Isotherm and Kinetic studies for the removal of perchlorate using modified adsorbent from aqueous solutions: Batch Process

George Ann M.[1*], Nair Jayakumaran Ananthakrishnan[2] and Nair Radhakrishnan Krishna Bhavan Bhaskaran[3]
1. LBS Center for Science and Technology, University of Kerala, Thiruvananthapuram- 695033, INDIA
2. Department of Biotechnology, Kariavattom Campus, University of Kerala, Thiruvananthapuram, 695581, INDIA
3. Department of Biotechnology and Biochemical Engineering, SCT College of Engineering, Thiruvananthapuram, 690518, INDIA
*annmgeorge16@yahoo.co.in

Abstract
The toxic monovalent inorganic anion perchlorate can be removed from aqueous solution by the process of adsorption using the rice husk modified by cetyl trimethyl ammonium bromide studied in a batch adsorption system. The performance of modified rice husk was characterized by SEM analysis. Dependence of pH, initial concentration, temperature and contact time on adsorption were studied. From the studies of equilibrium isothermal data of different models, Langmuir isotherm model showed favorable adsorption on modified rice husk. The increase in Freundlich constant with increase in temperature showed that adsorption was favorable at high temperature and the process was endothermic. The adsorption data showed good agreement with the pseudo second order kinetic model for different perchlorate concentrations.

The values of activation energy obtained using Arrhenius equation indicated that the adsorption of perchlorate onto modified rice husk was activated chemical sorption. The thermodynamic parameters have been evaluated to establish the feasibility of the adsorption of perchlorate. The negative values of Gibb's Free energy change confirm the feasibility of the process and the spontaneous nature of adsorption of perchlorate onto modified rice husk. Results indicated that modified rice husk is a potential low-cost adsorbent for removing perchlorate from water and waste water.

Keywords: Perchlorate, Rice husk, CTAB, Adsorption, Isotherm models, Kinetic.

Introduction

Perchlorate (ClO_4^-) consists of a central chloride atom surrounded by four oxygen atoms and it is a highly soluble anion (Fig.1).[6] The salts of this compound particularly ammonium perchlorate are used as ingredients in solid rocket fuels. The different forms of this anion like sodium perchlorate, potassium perchlorate, magnesium perchlorate and lithium perchlorate can also be used in highway safety flares, airbag inflators, fireworks, missiles, fuels, batteries, matches.[18,20] The perchlorate exposures causes various health issues to human which includes effects on nervous system, inhibition of thyroid activity and mental retardation in infants.[13]

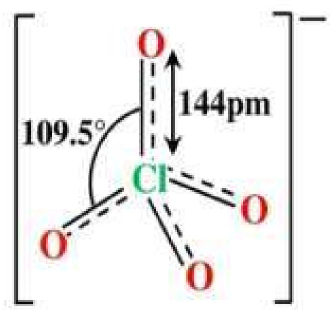

Fig. 1: Structure of perchlorate ion

Adsorption seems to be an attractive method for the removal of perchlorate from water using the low cost adsorbent rice husk which is available in the State of Kerala in India.[8,14] Because of the presence of various functional groups on the rice husk,[22] surface modification was done using cetyl trimethyl ammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$,CTAB)[16] which is a hydrophobic cationic surfactant.[4] The modified adsorbent enhances their adsorption capacity for perchlorate in water.[23] The experiments based on batch kinetic and batch equilibrium studies provide basic information about the effectiveness of adsorbent adsorbate system.

Material and Methods

Preparation of Adsorbent: Rice husk used in the present work was collected from Kariavattom, Thiruvananthapuram, Kerala - GPRS 8º 33' 51" N 76º 53' 11" E. The collected rice husk has been washed, dried and sieved to the particle size of 40 µm. For the modification process, this powdered rice husk was treated with 100 ml of 1% CTAB, $C_{19}H_{42}BrN$ (HIMEDIA) and kept in a temperature-controlled shaker at 100 rpm for 24 h.[16] The modified rice husk was then dried at 60°C overnight and was further stored in sealed glass containers to be used in all the experiments.

Adsorbate: Potassium perchlorate used in this study was of commercial quality (HIMEDIA) and was used without further purification. The ClO_4^- stock solution (1000 mg/L) was prepared. The solutions of various concentrations were finally prepared using the intermediate stock solutions based on the experimental needs.

Instrumentation

Analysis of perchlorate: In the present study, the residual concentration in ppm (mg/L) level was determined by using Combination Ion -Selective Electrode (OAKTON Ion 700 meter, Cole-Parmer.[24] 1mL of 2 molar ammonium sulphate was added to each sample prior to analysis. Before measuring the perchlorate ion concentration in the residual sample, the electrode was calibrated using 1000 ppm, 100 ppm, 10 ppm and 1ppm standard perchlorate solution. pH meter (OAKTON pH meter) was used for pH measurements.

Scanning electron microscope (SEM) analysis: The surface morphology of the untreated rice husk, modified rice husk, perchlorate adsorbed rice husk on unmodified and modified rice husk has to be characterised using a Scanning electron microscope (Model NOVA Nanosem 450) at an electron voltage of (10 kV).

Batch adsorption experiments: The adsorption of ClO_4^- on modified rice husk was investigated in batch mode experiments. Adsorption studies were performed to obtain rate of adsorption and equilibrium data. The experiments were conducted in conical flasks containing modified adsorbent with ClO_4^- solution. The flasks were agitated at 100 rpm for 1 h in an orbital shaker (Scigenics Biotech) at room temperature. Batch sorption studies were performed at different pH (2-10), adsorbent dose (0.1- 3 g), adsorbate concentration (20-100 ppm), temperature (20 - 40°C) and contact time ranging from 20 to 60 minutes. The pH was adjusted by 1M HCl or 1M NaCl.

