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ADSORPTION OF CR(III) FROM AQUEOUS SYSTEM BY LIME LOADED RICE HUSK CARBON

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Abstract:

Adsorption of Cr(III) from aqueous system is carried out by lime loaded rice husk carbon (LRHC). BET adsorption and BJH desorption analysis of LRHC show the pores are predominantly mesopores. The adsorption of Cr(III) depends on initial concentration of adsorbate, pH of the solution, carbon dosage, agitation time and temperature. As the concentration of Cr(III) is increased, adsorption capacity of LRHC is also increased. When the adsorbent dosage is increased from 1 g to 5 g, adsorption capacity is decreased. The adsorption capacity increases from pH 1 to 3. As the pH increased from 3 to 10, the adsorption capacity had been decreased. Freundlich, Langmuir, Temkin and Dubinin Radushkevich adsorption isotherm models indicate the occurrence of adsorption. Thermodynamic parameters show the bio-sorption is exothermic, spontaneous and reversible. The adsorption is more when the agitation time is 120 min. Kinetics shows the adsorption is pseudo second order reaction. Intra-particle diffusion illustrates the adsorption is both diffusion controlled and surface controlled process. IR spectrum indicates the adsorption is physisorption. SEM analysis of LRHC and metal adsorbed LRHC show the presence of Cr(III). EDX analysis of metal adsorbed LRHC indicate the adsorption of Cr(III).

Key Words: Biosorption, Cr(III), Kinetics, Rice Husk & Sorption Isotherm

1. Introduction:

Cations present in natural water are expected to perform key biological. In addition to Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}, few heavy metal ions like Mn^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+} and Ni^{2+} are useful to catalyze biochemical reactions in biological systems. These ions however in excess amounts can cause toxic effects. The discharge of heavy metals into water is a major concern because they accumulate in living organisms resulting in various disorders. The water containing chromium compounds result from leather tanning, electroplating and chromite industries. Cr(III) is an essential nutrient required for sugar and fat metabolisms. But its long term exposure has been linked to skin allergies and cancer. Chromium can be removed from water by adsorption method.

Modification of Rice Husk with Sulphuric Acid and Lime Treatment:

Cellulose has three hydroxyl groups involved in hydrogen bonding. Lignin and silica reduce binding between functional groupson rice husks' surfaces and adsorbate molecules. Therefore, rice husk[1] needs to be modified before being applied for adsorption of ions. Concentrated sulphuric acid breaks hydrogen bonds, increase porosity and surface area and penetrates into non-crystalline and crystalline domains. Lime treatment of rice husk breaks the covalent association between lingo-cellulose components, and de-polymerizing lignin.

2. Methodology:

The stock solution was prepared by dissolving chromic salt in requisite amount of water. The pH of the suspensions is adjusted with HCl or NaOH to the required value.

The rice husks were dried and treated with conH_2SO_4. The rice husk carbon is soaked with 2% lime solution and the carbon thus prepared was called lime loaded rice husk carbon (LRHC). Experiments were carried out with variables like initial concentrations of adsorbate, adsorbent dosage, time intervals, pH and temperatures usingorbital shaker at 160 rpm. The concentration of Cr(III)was analyzed by Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) method using Perkin Elmer Optima 5300 DV. Adsorption isotherm models were used to interpret the above data. Kinetic studies were carried out to find the order of the reaction and nature of process. Thermodynamics studies were carried out to study the feasibility process. Infrared (IR) spectra was taken from Jasco, FT-IR 4100. Scanning Electron Microscope (SEM) and Energy – dispersive X – ray spectroscopy (EDX) were taken fromSophisticated Analytical Instrument Facility (SAIF), IIT-Madras.

