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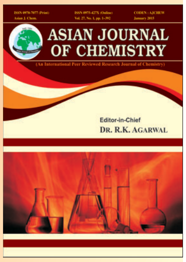

Removal of Chromium and Nickel Ions from Wastewater by Rice Husk Carbon

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Rice husk carbon was used as an adsorbent to remove nickel and chromium ions from a synthesized industrial wastewater. A laboratory experimental investigation was carried out to identify the effect of pH, initial concentration, dose and contact time on adsorption of nickel and chromium from the metals solution. Equilibrium adsorption experiments at 30 °C were carried out and fitted to Langmuir and Freundlich models. Results showed that pH 4.5 was the most suitable for nickel and 2 for chromium, while the maximum adsorbent capacity was at a dosage of 0.4 g/L, recording a sorption capacity of 1.337 mg/g of nickel and 1.581 mg/g for chromium and 90 min for nickel and chromium. Langmuir model had higher R^2 values of 0.997 and 0.917 for nickel and chromium respectively, which fitted the equilibrium adsorption process more than a Freundlich model for the two metals.

Keywords: Nickel, Chromium, Adsorption process, Activated rice husk, Freundlich isotherm.

INTRODUCTION

Nickel is a toxic heavy metal. The main source of nickel pollution in the water derives from industrial production processes such as silver refineries, electroplating, zinc base casting and storage battery industries[1]. Nickel occurs in two oxidation states in nature, namely Ni^0 and Ni^{2+}. Divalent nickel is toxic to most organisms in concentrations higher than 0.05 mg/L. It is carcinogenic in animals and is frequently encountered in raw wastewater effluent. The maximum permissible concentration of nickel in drinking water is 0.02 mg/L according to US-EPA report. Higher concentrations of nickel cause cancer related to lungs, nose and bone. Acute poisoning of divalent nickel causes headache, dizziness, sickness and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness[2]. Thereby, it is of great importance to eliminate nickel ions from wastewaters[3].

Hexavalent chromium (Cr^{6+}) is a hard oxidant and a group A carcinogen. The industrial sources of Cr^{6+} primarily include alloy and steel manufacturing, metal finishing, electroplating, leather tanning and pigments synthesis and dyeing industries[4]. The effluents from these industries contain Cr^{3+} and Cr^{6+} at concentrations ranging[4] from tenths to hundreds of mg/L. Contact with chromium can result in severe health problems ranging from simple skin irritation to lung carcinoma, therefore it should not be present in the leather fabrics. A variety of methods have been developed for removal of chromium compounds from industrial wastewater. Hexavalent chromium usually exists in wastewater as oxyanions such as chromate (CrO_4^{2-}) and dichromate($Cr_2O_7^{2-}$) and does not precipitate easily using conventional precipitation methods

For this reason, it is generally used the advanced treatment processes such as chemical reduction, ion exchange, reverse osmosis, electro dialysis and activated carbon adsorption. Since the cost of these processes is rather expensive, the use of agricultural residues or industrial by-product having biological activities have been received with considerable attention[4]. In recent years, a number of agricultural materials such as moss peat[5,6], coconut husk[7,8] (70 % removal of nickel ions), chitosan[9] (74 % removal), coirpith (66 % removal)[10], rice husk (74 % removal)[11,12], tea leaf (69 % removal)[13] and almond husk (64 % removal)[14] have been reported for the removal of toxic metals from aqueous solutions. Most of these materials contain functional groups associated with proteins, polysaccharides, lignin and cellulose as major constituents. Metal uptake is believed to occur through the sorption process involving the functional group mentioned above.

The aim of this research paper was to investigate on the effect of pH, contact time, initial concentration, temperature and dosage. Also determine the adsorption kinetics of activated rice husk so as to better understand and optimize its role as adsorbent for nickel and chromium ion in solution. While isotherm studies were used to model the adsorption process. Activated rice husk is low-cost and readily available and this knowledge will be a contribution to the global fight against pollution.

EXPERIMENTAL

Adsorbate: Metals solutions [nickel sulphate ($NiSO_4·6H_2O$) and potassium dichromate ($K_2Cr_2O_7$) were purchased from Sigma Aldrich]. Stock solutions (1000 mg/L) of Ni^{2+} were prepared by dissolving the required amounts of $NiSO_4$ or $K_2Cr_2O_7$ in deionized water. Aqueous solutions of metals were prepared in the laboratory based on metal concentration in the industrial effluent. Each metal solution was diluted with distilled water to obtain the desired initial concentration in the range 50-300 mg/L, to mimic the industrial wastewater. The distilled water that we used during our tests is characterized by a pH variance of 6.40 and 6.80 and a conductivity of 16.0 µS/cm.

A stock solution of metal was diluted to prepare working solutions. Buffer solutions (pH 4 and 7) were used to calibrate the pH meter. pH of each test solution was adjusted to the required value to 0.1N hydrochloric acid or dilute sodium hydroxide solutions.