The adsorption isotherm studies were carried out with perchlorate ion solutions of varying concentration (50, 100 and 200 mg/L) shaking at 100 rpm for 60 minutes. The experiments were performed at different temperatures ranging from 293 to 313 K at the optimum pH and optimum dosage of adsorbent. After attaining equilibrium, the samples were filtered and the residual perchlorate was measured using ion selective electrode. The amount of ClO_4^- adsorbed per unit adsorbent (mg/g) can be calculated using the formula:

$$q_e = \frac{C_i - C_e}{W} * V \quad (1)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_i and C_e are the initial and equilibrium concentration of ClO_4^- in solution (mg/L) respectively, V is the volume of ClO_4^- and W is the mass of the adsorbent in g .Adsorption kinetic tests were performed in a series of flasks containing 50 ml perchlorate ion solutions with initial concentration varying from 20 – 100 mg/L and the optimum dosage of MRH at 40 °C.

Results and Discussion

Scanning Electron Microscope (SEM) Analysis: The surface morphology of the adsorbent can be well understood using the SEM analysis. SEM images of rice husk, perchlorate adsorbed on unmodified rice husk, CTAB modified rice husk and perchlorate adsorbed on modified rice husk are shown in fig. 2. The micrographs clearly represent the uneven structure of rice husk (Fig. 2 a) and the porous structure shown by the modified rice husk (Fig. 2 b). These pores are heterogeneous and thus provide large surface area for the adsorption of ClO_4^-. These cavities are allowing the penetration of the anions and thus interact with the cations on the surface.

The images (Fig. 2 c) and (Fig. 2 d) show the surface changes of rice husk after adsorption of the anions. In the image (Fig. 2 d), the surface is more swollen than the image (Fig. 2 c) which indicates that higher adsorption process takes place in modified rice husk It is clear that the surface morphology of the rice husk before and after adsorption is different. The surface becomes smoother after the adsorption process. This indicates the adsorption of ClO_4^- to the surface groups of the modified rice husk. The surface heterogeneity has also decreased after the adsorption process.

Effect of pH: The effect of pH on removal of perchlorate has been investigated and at different pH ranging from 2.0 to 10[27] as illustrated in fig. 3. It has been observed that the % removal of ClO_4^- increases and reaches a maximum at pH 4 and then decreases. Theoretically the surface charge of an adsorbent was positive at lower pH and could readily adsorb negative charge perchlorate ions through electrostatic attraction. This condition is more effective for the adsorption of the anion (ClO_4^-). When the acidity in the aqueous solution decreases, deprotonation of the functional groups on the adsorbent surface may increase the negative charge in the solution and thus prevent the adsorption of the anionic compound ClO_4^-. At basic pH, the increase in the amount of OH^- ions competes with $ClO4^-$ ions in the solution which results in reduced adsorption of $ClO4^-$ ions.[27]

Therefore, further experiments were performed at pH 4. The above observation of reduction in removal efficiency down to the level of 92 % at pH above 4 was reported[26] using chitosan as the adsorbent. Similar results were obtained by Memon et al[15] in the adsorption of perchlorate on various types of activated commercial carbon using pH as master variable.

Effect of contact time and initial concentration: The effect of contact time on perchlorate (ClO_4^-) removal efficiency at different initial concentrations was investigated and reported in fig. 4. It is seen that the adsorption of ClO_4^- increased with increase in contact time and reaches a maximum value at 20 min, further increase in contact time did not yield any enhancement in the adsorption. During the process of adsorption, the adsorbate molecules will occupy the active sites. But after a period, the remaining active sites cannot be occupied because of the repulsive forces between the molecules on the adsorbent surface and the molecules in the bulk liquid phase. Similar observations were reported by Chen et al[29] in their studies on dye removal using adsorbents.

The initial concentration of the perchlorate also affects the rate of adsorption (Fig. 5). It has been observed that as the initial concentration of ClO_4^- increases from 20 to 100 mg/L, the percentage of adsorption decreases from 98.85 to 89.1 %. This can be due to the saturation of the limited number of active sites on the surface of the adsorbent at a particular concentration .Here the increase in concentration provides a driving force for the molecules to overcome the resistance between the phases and hence increases the adsorption rate. Thus, the initial concentration is having inverse relation to the adsorption due to the limited number of available active sites for the uptake of the anion. Similar results have been reported[5,12] on the adsorption of malachite green on neem saw dust.

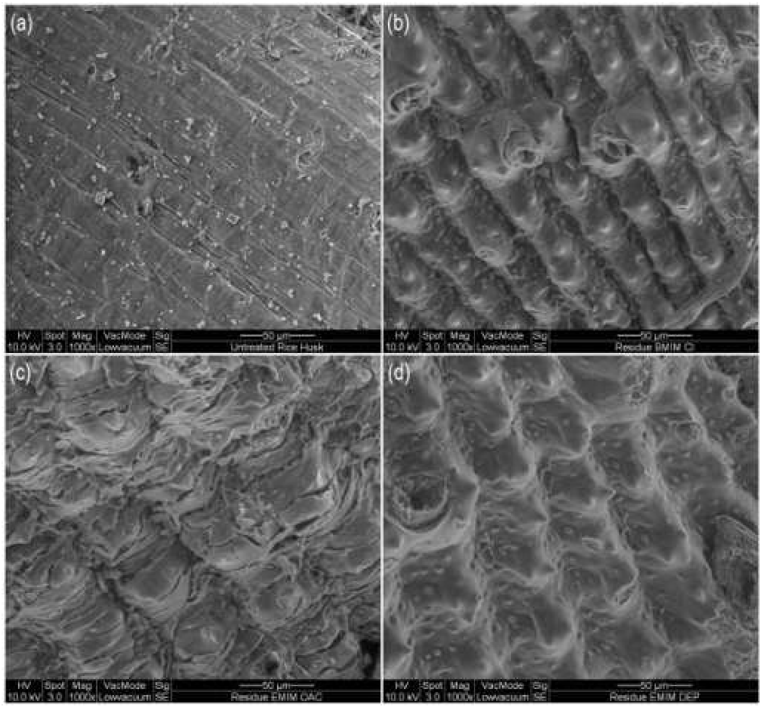

Fig. 2: Scanning electron micrograph (a) untreated rice husk, (b) modified rice husk, (c) perchlorate adsorption on unmodified rice husk (d) perchlorate adsorption on modified rice husk