3. Results and Discussion:

Brunauer, Emmett and Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore distribution:

BET surface area[2] was determined by nitrogen adsorption at 77.4 K using micrometrics ASAP 2010 volumetric adsorption analyzer. BET surface area is 19.9 m^2/g (Fig 1). The pore size distribution was calculated using BJH method. The analysis of adsorption / desorption curve shows that the pores are predominantly mesopores. BJH desorption pore area is 22.0 m^2/g. BJH desorption pore volume is 0.053 cm^3/g (Fig 2). BJH desorption pore diameter is 96.26 Å

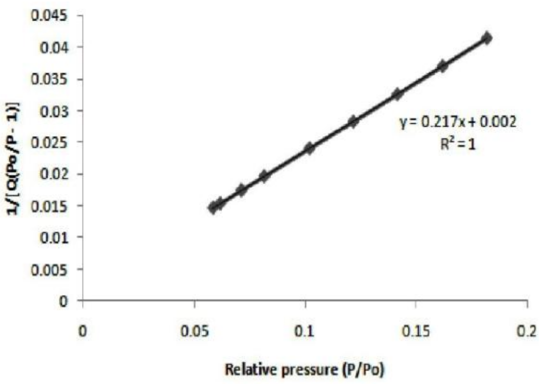

Figure 1: BET surface area plot

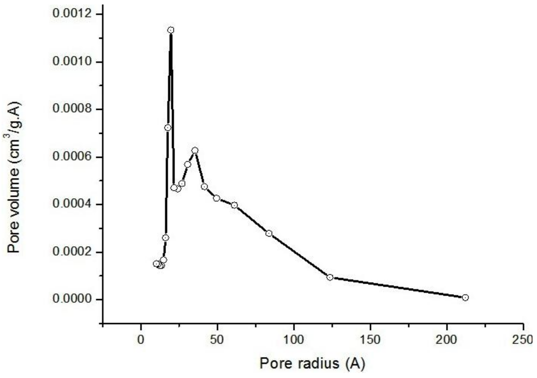

Figure 2: BJH desorption dV/dr pore volume

Effect of Initial Concentration:

Adsorption capacity is calculated using the equation (1)

$$q_e = \frac{(C_0 - C_e)\ V}{1000\ m} \quad .....(1)$$

As the concentration of Cr(III) increased[3] from 40 to 200 mg/L, the loading capacity increased while surface binding site remains constant, higher adsorption of Cr(III) occurs (Fig 3).

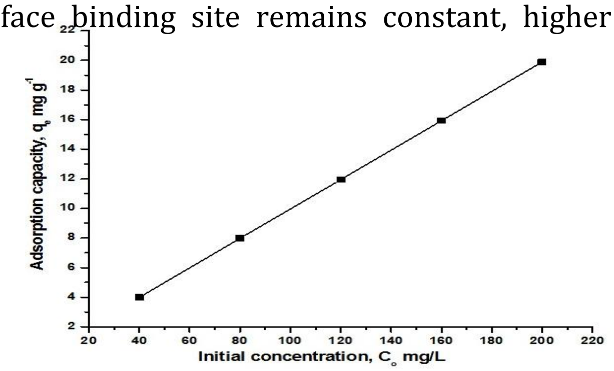

Figure 3: Effect of initial concentration of Cr(III) on adsorption capacity using 1 g of LRHC with pH 3 at 30°C for 2 h

3. Effect of Adsorbent Dosage:

When the adsorbent dosage[4] increased from 1g to 5g/100 ml, the adsorption capacity is decreased. With increase in adsorbent dosage, more surface area is available while the availability of Cr(III) ions remains constant. This indicates that the adsorption capacity is more at lower adsorbent dosage (Fig4).

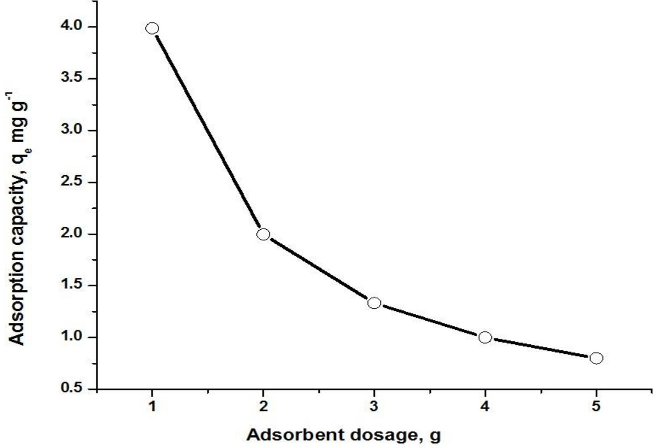

Figure 4: Effect of LRHC on adsorption capacity for 40 mg/L, Cr(III) with pH 3 at 30°C for 2 h

4. Adsorption Isotherms:

Adsorption isotherms indicate the nature of adsorption process.