Adsorbent preparation: The husk was washed with hot distilled water to remove water soluble impurities and dried in the sun. Then it was impregnated with H_3PO_4 (40 %) and carbonized at 450 ± 20 °C. For impregnation, the ratio of acid volume to weight of rice husk carbon was used as 2:1. This rice husk carbon was then washed with demineralized water and dried in an oven at 100 ± 5 ºC. Finally, it was ground and sieved to 170-200 mesh before utilizing it as rice husk carbon. The physico-chemical characteristic of rice husk is given in Table-1.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTIC OF RICE HUSK

Parameters	Value
Bulk density (g/mL)	0.73
Solid density (g/mL)	1.5
Moisture content (%)	6.62
Ash content (%)	45.97
Particle size (Mesh)	200.16
Surface area (M^2/g)	272.5
Surface acidity (meq/g)	0.1
Surface basicity (meq/g)	0.45

Adsorption experiment: The adsorption of Ni^{2+} and Cr^{6+} was conducted by contacting 200 mL of metal solutions with predetermined amounts of adsorbent in 250 mL beaker. The samples were agitated in a thermostated water bath at a speed of 500 rpm to ensure adequate mixing. At predetermined intervals (1, 3, 5, 7, 10, 15, 30, 45, 60 and 90 min), samples were drawn from the activated carbon/liquid mixtures and immediately filtered through a centrifuge lined with a Whatman 42 filter paper. All experiments were carried out at different temperatures in the range 293-323K. The supernatant was analyzed for solution metals by means of atomic absorption spectrophotometry (AAS).

The uptake of metal ions was calculated by the difference in their initial and final concentrations. The mass balance is expressed mathematically as:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (mg/g adsorbent), V is the volume of the metal solution (L), C_o is the initial concentration of metal ion in aqueous phase (mg/L), C_e is the final concentration of metal ion in aqueous phase (mg/L) and M is the mass of adsorbent used (g). The percentage adsorption was calculated as follows:

$$\text{Adsorption}\,(\%) = \frac{C_o - C_e}{C_e} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Effect of contact time: Equilibrium time is important operational parameter for an economical wastewater treatment process. The time required to achieve the adsorption equilibrium on the adsorption capacity of Ni^{2+} and Cr^{6+} is described in Fig. 1. Obviously, activated rice husk showed a good performance in adsorption during the first 30 min and there is no significant change from 30 to 90 min. A two-stage behaviour is observed. It is observed from the results that the uptake of Ni^{2+} and Cr^{6+} is initially quite high and slows down with the lapse of time leading gradually to an equilibrium condition. It also shows that a major fraction of Cr^{6+} and Ni^{2+} is adsorbed onto activated rice husk during the first 30 min, while only a very small part of the additional adsorption occurs during the following contact time. This clearly suggests that the adsorption of metal cations on the surface of the activated rice husk could take place in a single step and without any complexity. Thus, it is possible that during the initial stage of the process, the surface coverage is low and adsorptive ions occupy active surface sites rapidly in a random manner. As a result, the rate of uptake is higher. As time lapses the surface coverage increases, the rate of uptake becomes slower in the latter stages and ultimately an almost plateau region is attained when the surface becomes saturated[15,16].

Effect of pH: The effect of solution pH on the removal of nickel were investigated at pH 1.0-4.5, 303 K and an initial nickel ion concentration of 50 mg/L is shown in Fig. 2. As far as the metals are concerned, the removal efficiency was highly pH dependent.The percentage of removal of Ni^{2+} increased with an increase in pH. Furthermore, a rather fast uptake of Ni^{2+} ions and a small increase of pH values from 1 to 4.5 simultaneously occur within the first 30 min. The increase in metal removal with pH is due to a decline in competition between proton and metal species for surface sites; thereby decreasing in positive surface charge and resulting in a lower Coulombic repulsion of the adsorbed metal.

The graph reveals that the adsorption of Cr^{6+} on rice husk carbon increases with the decreased pH of the solution. It is evident from the plots that optimum pH is 2.0. Improved adsorption at low pH may be explained on the basis of the assumption that the large number of H^+ ions present in solution at low pH can neutralize the negatively charged rice husk carbon surface or convert the neutral groups to the positively charged groups. Hence, higher degree of adsorption of Cr^{6+} may be attributed due to the electrostatic force of attraction between the adsorbent and adsorbate.

The dependence of metal removal on the pH can be explained from the perspective of surface chemistry in an