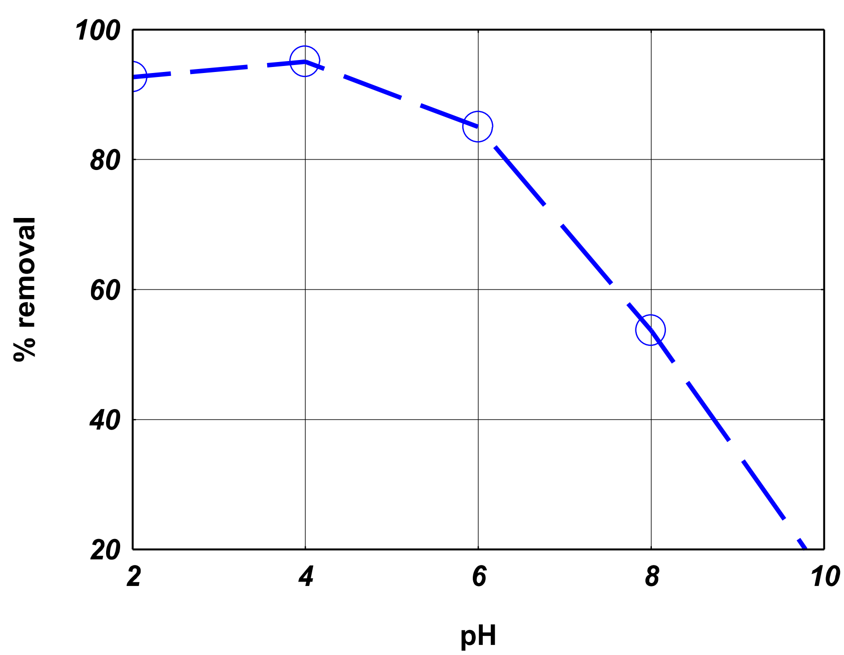

Fig. 3: Effect of pH on the adsorption of perchlorate by MRH (weight of the adsorbent =1g, contact time = 60 minutes, temperature= 27±2°C)

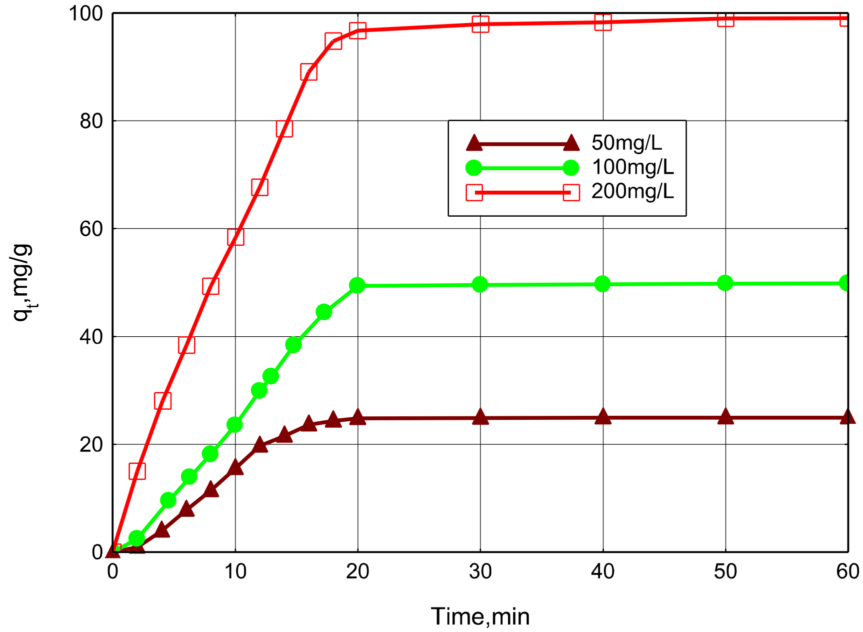

Fig. 4: Effect of time on the adsorption of ClO_4^- on MRH
(Weight of the adsorbent = 0.1g, agitation speed =100 rpm, contact time = 60 min, temperature = 40°C)

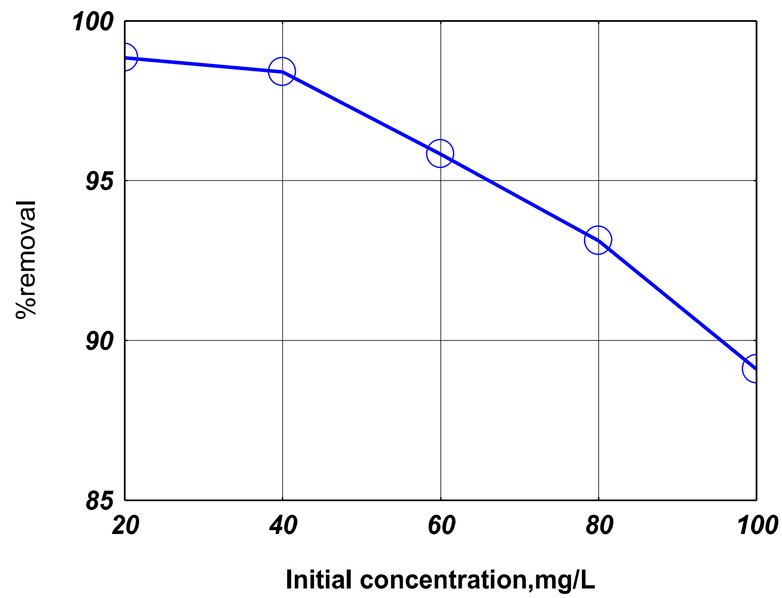

Fig. 5: Effect of initial concentration on the adsorption of ClO_4^- on MRH
(Weight of the adsorbent =1g, agitation speed =100 rpm, contact time = 60 minutes, temperature =25°C)