Freundlich Adsorption Isotherm:

Freundlich adsorption isotherm[5] was explained by the following equation (2)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad .....(2)$$

The values derived from Fig 5 aren = 1.253, 1/n = 0.798, K_F = 20.72 mg/g and R^2 = 0.993. The value of n between 1 to 10 represents favorable adsorption. The heterogeneity is 79.8 % and larger value of K_F indicates higher adsorption for heavy metal ions.

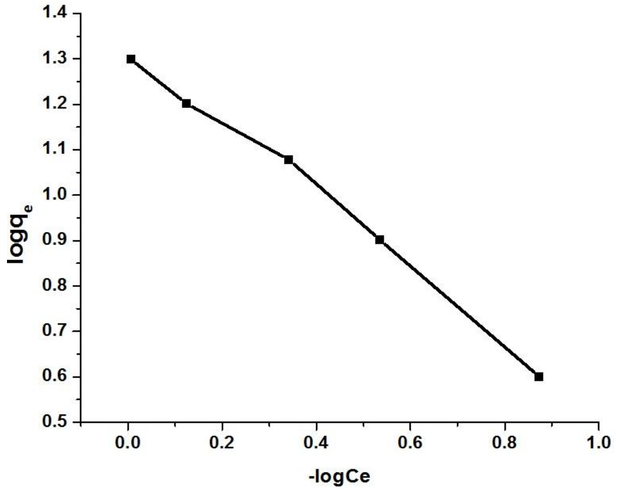

Figure 5: Freundlich isotherm

Langmuir Adsorption Isotherm:

The equilibrium data[6] was explained by the equation (3)

$$C_e/q_e = 1/q_{max}K_L + C_e/q_{max} \qquad .....(3)$$

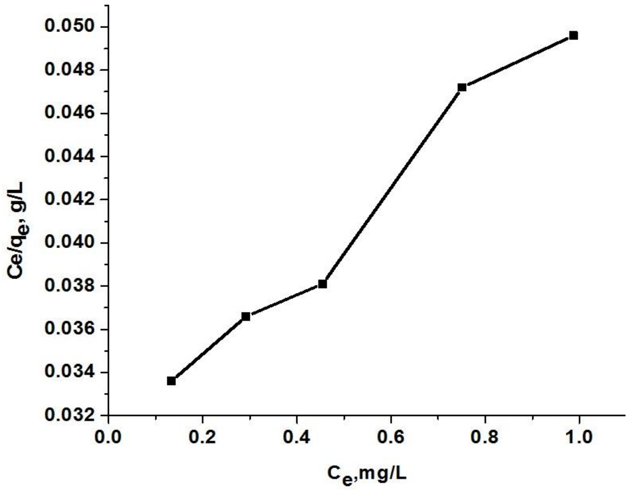

Figure 6: Langmuir isotherm

The values of q_{max} = 50.251 mg/g, K_L = 0.650 L/mg and R^2 = 0.970 show adsorption of Cr(III) (Fig 6). The feasibility of Langmuir adsorption isotherm is expressed in terms of a dimensionless constant equilibrium parameter R_L, which is defined as $R_L = 1/(1+K_L C_o) = 0.037$

The R_L values between 0 and 1 indicate favourable adsorption.