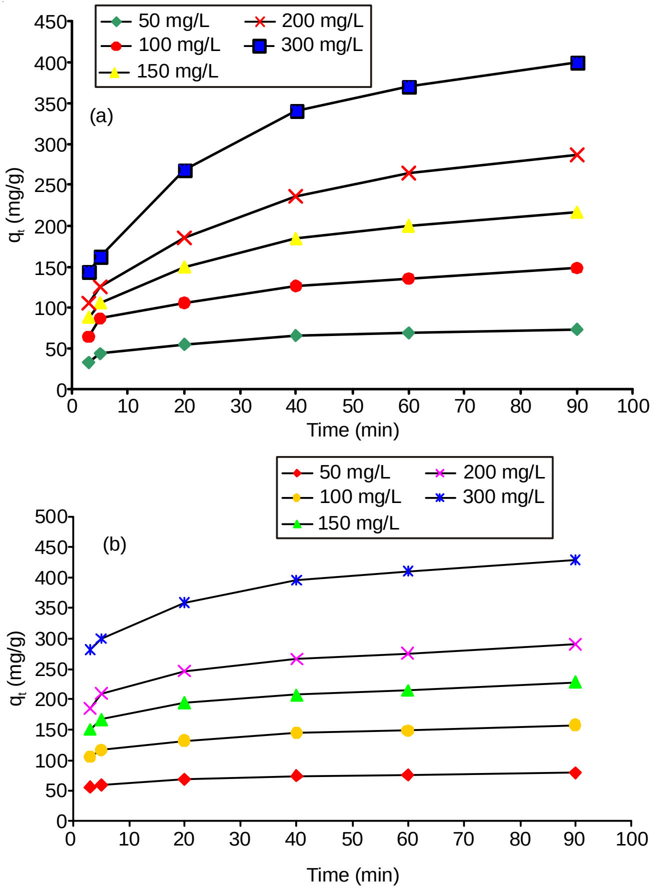

Fig. 1. Effect of contact time on the adsorption of (a) chromium(VI) pH = 2, (b) nickel pH = 4.5 (initial concentration = 50 to 300 mg/L, rice husk carbon dose = 0.1 g/200 mL, 500 rpm, contact time = 90 min and temperature = 303 K)

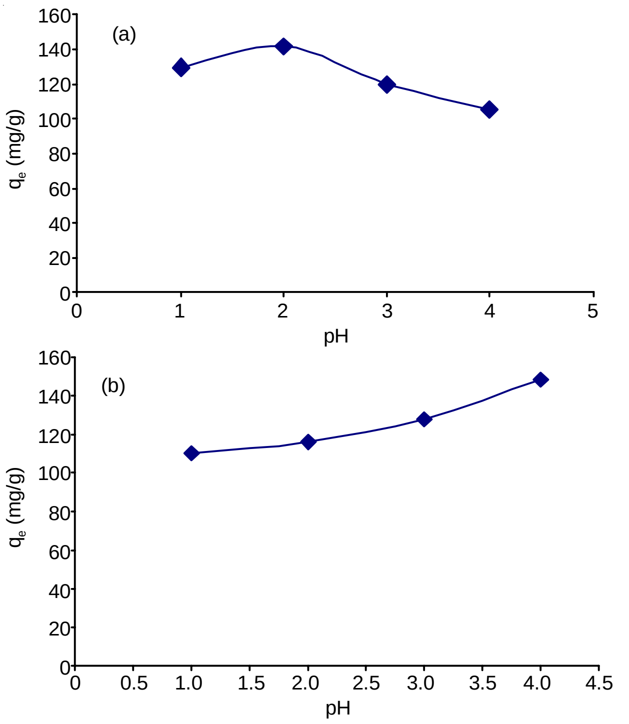

Fig. 2. Effect of pH for the adsorption of (a) chromium(VI) and (b) nickel(II) (initial concentration = 100 mg/L, rice husk carbon dose = 0.1 g/200 mL, stirring speed = 500 rpm, temperature = 303 K and time = 90 min)

aqueous phase. The surface charge is neutral at the zero point of charge pHpzc, which is 6.3 for rice husk. Below the pHpzc, the adsorbent surface is positively charged and anion adsorption occurred by simple electrostatic attraction. Above the pHpzc, the adsorbent surface is negatively charged and cation adsorption occurred.

At a pH lower than pHpzc, the percentage of adsorption should be reduced to nearly zero; while it is not the case for present research. It was found that at a pH lower than pHpzc, the amount of Ni ions was still adsorbed onto the rice husk, which suggested that ion exchange between Ni(II) and H^+ may play a role during this pH range[16-18].

When pHzpc < 6.3, the surface is protonated and the positively charged surface attracts CrO_4^{2-} On the other hand, at pH > pHzpc of the rice husk carbon it can be excepted that there is no Cr^{6+} adsorbed on the rice husk if electrostatic repulsion is the only mechanism during this pH range. However, a certain amount of Cr^{6+} ions were still adsorbed on rice husk at pH > pHzpc and hence some other mechanisms must be in place. Since the affinity of CrO_4^{2-} with rice husk is higher than that of OH^-, CrO_4^{2-} can replace OH^- from the surface of the hydrolyzed rice husk.

When pH ≤ pHzpc, the surface is hydroxylated and the negatively charged surface exchanges CrO_4^{2-} Taken together, the mechanisms of Cr^{6+} adsorption onto rice husk are electrostatic attraction and ion exchange.

Effect of amount adsorbed: Since an optimum adsorbent dose is essentially required to maximize the interactions between metal ions and adsorption sites of adsorbent in the solution, the effect of adsorbent dose of Cr^{6+} and Ni^{2+} ions adsorption was investigated. Fig. 3 showed that the increase in the dose of the adsorbents (rice husk carbon concentrations of 0.1-0.4 g/200 mL) increases Cr^{6+} and Ni^{2+} uptake. Namely, the percentage removal increases as the adsorbent doses increases These observations suggest that the increase in rice husk concentration leads to increase in the adsorbent surface area and the availability of more adsorption sites for metal ions adsorption. Therefore, the maximum removal efficiency of metal is 79.58 % at 0.4 g/mL dose of rice husk carbon. Furthermore, as shown in Fig. 3, the amount of metal ion adsorbed per unit weight of adsorbents (q) increase with the increase in rice husk doses. The initial increment in adsorption capacity with an increase in adsorbent dosage was expected, Since a number of adsorbent particles increases and thus more surface areas were available for metals attachment same trend was reported by Dakiky *et al.*[19] and Acar & Eren[20]. It is plausible to suggest that with a higher dosage of adsorbent there would be greater availability of the exchangeable site of metal ions.