Effect of temperature: The influence of temperature on the adsorption rate was studied (Fig. 6). The adsorption of perchlorate increased with rise in temperature up to 40^{0}C and then drops drastically. This indicates that with increase in temperature, the available active sites, porosity and kinetic energy increase but the viscosity of the molecules decreases.[7] The chemisorption rate also increases and thereby increases the activation energy due to the rise in temperature.[5] But after certain level the adsorption rate decreases because of the bond breaking between adsorbate and adsorbed molecules. The tendency of the metal ion to escape from the biomass surface to the solution phase leads to the decrease in boundary layer, thereby decreases the rate of adsorption as reported by Aksu and Kutsal.[2]

Similar results were reported by Horsfall et al[10] on the adsorption of Pb^{2+} and Cd^{2+} from aqueous solutions. This finding is in agreement with the observations of Chowdhury et al[5] on the biosorption of malachite green on to modified rice husk.

Adsorption Isotherms: In the present study, the experimental data on batch adsorption have been fitted using three isotherm models namely Langmuir, Freundlich and Temkin.[5] The results are shown in table 1 and the modelled isotherms are plotted in fig. 7.

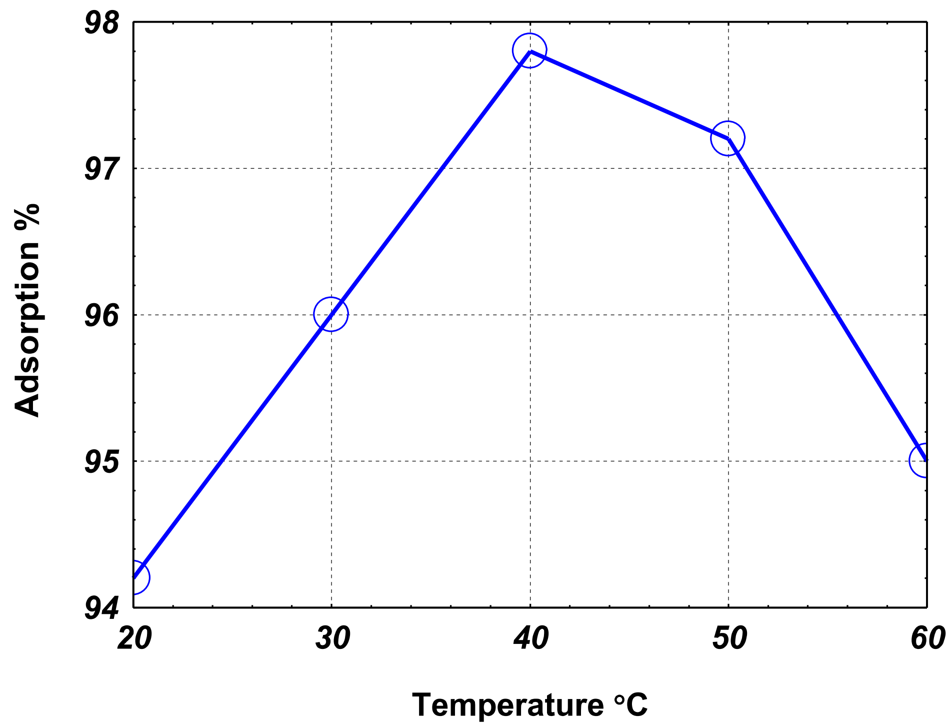

Fig. 6: Effect of Temperature on the adsorption of ClO_4^- on MRH
(conditions: Weight of the adsorbent =1g, agitation speed =100 rpm, contact time = 60 minutes)

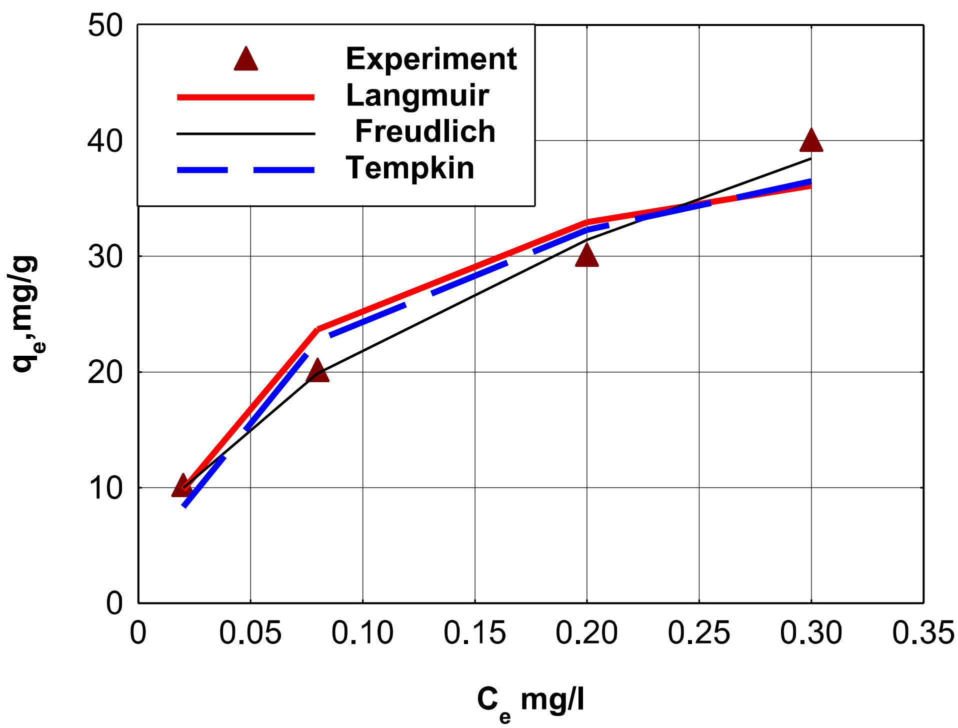

Fig. 7: Comparison of measured and modelled isotherm profile
(Weight of adsorbent = 0.1g, 30°C, Contact time = 60 minutes, pH=4).

