at equilibrium onto carbon, (C_e) equilibrium liquid- phase concentration of Cr (VI) and Cu(II) ions, Q_m is a constant and reflect a complete monolayer (mgg^{-1}) K_a is the adsorption equilibrium constant (Lmg^{-1}) that is related to the apparent energy of sorption.

The Langmuir isotherm equation (1) can be literalized into the following form.

Langmuir-1

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \left(\frac{1}{Q_m} \times C_e \right) \quad (2)$$

A Plot of C_e/q_e versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $(1/K_a Q_m)$.

The applicability of the linear form of Langmuir model to RAS was proved by the high correlation coefficients $R^2=0.9994 \text{ mg/g}^{-1}$ for Cu (II) and 0.9817 mg/g^{-1} for Cr (VI)

ion. This suggests that the Langmuir isotherm provides a good model of the sorption system.

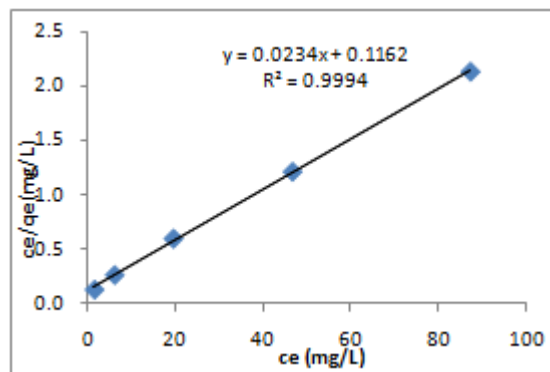


Figure 7: Langmuir plot for adsorption of Cu (VI) onto RAS

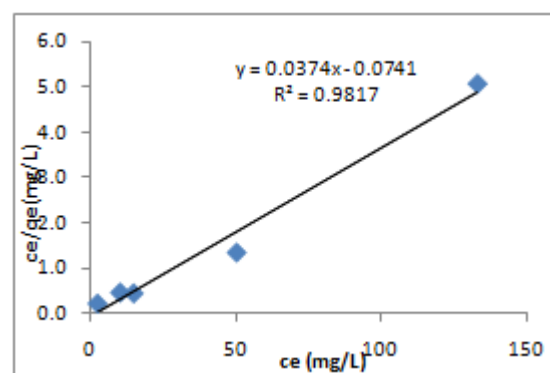


Figure 8: Langmuir plot for adsorption of Cr (VI) onto RAS

6.2 The Freundlich isotherm:

The Freundlich isotherm models earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation [21].

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where K_F is a constant for the system, related to the bonding energy, K_F can be defined as the adsorption or distribution co-efficient and represents the quantity of metal absorbed onto adsorbent for unit equilibrium concentration $1/n$ is indicating the adsorption intensity of metal onto the adsorbent surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of co-operative adsorption equation 4. and the Freundlich constants can be determined.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The applicability of the Freundlich adsorption isotherm was also analyzed using the same set of experimental data, by

plotting $\log(q_e)$ versus $\log(C_e)$. The data obtained from linear Freundlich isotherm plot for the adsorption of the metal onto RAS presented in table 1. The correlation coefficients for Cu (II) are 0.944 mg g^{-1} and Cr (VI) 0.5199 mg g^{-1} showed that the Freundlich model Cu (II) is comparable to the Langmuir model. The $1/n$ is lower than the 1.0 indicating Cu (II) ions is favorably adsorbed by RAS [22].