Effect of initial concentration: Fig. 4 showed the effect of varying the initial concentration of Ni^{2+} ions from 50 to 300 mg/L on the adsorption under the optimized condition at pH 2,4 for chromium and nickel, 30 °C and 0.1 g of rice husk carbon.

It can be seen from the figure that, with increasing Cr^{6+} and Ni^{2+} initial concentration, there is a decrease in % removal of Cr^{6+} and Ni^{2+} for adsorbent. This can be explained with the fact that the adsorbent had a limited number of active sites, which would have become saturated above a certain

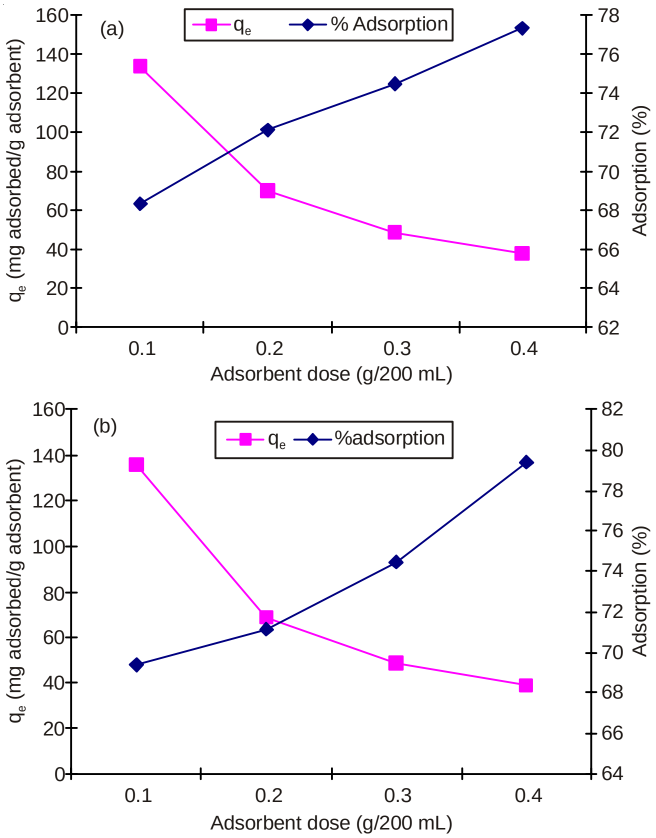

Fig. 3. Effect of adsorbent dose of rice husk carbon on % adsorption and q_e, initial concentration [Ni^{2+}] and [Cr^{6+}] = 100 mg/L, pH = 4.5, stirring speed = 500 rpm, temperature = 303 K

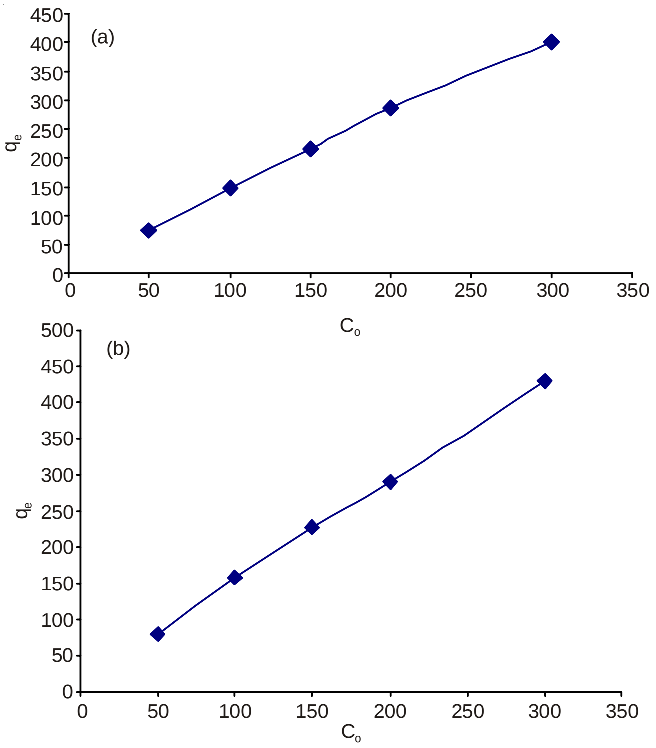

Fig. 4. Relationship between q_e and initial concentration for (a) chromium and (b) nickel

concentration. Similar observations have also been reported from other researches[21-23]. In another word, at higher concentration of metal ions, the most superficial groups are already occupied and in consequence the diffusion of metal ions to the unreacted functional group is inhibited.

Temperature effect and thermodynamic parameters: Effects of temperature on the adsorption of nickel and chromium ions by rice husk carbon were investigated at 301-313 K and an initial metal ion concentration of 100 mg/L and 500 rpm for chromium and nickel, optimum pH values of 2 for chromium and 4.5 for nickel and 0.1 g/200 mL of rice husk carbon.

As shown in Fig. 5, the adsorption capacities for rice husk carbon increased with the increase in temperature, revealing both the adsorption processes were endothermic. The increase in adsorption with temperature may be attributed to either increase the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of the adsorbate in the boundary layer decreases[24].