The following equilibrium models have been used in the present study to investigate the suitable adsorption isotherm.

Langmuir Isotherm: Langmuir isotherm model is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L\, q_m} \qquad (2)$$

where q_e (mg/g)= equilibrium adsorption capacity, q_m (mg/g)= maximum adsorption, K_L (L/mg)= Langmuir constant and C_e (mg/L)= equilibrium adsorbate concentration in solution.

The comparison of the experimental data on adsorption of perchlorate is shown in fig. 8. The high value of correlation coefficient (R^2) obtained indicates a good agreement between the experimental values and isotherm. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L,

$$R_L = \frac{1}{(1+K_L\, C_o)} \qquad (3)$$

The calculated values of R_L are included in table 1. For an initial concentration (C_0) of 80 mg/L, all R_L values are between zero and unity thus showing favorable adsorption means that equilibrium isotherms can be explained by Langmuir model. The value of q_m increases with temperature confirming the process of adsorption as endothermic. The maximum adsorption capacity (50mg/g at 313K) for ClO_4^- uptake onto MRH shows agreement with experimental data.

The q_m values obtained in this study were comparable with previous reported values for the adsorbent such as wheat bran, rice bran, saw dust etc.[9,25] The q_m values obtained for the perchlorate adsorption by granular ferric hydroxide was about 20mg/g at pH 6.0 to 6.5 at room temperature.[30]

Freundlich Isotherm: The equation of Freundlich is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact:[5]

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4)$$

where K_F (mg/g) (L/g^{-1}) is the Freundlich constant and n is the heterogeneity factor.

The increase in adsorption with temperature suggests an endothermic process of adsorption. Freundlich isotherm model and comparison of experimental data for the perchlorate adsorption onto MRH have been made in this study and represented in fig. 9 which showed good agreement between experiment and the model.[19] The obtained values of $\frac{1}{n}$ indicated a higher adsorbent ability.

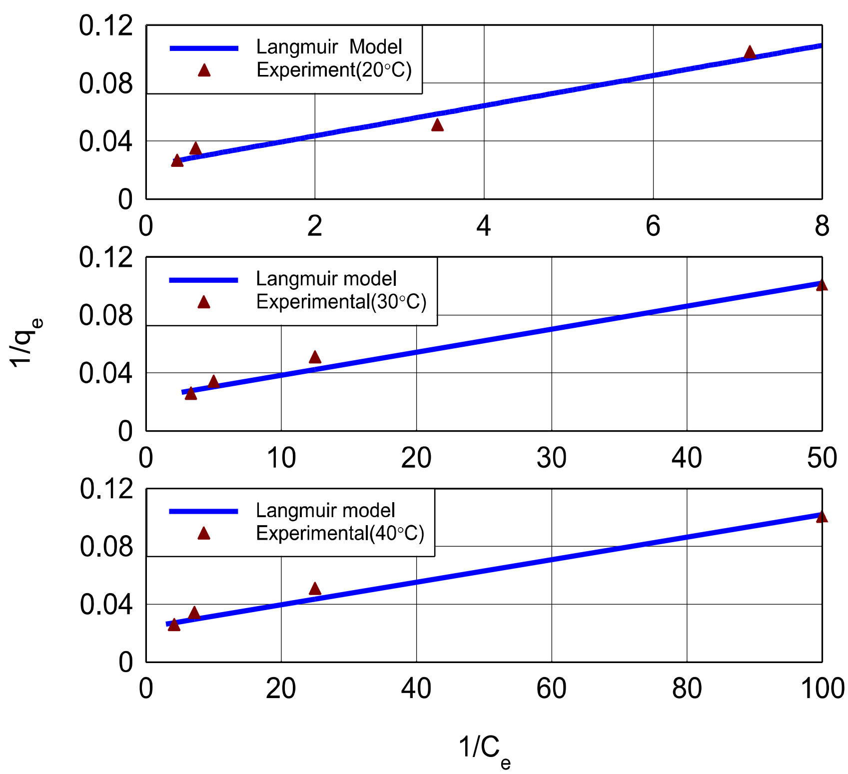

Fig. 8: Langmuir isotherm model and experiment comparison for the perchlorate adsorption on to Modified Rice husk

Table 1
Model parameters based on present study for adsorption of Perchlorate onto MRH

Isotherm	**parameters**	**T(K)**		
		293	**303**	**313**
Langmuir	q_m (mg g^{-1})	43.85	44.64	50.0
	K_L(Lmg^{-1})	2.19	14.08	25.0
	R^2	0.97	0.99	0.99
	R_L	0.00567	0.000887	0.000484
Freundlich	K_F (mgg^{-1}) (L $mg^{-1})^{1/n}$	25.70	70.10	75.94
	$\frac{1}{n}$	0.4	0.52	0.43
	R^2	0.91	0.98	0.992
Temkin	K_T (Lmg^{-1})	26.84	111.22	201.29
	B_T	8.51	10.4	10.5
	R^2	0.995	0.99	0.99