Temkin Isotherm:

Temkin isotherm[7] equation (4) is

$$q_e = B_1 \ln k_T + B_1 \ln C_e \text{ where } B_1 = RT/b_T \qquad .....(4)$$

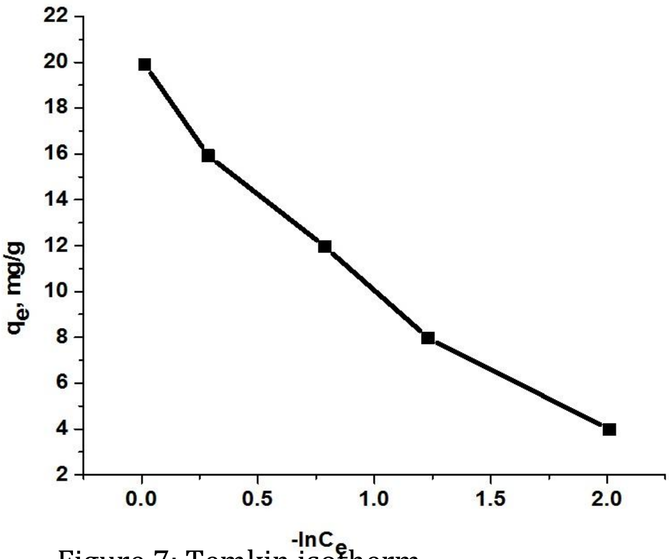

Figure 7: Temkin isotherm

The values of K_T = 10.94 L/g, B_1 = 7.8223 J/mol and R^2 =0.971 indicate the process is physical adsorption in nature (Fig 7).

Dubinin–Radushkevich Isotherm Model:

Dubinin–Radushkevich isotherm[8]equation (5) is.

$$q_e = q_s\, e^{-\beta\varepsilon 2} \qquad .....(5)$$

Where ε = Polanyi potential = RT ln $(1 + 1/C_e)$,

$$E=1 / (2\beta)^{0.5}$$

The values of q_s and β were obtained from the linear plots of $\ln q_e$ Vs ε^2 (Fig 8). The values of q_s = 21.1 mg/g, E=2.887 kJ/mg and R^2 = 0.974. The value of E less than 8 kJ/mol indicates the adsorption process of metal ions was physical nature.

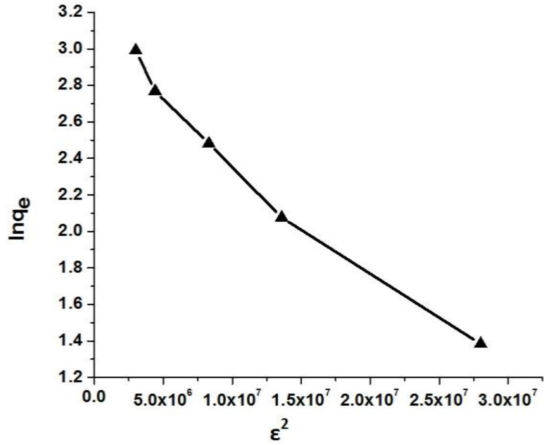

Figure 8 Dubinin–Radushkevich isotherm

5. Effect of pH:

The pH of an aqueous solution[9]controls uptake of heavy metals from aqueous system. As the pH increased from 1 to 3, the adsorption of Cr(III) ions was increased (Fig 9). The adsorption decreases from pH 3 to 10. As pH increases, competition between ions decreases which enhances the adsorption of the positively charged metal ions through electrostatic forces of attraction. It is speculated that the electrostatic attraction and ion exchange were the principal mechanism for the adsorption behavior

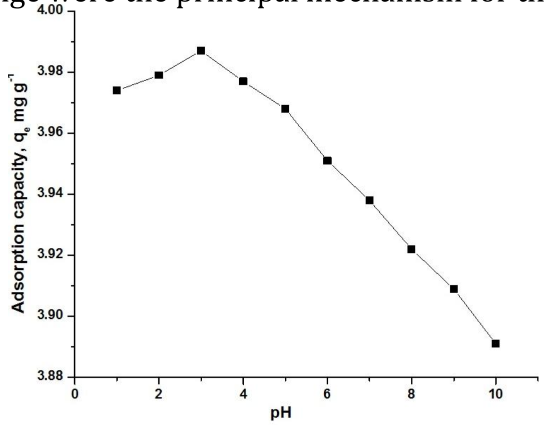

Figure 9: Effect of pH on adsorption capacity for 40 mg/L, Cr(III) using 1 g of LRHC for 2 h at 30°C