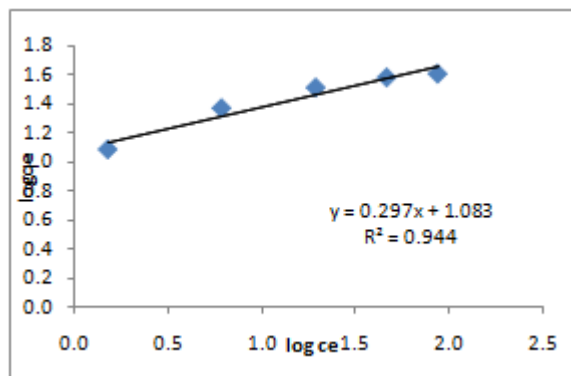


Figure 9: Freundlich plot for adsorption of Cu (II) onto RAS

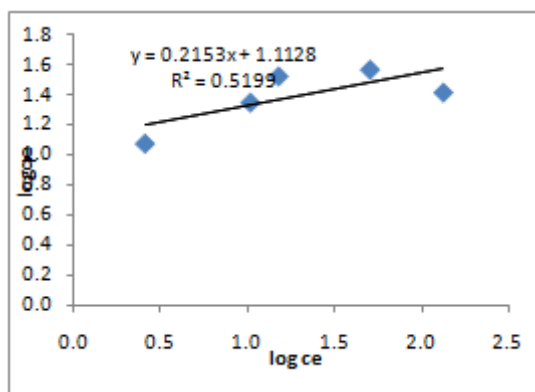


Figure 10: Freundlich plot for adsorption of Cr (VI) onto RAS

6.3 The Temkin isotherm

Temkin adsorption isotherm model was used to evaluate the adsorption potentials of the RAS for Cu (II) ions and Cr (VI) ions. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (5)$$

The Temkin isotherm equation (5) can be simplified to the following equation.

$$q_e = \beta \ln a + \beta \ln C_e \quad (6)$$

where $\beta = (RT)/b$, T is the absolute temperature in Kelvin and R is the Universal gas constant, $8.134 \text{ J (mol K)}^{-1}$.

The constant b is related to the heat of adsorption. The adsorption data were analyzed according to the linear form of Temkin isotherm equation [6]. Examination of the data shows that the Cu (II) adsorption the linear isotherm constants and coefficients of determination are presented in table 2. The correlation coefficient R^2 obtained from Temkin

model were comparable to that obtained for Langmuir and Freundlich equations which explain the applicability of Temkin model to the adsorption of Cu (II) onto RAS [23].

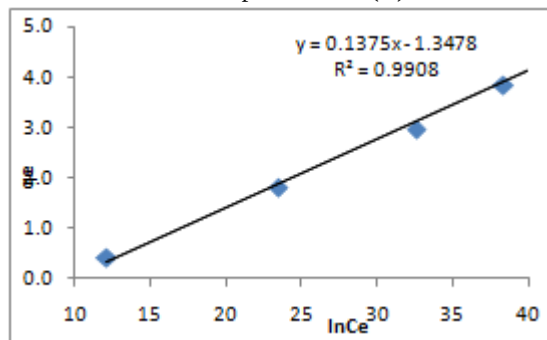


Figure 11: Temkin plot for adsorption of Cu (II) onto RAS

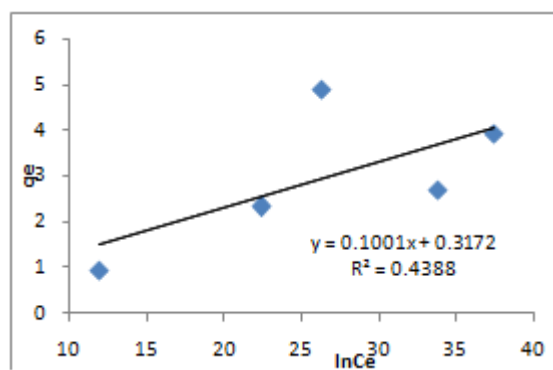


Figure 12: Temkin plot for adsorption of Cr (VI) onto RAS

6.4 The Dubinin-Radushkevich (D-R) Isotherm The D-R model was also to estimate the porosity apparent free energy and the characteristics of adsorption. It can be used to describe adsorption on both homogenous and heterogeneous surfaces. The D-R equation can be defined by the following equation: 7.

$$\ln q_e = \ln Q_m - K \epsilon^2 \quad (7)$$

Where K is a constant related to the adsorption energy, Q_m (mg g^{-1}) is the theoretical saturation Capacity is the ϵ Polanyi potential, calculated from equation

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

The slope of the plot of $\ln q_e$ versus ϵ^2 gives K ($\text{mol}^2 (\text{KJ}^2)^{-1}$) and the intercept yields the adsorption capacity Q_m (mg g^{-1}). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation. 9

$$E = 1/\sqrt{2K} \quad (9)$$

The calculated value of D-R parameters is given in table 2. The saturation adsorption capacity Q_m obtained using D-R isotherm model for adsorption of Cu (II) and Cr (VI) onto RAS is 0.9656 mg g^{-1} and 0.8369 mg g^{-1} at $0.2 \text{ g}/50 \text{ mL}$ adsorbent dose. This is close to that obtained ($0.9817 \text{ mg g}^{-1}/0.9994 \text{ mg g}^{-1}$) from the Langmuir isotherm model (table 2) The values of E calculated using equation .9 is $0.2659 \text{ kJ mol}^{-1}/0.3322 \text{ kJ mol}^{-1}$ which indicates that the physical sorption

process plays a significant role in the adsorption of Cu (II) and Cr (VI) onto RAS [24].