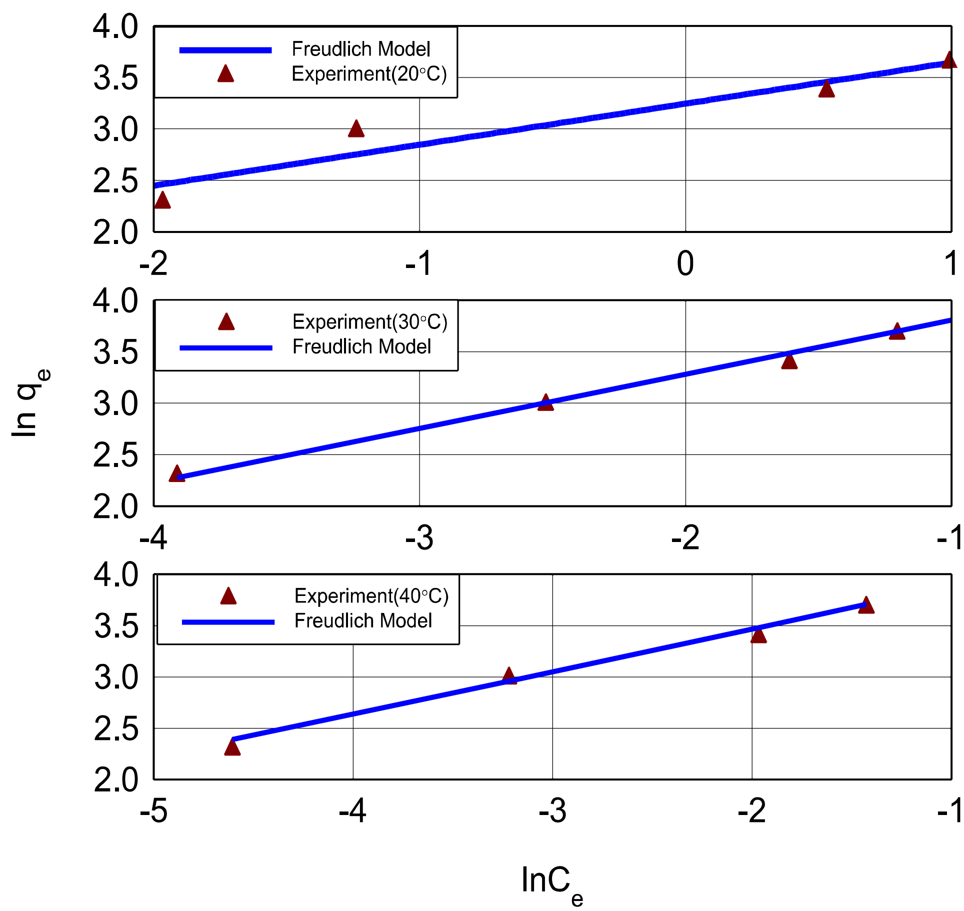

Fig. 9: Freundlich isotherm model and experiment comparison for the perchlorate adsorption on to Modified Rice Husk

The increase in Freundlich constant with increase in temperature shows adsorption was favorable at high temperature and the process is endothermic in nature. The R^2 values of Freundlich isotherm were found lower than that of the Langmuir isotherm, indicating a better fit of the present experimental data with the Langmuir model compared to the Freundlich model.[29] Table 1 gives different isotherm model parameter values based on the present investigation.

Temkin Isotherm Model: Temkin Isotherm Model[1] is expressed as:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (5)$$

where K_T (L/g) is Temkin adsorption potential and B_T is Temkin constant.

The comparison of the present experimental data on the perchlorate adsorption onto MRH with the Temkin isotherm is indicated in fig. 10 and observed a good agreement. Smaller value of B_T indicated the favorability of adsorption of perchlorate and the increase in B_T values with increase in temperature indicated endothermic adsorption. Table 1 gives different isotherm model parameter values based on the present investigation.

Adsorption Kinetics: To find out the adsorption mechanism, several kinetic models such as pseudo–first order, pseudo–second order and Elovich model have been applied in this study.

Pseudo-first order kinetic model: This model is applied at the initial stage of adsorption process.[29] The adsorption rate constant based on the adsorption capacity was determined from the pseudo first order kinetic model[17] (Table 2). It is expressed as:

$$\log(q_e-q_t) = \log q_e - \frac{k1}{2.303}t \qquad (6)$$

where q_e and q_t (mg/g)= amount of adsorbate adsorbed at equilibrium and at time t respectively and k_1 (min^{-1}) pseudo-first order adsorption rate constant.

The plot of log (q_e-q_t) verses t gave a straight line for the pseudo-first order adsorption kinetics to obtain the rate parameters. The values of k_1, calculated value of the adsorptive capacity $q_{e\ cal}$, experimental value of adsorptive capacity $q_{e\ exp}$ and the correlation coefficient R^2 obtained from the plot are given in table 2.

The kinetic parameters of the first order rate equation are given in table 2. It is found that the experimental results did not provide an accurate fit of the first order kinetics (Table 2) which indicated that the adsorption of ClO_4^- on to MRH did not follow pseudo-first-order kinetics. This can be due to the external resistance at the beginning of the adsorption process[11].