6. Effect of Contact Time:

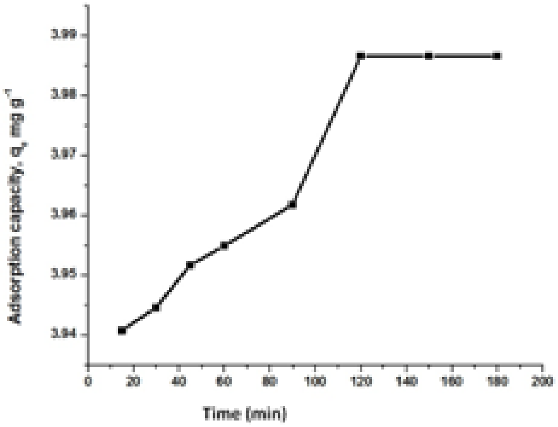

Figure 10: Effect of contact time on adsorption capacity for 40 mg/L, Cr(III) using 1 g of LRHC with pH 3 at 30°C

As the contact time is increased, the adsorption of Cr(III) ions was increased up to 2 h and then remains constant(Fig10).The initial adsorption rate was very fast which may be due to the existence of greater number of vacant sites available for metal ions adsorption. As the remaining vacant adsorption sites decreased, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and liquid surface.

7. Kinetic Study:

Adsorption kinetics describes the solute uptake rate which in turns controls the residence time.

Pseudo First Order Model: Lagergren equation (6) is

$$\log (q_e - q) = \log q_e - k_1 t / 2.303 \qquad .....(6)$$

Lagergren plot[10] of $\log(q_e - q)$ versus time was shown in Fig 11. The experimental value of adsorption capacity is 3.987 mg/g whereas the calculated value of adsorption capacity is 0.0523 mg/g. The rate constant (k_1) was 0.043. Correlation coefficient (R^2) was 0.992. The above results indicate that first order mechanism is not followed in this process.

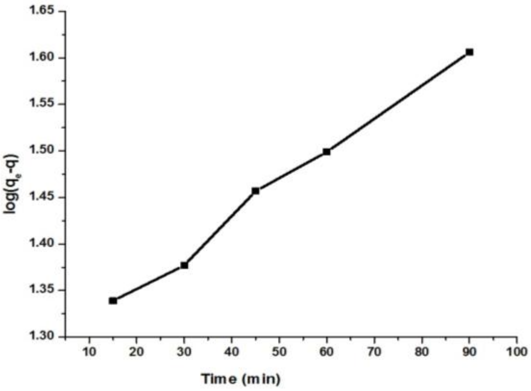

Figure 11: Pseudo first order plot

Pseudo Second Order Model: The pseudo second order rate equation (7) is

$$t/q = 1/ k_2 q_e^2 + t/q_e \qquad .....(7)$$

The kinetic data of LRHC for pseudo second order models[11] are shown in Fig 12. The experimental value of adsorption capacity for Cr(III) is 3.987 mg/g whereas the calculated value of adsorption capacity 3.995 mg/g and R^2 =1. This indicates that pseudo second order mechanism is followed in this process.

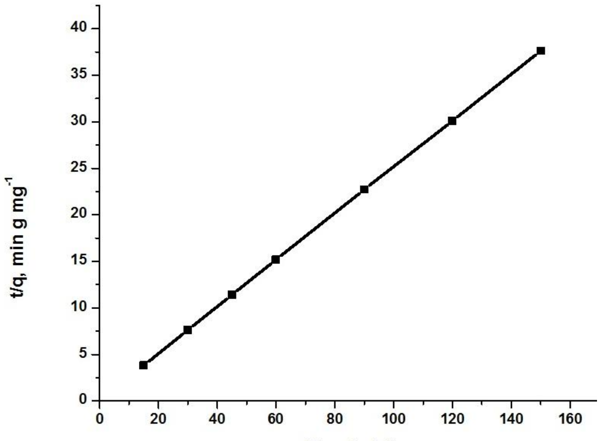

Figure 12: Pseudo second order plot

Intra-Particle Diffusion Model: The intra-particle diffusion equation (8) by Weber-Morris[12] is

$$q_t = K_p t^{1/2} + I \qquad .....(8)$$

The plot of q_t versus $t^{1/2}$ for LRHC is given in Fig 13. The deviation of straight line from the origin indicates that the pore diffusion is not the sole rate controlling step.