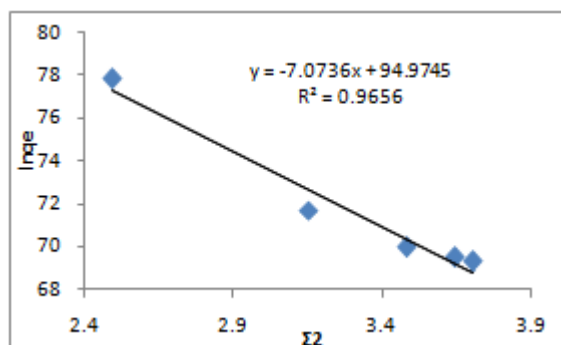


Figure 13: D-R plot for adsorption of Cu (II) onto RAS

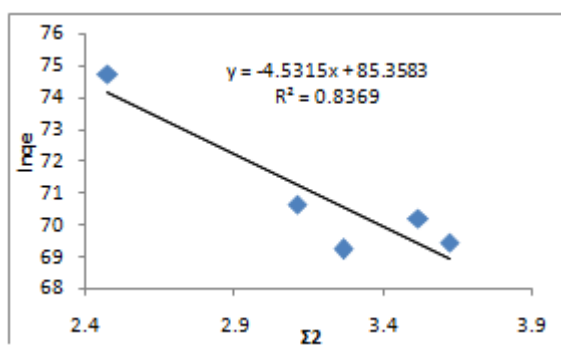


Figure 14: D-R plot for adsorption of Cr (VI) onto RAS

Table 2: Comparison of the coefficients isotherm parameters for Cu (II) and Cr (VI) adsorption onto RAS

S.No	Isotherm Model	Metal Cu(II)	Metal Cr(VI)
1	Langmuir		
	$Q_m(\text{mg.g}^{-1})$	42.73	26.73
	$K_a(\text{L.mg}^{-1})$	0.2013	2.7713
2	Freundlich		
	$1/n$	4.644	0.297
	$K_f(\text{mg.g}^{-1})$	12.96	12.10
3	Temkin		
	$\alpha(\text{L.g}^{-1})$	5.3502	5.5594
	$\beta(\text{mg.L}^{-1})$	0.1375	0.1375
4	Dubinin-Radushkevich		
	$Q_m(\text{mg.g}^{-1})$	218.73	196.58
	$K (\times 10^{-5} \text{mol}^2 \text{KJ}^{-2})$	7.0736	4.5315
	$E(\text{KJ mol}^{-1})$	0.2659	0.3322
	R^2	0.9656	0.8369

7. Adsorption Kinetics

7.1 Kinetic Models Applied To the Adsorption of Cu (II) Cr (VI) onto RAS

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; Kinetic models are used to test experimental data from the adsorption of Cu (II) and Cr (VI) adsorption onto RAS. The kinetics of Cu (II) and Cr(VI) adsorption onto RAS required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of

adsorption rate, give important information for designing and modeling the adsorption processes. Thus the kinetics of Cu (II) and Cr (VI) onto RAS were analyzed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close or equal to 1) higher value is the more applicable model to the kinetics of Cu (II) and Cr(VI) adsorption onto RAS [25].

7.2 Pseudo- First –Order Equation

The pseudo-first order equation of Lagergren is generally expresses as follows:

$$dq_t/dt = k_1(q_e - q_t) \quad (10)$$

Where q_e and q_t (mg.g^{-1}) are the adsorption capacity at equilibrium and at time t respectively, k_1 (L.min^{-1}) is the rate constant of pseudo-first-order adsorption [26]. Integrating Eq. (10) for the boundary conditions $t = 0 \rightarrow t$ and $q_t = 0 \rightarrow q_t$ gives

$$\log(q_e/(q_e - q_t)) = k_1/2.303 \times t \quad (11)$$

Equation (11) linear form:

$$\log(q_e - q_t) = \log(q_e) - k_1/2.303 \times t \quad (12)$$

The values of q_e and k_1 for the pseudo-first-order kinetic model were determined from the intercepts and the slopes of the plots of $\log(q_e - q_t)$ versus time (Figure 15) The K values R^2 values and q_e values are summarized in Table 2.