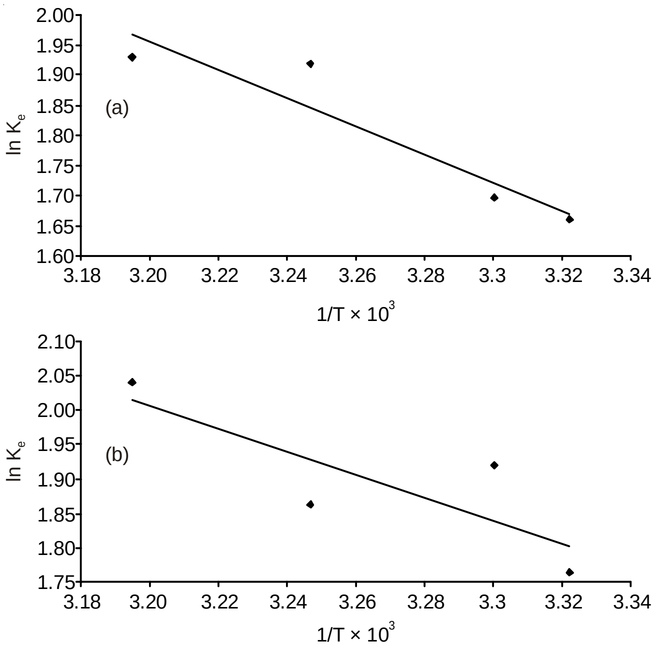

Fig. 5. Relationship between ln (K_e) and reciprocal of temperature, at constant initial concentration of 100 mg/L, 0.1 g/200 mL of rice husk carbon and 500 rpm for (a) chromium and (b) nickel

Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperature.

Another possible explanation was that the metal ions were well hydrated. They have to lose part of the hydration sheath in order to be adsorbed. This dehydration process of metal ions needed energy and superseded the exothermicity of the ion adsorption on the surface[25].

Temperature is an important parameter in the adsorption process and to determine the spontaneity of the process in engineering practice, thermodynamic parameters such as enthalpy change (ΔH^o), entropy change (ΔS^o) and free energy change (ΔG^o) are crucial and must be taken into consideration.

These thermodynamic parameters are obtained from adsorption experiments at various temperatures (293, 303, 313 and 323 K) and estimated (Table-2) using the following equations:

$$K = q_e/C_e \tag{3}$$

$$\Delta G = -RT \ln K_c \tag{4}$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

where K_c is the equilibrium constant, q_e (mg L^{-1}) is the concentration of Ni^{2+} and Cr^{6+} adsorbed on solid at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of Ni^{2+} and Cr^{6+} in the solution R (8.314 J K^{-1} mol^{-1}) is the gas constant and T (K) is temperature. The values of ΔH and ΔS are obtained from the slope and intercept of the van't Hoff plot of ln K *versus* 1/T as indicated in the inset of Fig. 6. From the slope (-ΔH/R), the changes of enthalpy (ΔH) at 239-323 K could be determined to be 19.51 kJ/mol for chromium and 13.82 and from the intercept (ΔS°/R), while the changes of entropy is 0.078 kJ/mol and 0.091 for nickel. The positive value of ΔH° confirmed the endothermic nature of adsorption which was also supported by the increase in value of Ni^{2+} and Cr^{6+} uptake with the rise in temperature. The positive value of ΔS° suggested the increasing randomness at the solid/liquid interface during the adsorption of Ni^{2+} and Cr^{6+} ions on rice husk[26].

TABLE-2
THERMODYNAMIC PARAMETERS FOR ADSORPTION PROCESS

Temp. (K)	ΔG° (J/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
Chromium			
301	-23668.79	19.51	0.078
303	-23826.18		
308	-24219.68		
313	-24613.17		
Nickel			
301	-18319.67	13.81	0.061
303	-18441.49		
308	-18746.03		
313	-19050.58		

The negative values for ΔG° indicate that adsorption is a feasible and spontaneous process, where no energy input from outside of the system is required. The increase of negativity ΔG° values with temperature implies that the adsorption reaction is more spontaneous and more favourable at high temperature.

Kinetic studies: The kinetics of adsorption describe the rate of metal ion uptake on activated rice husk and this rate controls the equilibrium time. The kinetics of adsorbate uptake are required for selecting optimum operating condition for the full scale adsorption process[27]. The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. The kinetics of the adsorption data were analyzed using different kinetic models such as pseudo-first order (Fig. 6) and pseudo-second order (Fig. 7) models.

Pseudo first order model (Lagergren equation)[28]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

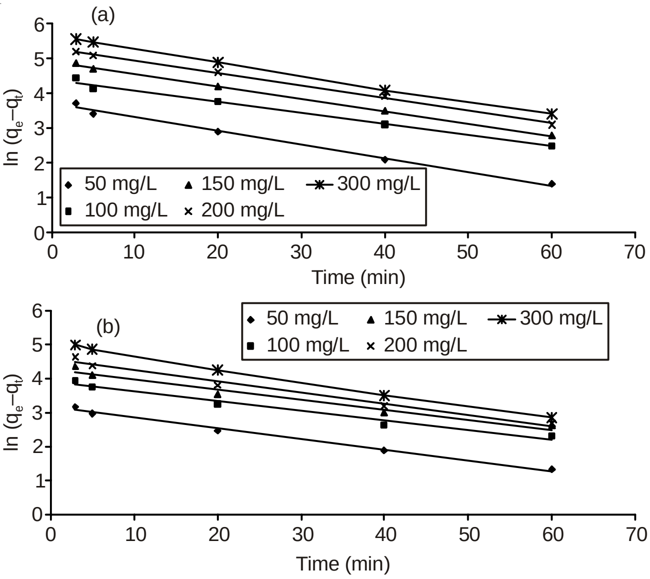

Fig. 6. Pseudo-first order kinetic fit for adsorption of (a) chromium and (b) nickel onto rice husk at different initial concentrations, 0.1 g/200 mL rice husk carbon, 500 rpm and 301 K