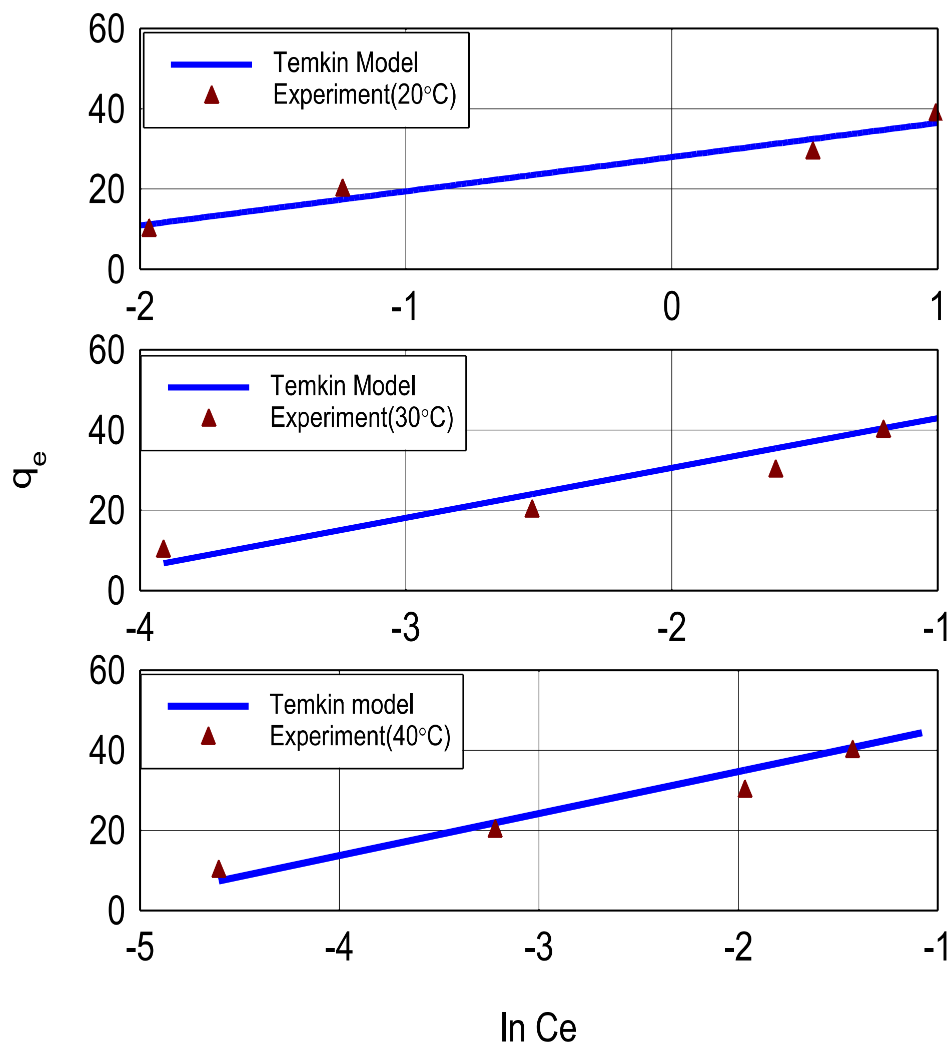

Fig. 10: Temkin isotherm model and experiment comparison for the perchlorate adsorption onto Modified Rice husk

Table 2
Kinetic Parameters for adsorption of Perchlorate onto modified Rice husk at 40°C.

C_o(mg/L)	$q_{e, exp}$(mg/g)	Pseudo first order			Pseudo second order		
		k_1(min^{-1})	$q_{e, cal}$(mg/g)	R^2	k_2(g/mg min)	$q_{e, cal}$(mg/g)	R^2
50	24.97	0.198	0.984	0.981	0.188	25.06	0.99
100	49.88	0.149	2.03	0.938	0.06	50.25	0.99
200	99.05	0.274	35.51	0.841	0.013	100.3	0.99

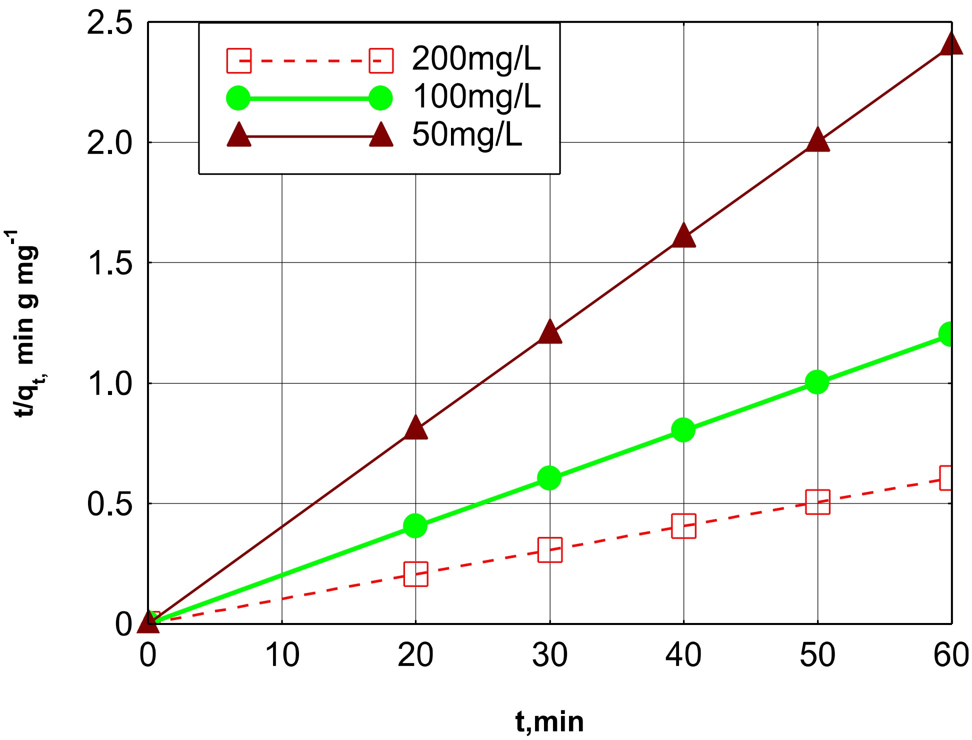

Fig. 11: Pseudo-Second order plot for the adsorption of perchlorate on MRH
(Weight of adsorbent = 0.1g, 40°C, Contact time = 60 min, pH=4)

Pseudo-second order kinetic model: The pseudo -second order rate expression, which has been applied for analyzing chemisorption kinetics from liquid solutions[28] is linearly expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where k_2 is the second order adsorption rate constant (g/mg/min), q_e is the adsorption capacity calculated by the pseudo –second order kinetic model (mg/g).

The plots t/q_t verses t gives a straight-line relation for the initial ClO_4^- studied (Fig. 11) and coefficient of correlation (R^2) very close to 1 (Table 2) confirms the applicability of the pseudo–second order equation to describe the adsorption process of ClO_4^- on MRH. The kinetic parameters of the second order rate equation based on the present study are given in table 2.

The values of $q_{e, cal}$ and k_2 were calculated from the linear plot of t/q_t verses t with slope of $1/q_e$ and intercept $1/k_2q_e^2$.The results showed that the second order rate constant k_2 decreased with an increase in initial concentration of perchlorate (ClO_4^-). The $q_{e\ cal}$ values agreed well with the experimental data $q_{e\ exp}$ (Table 2). This indicates the chemical behaviour of adsorption of ClO_4^- onto MRH and supports the assumption behind the model that the rate limiting step in adsorption of heavy metals is chemisorption involving sharing or exchange of electrons between adsorbent and metal ions.