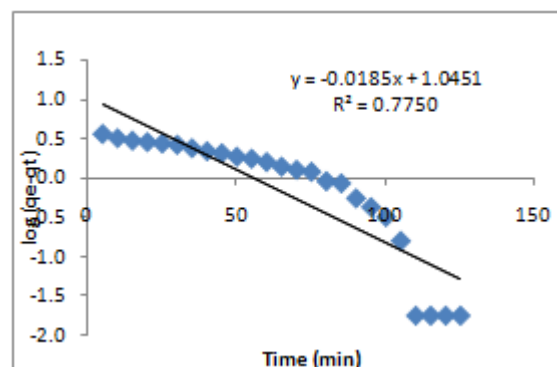


Figure 15: Pseudo- first-order kinetics for Cu (II) onto RAS.

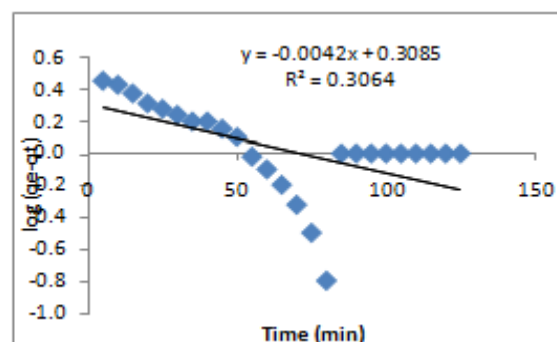


Figure 16: Pseudo- first-order kinetics for Cr(VI) onto RAS.

7.3 Pseudo-Second-order-equation

The adsorption Kinetics may be described by the Pseudo-Second-order model. The differential equation is generally given as follows:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (13)$$

Where k_2 ($\text{g}(\text{mg min})^{-1}$) is the second-order rate constant of adsorption. Integrating Eq.(13). For the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$ is simplified as can be rearranged and linear equation is: [27]

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2}\right) + 1/q_e(t) \quad (14)$$

This second-order rate constants were used to calculate the initial sorption rate

$$h = k_2 q_e^2 \quad (15)$$

Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t . The linear plots of t/q_t versus t show good agreement between experimental and calculated q_e values at $0.2\text{mg}/50\text{mL}$ adsorbent concentrations (table 2). The correlation coefficients for the Second-order Kinetic model are for Cu (II) is 0.9935 and for Cr (VI) is 0.9979 the adsorption constant (q_m) was close to experimental value, which led to believe that pseudo-second-order Kinetic model provided good correlation for the bio adsorption of Cu (II) and Cr (VI) onto RAS [28].

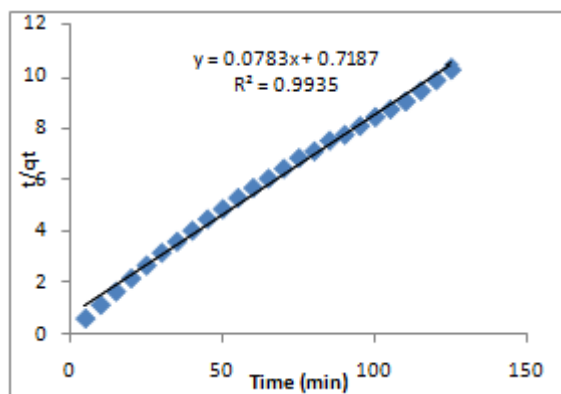


Figure 17: Pseudo- second-order kinetics for Cu (II) onto RAS

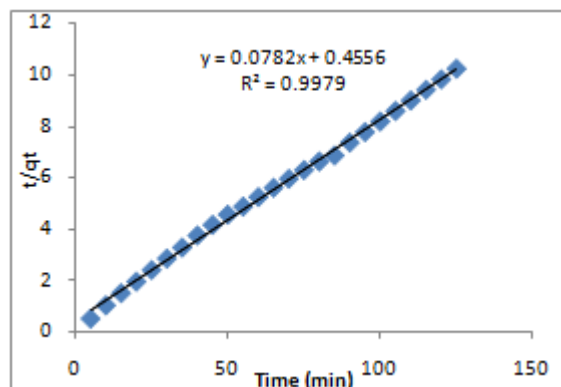


Figure 18: Pseudo- second-order kinetics for Cr (VI) onto RAS.