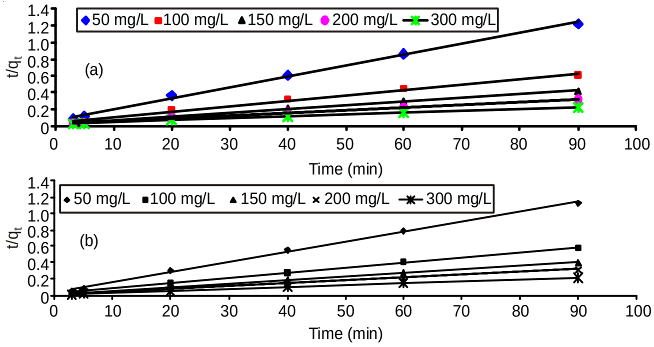

Fig. 7. Pseudo-second order kinetic fit for adsorption of (a) chromium and (b) nickel onto rice husk at different initial concentrations, 0.1 g/200 mL rice husk dose, 500 rpm and 301 K

Pseudo second order[29]:

$$t/q = t/q_e + k_2 q_e^2 \tag{7}$$

The pseudo second order reaction rate model was found to be the best to describe the kinetic data. The applicability of this model showed that sorption process is complex and involve more than one mechanism.

The rate constant k, the correlation coefficient R^2 at equilibrium state was calculated in Table-3.

Adsorption isotherm studies

Langmuir adsorption isotherm: Langmuir is the simplest type at theoretical isotherm. Langmuir adsorption isotherm describes quantitatively the formation of monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases.. The Langmuir adsorption is based on the view that every adsorption site is identically and energically equivalent (thermodynamically, each site can hold one adsorbate molecule). The Langmuir isotherm assumes that the ability of molecule to bind and adsorbed is independent of whether or not neighboring site are occupied. This means, there will

TABLE-3
COMPARISON OF THE PSEUDO FIRST-ORDER AND PSEUDO-SECOND ORDER ADSORPTION RATE CONSTANT FOR DIFFERENT INITIAL CONCENTRATION

Initial concentration (ppm)	Pseudo-first order			Pseudo-second order		
	q_e (mg/g) calculated	K_1 (min)	R^2	q_e (mg/g) calculated	K_2 (g mg^{-1} min^{-1})	R^2
			Chromium			
50	39.97	0.039	0.943	77.06	0.00247	0.999
75	81.59	0.032	0.993	153.92	0.00104	0.992
100	137.14	0.036	0.988	228.46	0.00059	0.999
150	201.17	0.036	0.999	307.17	0.00036	0.983
200	284.06	0.038	0.997	431.64	0.00026	0.983
			Nickel			
50	23.83	0.0314	0.992	80.71	0.00475	0.998
75	49.83	0.0286	0.974	159.63	0.00214	0.998
100	72.25	0.0296	0.962	230.28	0.00152	0.998
150	99.13	0.0332	0.979	295.06	0.00115	09976
200	155.85	0.0372	0.978	437.83	0.00076	0.998

be no interactions between the adjacent molecules on the surface and immobile adsorbtion. Also mean, trans-migration of the adsorbate in the plane of the surface is precluded. In this case, the Langmuir isotherm is valid for the dynamic equilibrium (adsorption-desorption) processes on completely homogenous surface with negligible interaction between adsorbed molecules that exhibit the form[29,30].

$$q_e = (Q \times b \times C_e)/(1 + b) \times C_e \quad (8)$$

where C_e = the equilibrium concentration in solution; q_e = the amount adsorbed for unit mass of adsorbent; Q and b are related to standard monolayer adsorption capacity and Langmuir constant respectively.

$$q_{max} = Q \times b \quad (9)$$

q_{max} = the constant related to overall solute absorptivity.

Equation 8 could be re-written as:

$$C_e/q_e = [(1/(b^*q_{max})] + (1/q_{max}) \times C_e \quad (10)$$

In summary, the Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests the uptake occurs on homogenous surface by monolayer sorption without interaction between adsorbed molecules. The Langmuir isotherm assumes that adsorption sites on the adsorbed surfaces are occupied by the adsorbate in the solution. Therefore, the Langmuir constant (b) represents the degree of adsorption affinity of adsorbate. The maximum adsorption capacity (Q) associated with complete monolayer cover is typically expressed in (mg/g). High values of b indicate for much stronger affinity of metal ion adsorption.

The shape of the isotherm assuming the (x) axis represents the concentration of adsorbing material in the contacting liquid is a gradual positive curve that flattens to a constant value.

A plot of C_e/q_e *versus* q_e gives a straight line of slope $1/q_{max}$ and intercept $(1/q_{max}{*}b)$ as shown in Fig. 8.

The essential features of Langmuir can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is favourable or unfavourable.

The separation factor, R_L is defined by

$$R_L = (1/(1 + bC_f)$$

where C_f is the final Cr(VI) and Ni^{2+} concentration (mg dm^{-3}) and b is the Langmuir adsorption equilibrium constant (dm^3 mg^{-1}).