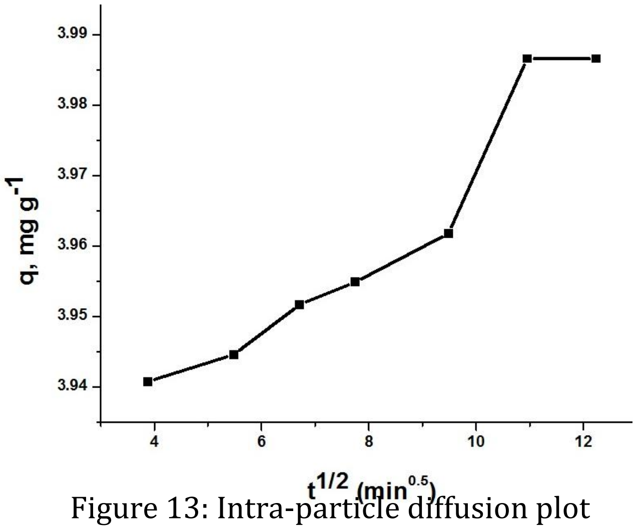

Figure 13: Intra-particle diffusion plot

8. Effect of Temperature:

The effect of temperature on the adsorption capacity of Cr(III) using 1 g of LRHC with pH 3 for 2 h were shown in Fig 14. The results show that the adsorption capacity of LRHC decreases with increase in temperature

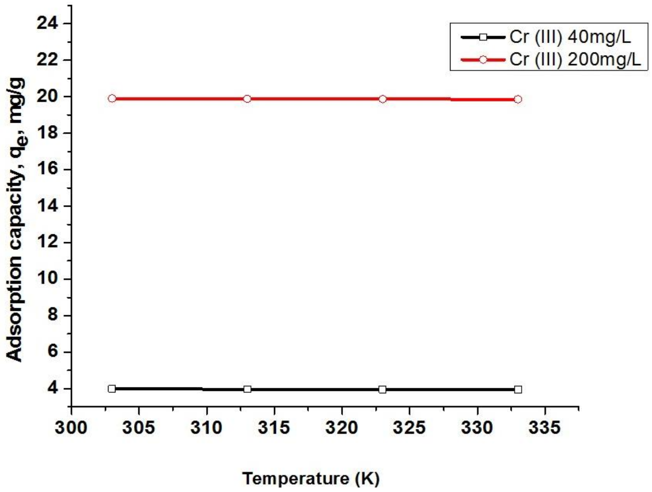

Figure 14: Effect of temperature on adsorption capacity for 40 mg/L, Cr(III) using 1 g of LRHC with pH 3 for 2 h

9. Thermodynamics:

The changes occurred during biosorption can be explained by the three main important thermodynamic parameters namely Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS).

Effect of Temperature on Equilibrium Constant: Temperature dependence of equilibrium constant[13] can be explained by equation (9).

$$\log K_c = \Delta S^o / 2.303R - \Delta H^o / 2.303RT \qquad .....(9)$$

When the temperature is increased from 303K to 333K, the equilibrium constants for adsorption of Cr(III) ions are decreased. The values for ΔG, ΔH & ΔSat lower concentration comes to -12.267 kJ/mol, -42.583 kJ/mol & -179 J/mol and at higher concentration comes to -13.467 kJ/mol, -10.856 kJ/mol&8 J/mol. The Gibbs free energy change is negative (ΔG < 0) which shows the biosorption is spontaneous. The negative value of heat of the reaction, (ΔH < 0) indicates that biosorption is exothermic and it can liberate energy without any external aid. The change in entropy below zero (ΔS < 0) indicates the affinity of adsorbent material for Cr(III) ions.The effect of temperature on equilibrium constant is given in Fig 15.