7.4 Elovich Equation

The Elovich equation is another rate equation based on the adsorption capacity generally expressed as

$$dq_t/dt = B_E \exp(-A_E q_t) \quad (16)$$

Where B_E is the initial adsorption rate ($\text{mg}(\text{g min}^{-1})$) and A_E is the de-sorption constant (g mg^{-1}) during any experiment. It is simplified by assuming $A_E B_E \gg t$ and by applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$ equation (16) can be written as follows [29]:

$$q_t = 1/A_E \ln(B_E A_E) + 1/A_E \ln(t) \quad (17)$$

If Cr (VI) adsorption by RAS fits the Elovich model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/A_E)$ and an intercept of $(1/A_E) \ln(A_E B_E)$. Thus, the constants can be obtained from the slope and the intercept of the straight line (table 3). The initial adsorption rate A_E for Cu(II) is 1.4401 and for Cr(VI) is 1.2039 $\text{mg}(\text{g min})^{-1}$ for the initial Cu(II) and Cr (VI) concentration of 50mgL^{-1} on RAS dose 0.2g mL^{-1} . Similar pattern is mentioned above for the Initial adsorption rate, h , obtained from pseudo-second-order model [30].

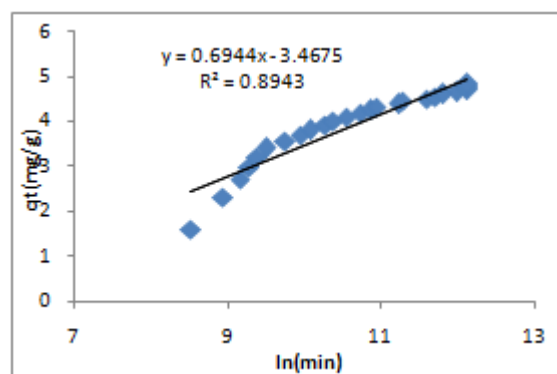


Figure 19: Elovich plot for Cu (II) onto RAS

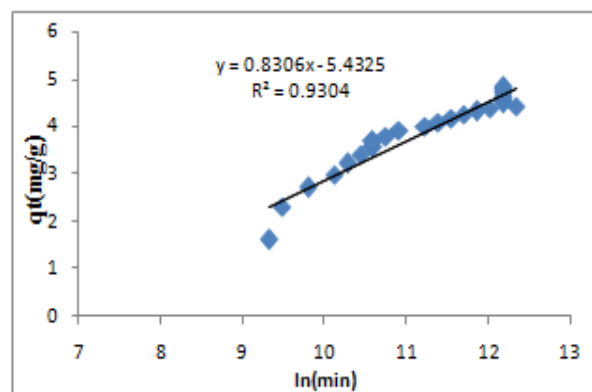


Figure 20: Elovich plot for Cr (VI) onto RAS

7.5 The Intraparticle Diffusion Model

The adsorption mechanism of adsorbent follows three steps viz, film diffusion, pore diffusion and intra-particle transport. The slowest of the three steps controls the overall rate of the process. The slowest of the three steps controls the overall rate of the process. Generally, pore diffusion and intra-particle diffusion are often rate-limiting in a batch reactor, which for continuous flow system film diffusion is

more likely the rate limiting step. The liner form of intra particle diffusion model can be expressed as follows.

$$q_t = K_{diff} \frac{1}{2} + B_L \quad (18)$$

Where K_{diff} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intra-particle diffusion rate constant. The correlation coefficients of the plot range 0.9824 and 0.9587 for the adsorption of Cu (II) and Cr (VI) ions by RAS. If intra-particle diffusion is the sole rate-limiting step, it is for the q_t versus $t_{1/2}$ plots to pass through the origin, which is not the case in this study, it may be concluded that surface adsorption and intra-particle diffusion were currently operating during the Chromium-adsorbent interactions. The evidence for such conclusion is the rate constants of Second-order and intra-particle diffusion, where their values are the highest among other kinetic models.