The parameter indicates the isotherm shape according to $R_L > 1$ is unfavourable, $R_L = 1$ is linear, $0 < R_L < 1$ is favourable and $R_L = 0$ is irreversible. The values of R_L are in the range of $(0 < R_L < 1)$, it indicates that the adsorption of Cr^{6+} and Ni^{2+} on to rice husk carbon is favourable. Thus rice husk carbon is an efficient adsorbent.

The value of R^2 can give more information about the suitability of adsorption model. Higher values of the correlation coefficient and Freundlich isotherm equation can satisfactorily describe the adsorption of Cr^{6+} and Ni^{2+} on activated rice husk carbon. The adsorption of Cr^{6+} and Ni^{2+} is shown in Fig. 8. The related parameters of the isotherm are presented (Table-4).

Freundlich isotherm: The Freundlich isotherm equation is used for the description of multilayer adsorption with the interaction between adsorbed molecules. The model predicts that the adsorbate concentration in the solution will be increasing. The model applies to the adsorption onto heterogeneous surfaces with uniform energy distribution and reversible adsorption. The non-linear form of the Freundlich equation may be written as:

TABLE-4
ADSORPTION ISOTHERM PARAMETERS

C_o (mg/L)	Langmuir isotherm								Freundlich isotherm					
	q_{max} (mg/g)		b		R^2		R_L		1/n		K_f		R^2	
	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)
50	956.1	803.98	0.0076	0.013	0.995	0.915	0.730	0.618	0.789	0.726	11.64	17.86	0.9942	0.998
100							1	1						
150							1	1						
200							1	1						
300							1	1						

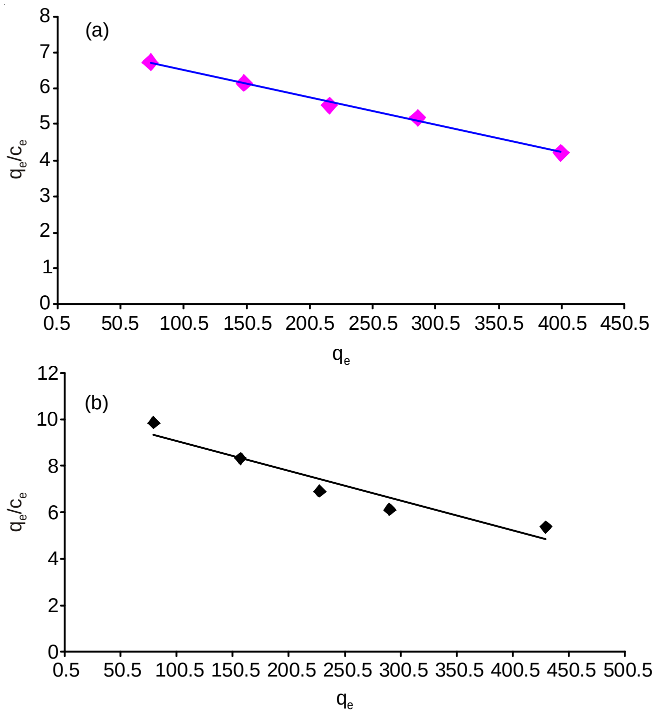

Fig. 8. Linear Langmuir adsorption isotherm for (a) chromium(VI) ions (b) nickel(II) ions with rice husk at 303 K

$$q_e = K_f C_e 1/n \quad \text{where } n > 1 \qquad (11)$$

The linearized form of Freundlich isotherm given by the equation:

$$\log q_e = \log K_f + (1/n) \log C_e \qquad (12)$$

where, q_e = amount adsorbed per unit weight of the adsorbent at equilibrium (mg g^{-1}); C_e = equilibrium concentration of the adsorbate in solution after adsorption (mg dm^3) = (mg/L); K_f = empirical Freundlich constant or capacity factor (mg g^{-1}); 1/n = Freundlich exponent.

Non-linear behaviour of adsorption indicates that adsorption energy barrier increase exponentially with increasing fractional filled sites on the adsorbent. The Freundlich isotherm parameter (1/n) measures the adsorption intensity of metal ion on adsorbent.

The Freundlich constant K_f and n can be obtained by plotting log q_e *versus* log C_e as presented in the previous equation. From the plot (Fig. 9), the values K_f and n can be obtained. Other than the homogenous surface, the Freundlich equations are also suitable for a highly heterogeneous surface and an adsorption isotherm indicates the multi layer adsorption. The value of 1/n less than unity is an indication that significant adsorption takes place at low concentration but in the increase in the amount adsorbed with concentration become less significant at higher concentration.Thus, the adsorption pattern of metal ions on activated rice husk was well fitted by Langmuir as well as Freundlich isotherm in the experimental concentration range according to the values of correlation coefficient R^2. The Langmuir and Freundlich isotherm models provided that the best fit for experimental data which indicated monolayer as well as multilayer adsorption[31-33].

Characterization of adsorbent: The morphology of the prepared adsorbents was recorded using scanning electron microscope (SEM) (FEI Quanta 200) operated at 20 KV accelerating voltage. As shown in Fig. 10, it has been observed that there is no significance change in morphology and granular size/shape of activated rice husk layered, loosely packed structure with lots of cavities, cracks, irregular protrusions with widely dispersed pores in both grades of carbon are observed by scanning electron micrograph (Fig. 10a). This is due to the fact that all these grades of carbon are bituminous coal based samples. It is also observed that the packed structure are observed after adsorption of nickel and chromium ions (Fig. 10b and 10c).