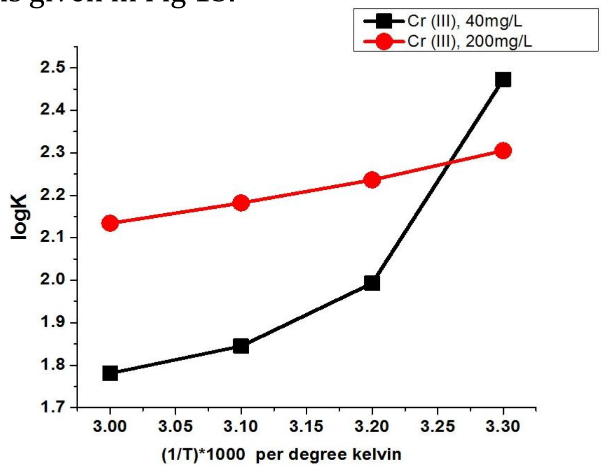

Figure 15: Effect of temperature on equilibrium constant for adsorption of Cr(III) for 1 g of LRHC with pH 3 for 2 h

10. FT-IR Study:

The Fourier Transform – Infrared spectra[14] of raw LRHC and metal ion loaded LRHC are given in Fig 16 and Fig 17. It is evident from the spectra that the positions of the spectra remain unaltered after the adsorption of metal ion from the solution. Thus the adsorption of metal ions on the adsorbent is by physical forces only and not by chemical forces which might alter the chemical nature of the adsorbent and consequently the position of the peaks.

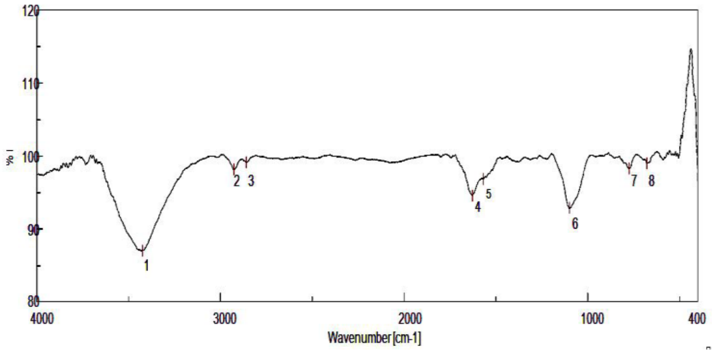

Figure 16: Infra-red spectra of LRHC

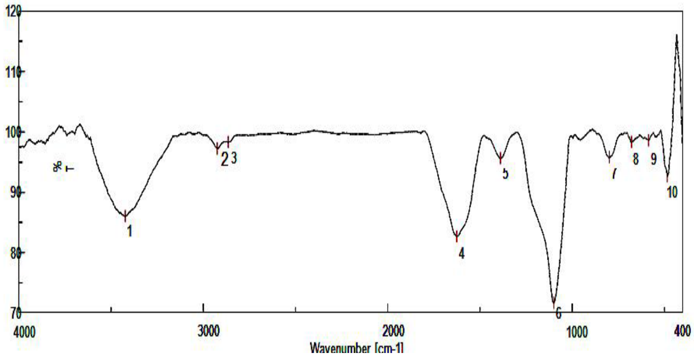

Figure 17 Infra-red spectra of Cr(III) adsorbed LRHC

11. SEM and EDX Study:

SEM images[15] of LRHCand metal adsorbed LRHCtaken at magnitude 1000x was given in Fig 18 and Fig 19. The bright spots show the presence of tiny holes on the crystalline structure of LRHC. After treatment with metal ions the bright spots become black indicating the adsorption of metal ions on the surface of LRHC.EDX analysis of LRHCand metal adsorbed LRHCwas given in Fig 20 and Fig 21. Peak indicates the presence of Cr(III).