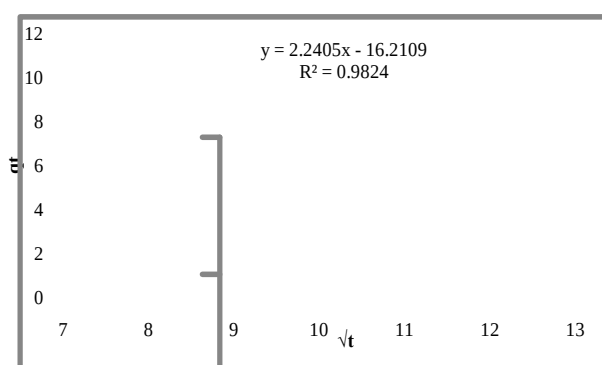


Figure 21: Intra-particle diffusion plot for Cr (VI) onto RAS

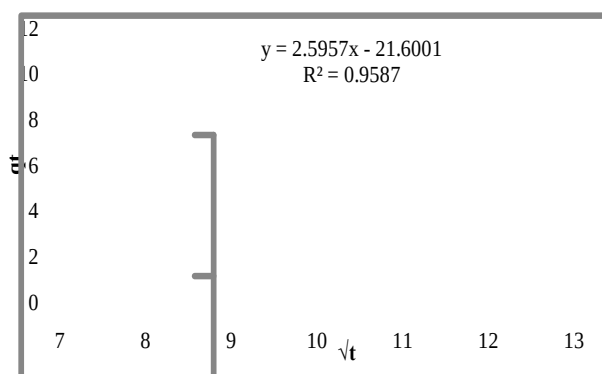


Figure 22: Intra-particle diffusion plot for Cu(II) onto RAS

Table 3: Comparison of first order and second order adsorption data

S. No	Kinetic models	Parameters	Adsorption of Cu (II) onto RAS	Adsorption onto RAS of Cr(VI)
1	First-order kinetic model	K_1 q_e R^2	0.0426 11.094 0.7750	0.0097 2.0248 0.3064
2	Second-order kinetic model	K_2 q_e R^2	0.004 12.77 0.9935	0.003 12.78 0.9979
3	Exp	q_e	12.14	12.18

k_1 (min^{-1}) k_2 (mg min^{-1}), q_e (mg g^{-1})

Table 4: Comparison parameter obtained from the Elovich kinetic model and intraparticle diffusion model

S.No	Kinetic models	Parameters	Adsorption of Cu (II) onto RAS	Adsorption of Cr (VI) onto RAS
1	Elovich	A_E B_E R^2	1.4401 102.306 0.8943	1.2039 574.39 0.9304
2	Intra particle Diffusion	K_{diff} C R^2	2.2405 16.2109 0.9824	2.5957 21.600 0.9587

8. Conclusion

From this study, it was found that Cu (II) has a lower adsorption efficiency compared to Cr (VI) at any given parameters. The equilibrium adsorption is practically achieved in 1 hr 20 min for Cu (II) onto RAS, and 1 hr 30 min are taken for the adsorption of Cr (VI) onto RAS at 5 and 2 pH respectively. The removal efficiency increased agitation time and with initial metal concentrations. The equilibrium data were best described by the Langmuir isotherm model and the adsorption kinetics can be successfully fitted to pseudo-second-order kinetic model with intraparticle diffusion as one of the rate-limiting steps. The Annona Squamosa seed used in this work are freely and abundantly available. The preparation of RAS is agreeing with principles of green chemistry and less time is required to possess high adsorption of Cu (II) and Cr (VI) ions [31]. Therefore, the ecofriendly adsorbent RAS is expected to be environmentally and economically feasible for the removal of Cu(II) and Cr(VI) ions from aqueous solutions. The present study concludes that the RAS was low-cost adsorbents as alternatives to commercial activated carbon for the removal of Cu (II) and Cr (VI) from water and waste water.

9. Future Scope

In addition to my research work there are all possibilities that adsorption rate of the adsorbent may increase by using alternate method of Sulphuric acid activation. The benefit of the research work is to eliminate the water pollution and save the environment.

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