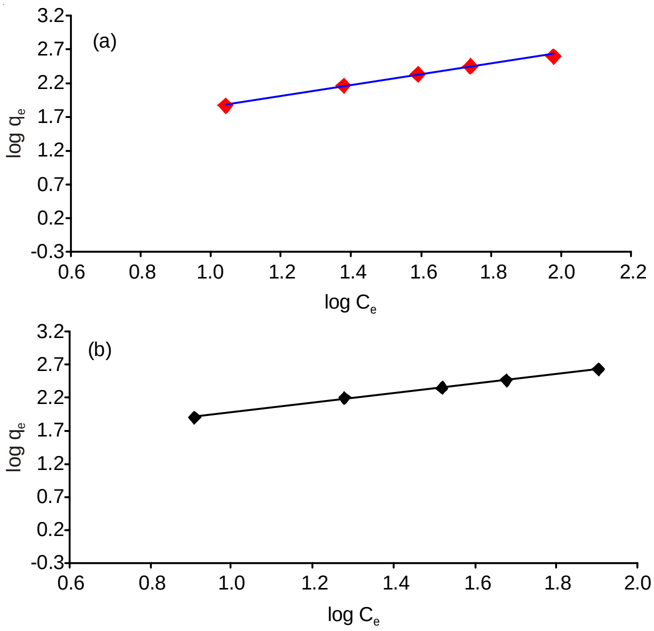

Fig. 9. Linear Freundlich adsorption isotherm for (a) chromium(VI) ions (b) nickel(II) ions with rice husk at 303 K

Conclusion

In this study, the performance of activated rice husk for the removal of Ni^{2+} and Cr^{6+} ions in aqueous solution has been evaluated. It has been demonstrated that these metal ions can be effectively removed by using relatively small amounts of particles due to their large surface area and presence of functional groups. The parameters for the adsorption procedure were optimized: initial solution pH (4.5) and (2) for Ni^{2+} and Cr^{6+} and sorbent mass (0.1 g). The experimental data were fitted using isotherm models *viz*., Langmuir and Freundlich. The experimental data were fitted pseudo second order.

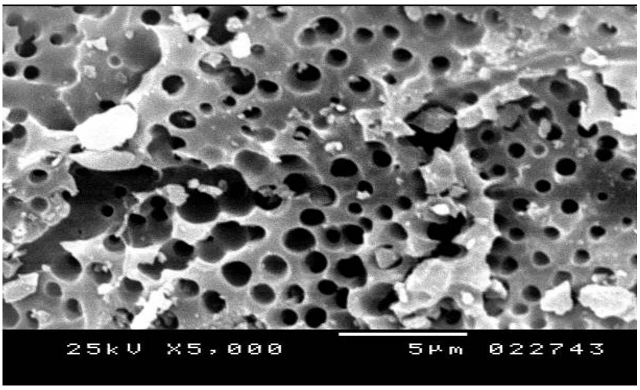

Fig. 10a. Rice husk carbon before adsorption

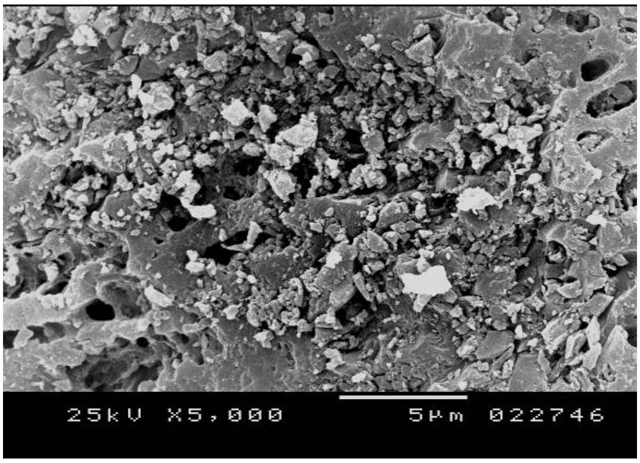

Fig.10b. Rice husk carbon after nickel adsorption

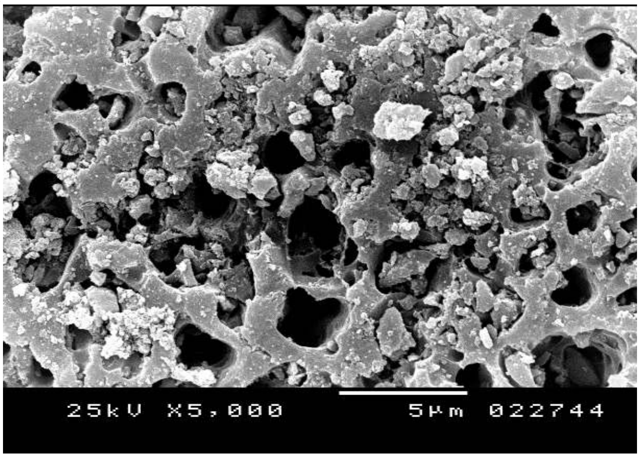

Fig.10c. Rice husk carbon after chromium adsorption

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