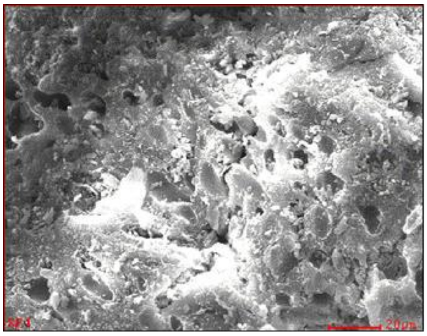

Figure 18: SEM images of LRHC

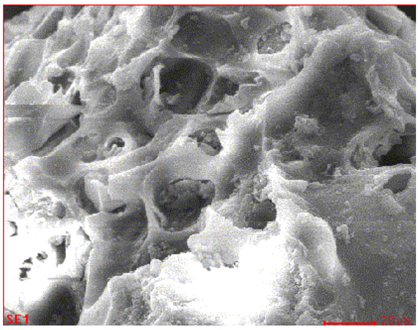

Figure 19: SEM images of Cr(III) adsorbed LRHC

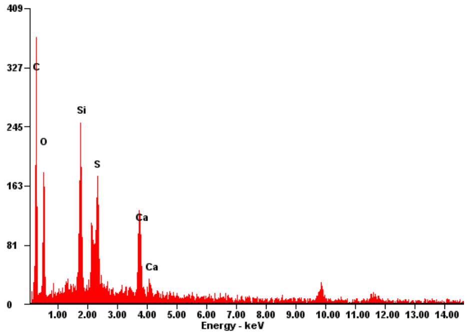

Figure 20: EDX of LRHC

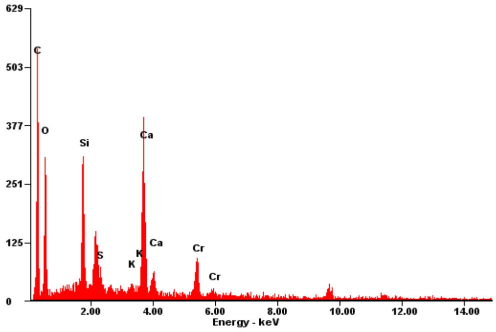

Figure 21: EDX of Cr(III)adsorbed LRHC

12. Conclusion:

Lime loaded rice rusk carbon can be used as an adsorbent for the adsorption of Cr(III) ions. The adsorption decreases with increase in adsorbent dosage and increases with increase in adsorbate concentration. The maximum adsorption of Cr(III) was found at pH 3. The result was supported by the study of Freundlich, Langmuir, Temkin and Dubinin Radushkevich adsorption isotherms. The maximum adsorption occurs at 120 min. Kinetics shows the adsorption is of pseudo second order. Thermodynamics show the adsorption is feasible. FT-IR shows the adsorption is physical nature. SEM & EDX studies illustrate the adsorption process. It may be concluded that lime loaded rice rusk carbon may be used as a low cost, natural and abundant resource for the adsorption of Cr(III) ions from aqueous system.

13. List of Notations:

C_o	Initial concentration of metal ion (mg/L)
m	Mass of LRHC carbon (g)
V	Volume of the sample (mL)
q_e	Adsorption capacity (mg/g)
K_F	Freundlich constant, indicator of adsorption capacity
C_e	Equilibrium concentration of metal ion (mg/L)
n	Constant, measure of intensity of adsorption.
R^2	Correlation Co-efficient

q_{max}	Constant for monolayer adsorption capacity (mg/g)
K_L	Constant for energy of adsorption (L/mg)
R_L	Equilibrium parameter
K_T	Temkin isotherm equilibrium binding constant (L/g),
b_T	Temkin isotherm constant,
R	Universal gas constant (8.314 J/mol/K),
T	Temperature in Kelvin
B_1	Constant related to heat of sorption (J/mol)
q_s	Theoretical isotherm saturation capacity (mg/g);
β	Dubinin–Radushkevich isotherm constant (mol^2/kJ^2)
ε	Polanyi potential
E	Mean free energy, kJ/mol
q	Adsorption capacity at time t, (mg/g)
k_1	Rate constant for pseudo first order adsorption (min^{-1})
k_2	Rate constant for pseudo second order adsorption (g/mg min).
k_p	Intra-particle diffusion rate constant (mg/g $min^{0.5}$)
I	Constant that gives idea about the thickness of the boundary layer, (mg/g)
ΔG	Gibbs free energy change, kJ/mol
K_c	Thermodynamic equilibrium constant for the adsorption
ΔS	Entropy change, J/mol
ΔH	Enthalpy change, kJ/mol

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