Similar results were obtained for the removal of ClO_4^- using quaternary ammonium functionalized cross linked chitosan beads.[21]

From the pseudo -second-order kinetic model, the initial adsorption rate h (mg $g^{-1}min^{-1}$) at different temperatures was calculated using the following equation:

$$h = k_2 q_e{}^2 \qquad (8)$$

The value of h increases with increase in temperature indicating that higher temperature favours the adsorption process by increasing the rate of adsorption and capacity (Table 3). The above results support the process of adsorption of perchlorate onto MRH on account of chemisorption. Similar results were previously reported by Chowdhury et al.[5]

Elovich equation: The Elovich equation assumes that the active sites of a solid surface are heterogeneous in nature and thus exhibit different activation energies for chemisorption.

The Elovich equation is given below:

$$q_t = \frac{\ln(\alpha\,\beta)}{\beta} + \frac{\ln(t)}{\beta} \qquad (9)$$

where α is the initial adsorption rate (mg/g min) and β is the desorption constant related to the extent of surface coverage and activation energy for chemisorption (g/mg). From the plot of q_t verses ln (t) (Fig.12), the Elovich constants α and β were obtained from the intercept and slope. The values obtained for α (Table 4) are found to be increasing with initial concentration and the values of β decreased with increase in initial concentration.[29] The correlation coefficient R^2 were obtained in the range of 0.96-0.99 for all initial concentration (50 mg/L to 200 mg/L) and was found to be lower than pseudo second order model as shown in table 2.

Table 3
Kinetic Parameters for adsorption of Perchlorate onto modified Rice husk at 20°C and 40°C for an initial concentration of 50 mg/L

C_o(mg/L)	Temperature (^{o}C)	$q_{e,exp}$ (mg/g)	Pseudo second order			$h = k_2 q_e{}^2$
			k_2 (g mg^{-1} min^{-1})	$q_{e, cal}$ (mg/g)	R^2	(mg g^{-1} min^{-1})
50	20	24.40	0.012	25.60	0.99	7.50
50	40	24.97	0.188	25.10	0.99	118.90

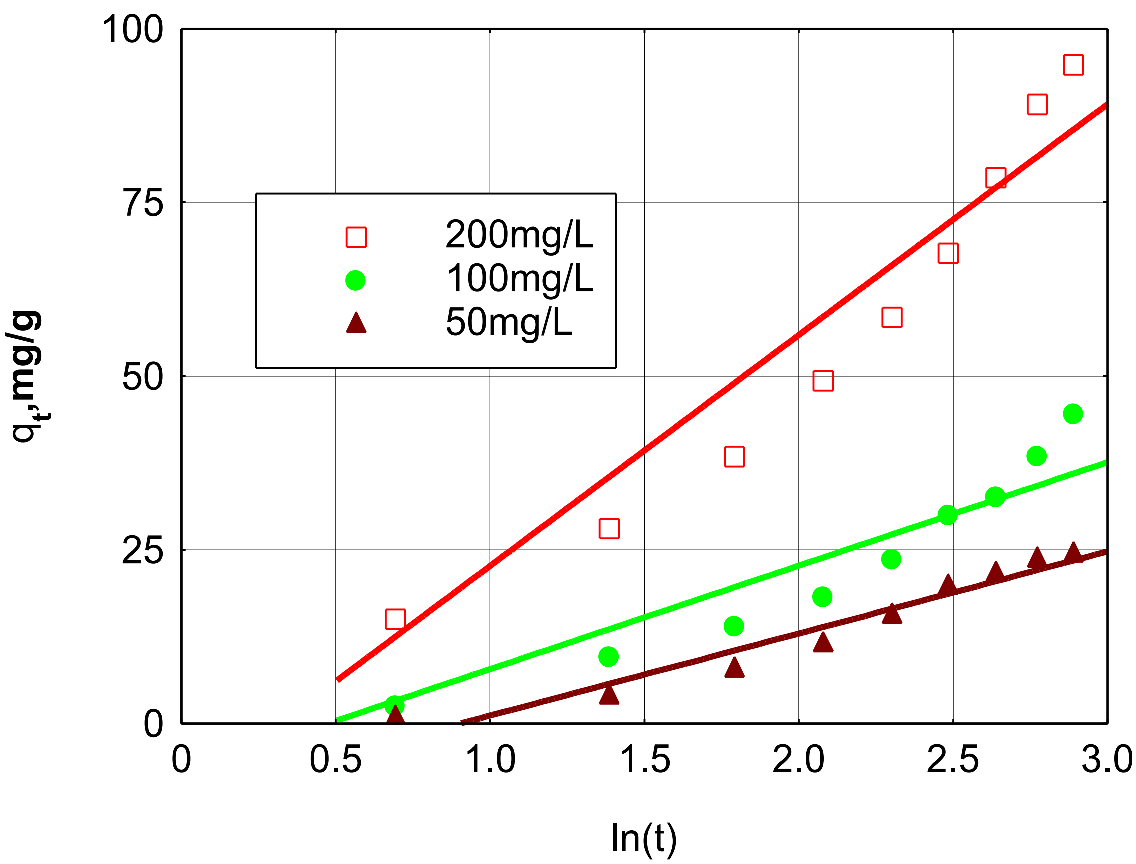

Fig. 12: Elovich kinetic model plot for the adsorption of perchlorate on MRH (Wt. of adsorbent =0.1g, 40°C, Contact time = 20 minute pH=4) for initial concentrations of 50 mg/L, 100 mg/L, 200 mg/L.

Activation Parameters: From the pseudo-second order constant k_2 (Table 4), the activation energy Ea for the adsorption of perchlorate on modified rice husk was determined. Arrhenius equation is expressed as:

$$\ln k = \ln A - \frac{Ea}{RT} \quad (10)$$

ln k versus 1/T is plotted (Figure not shown), Ea is obtained from the slope of the linear plot. The magnitude of Ea is 106.4 kJ/mol points to an activated chemical adsorption process.[3]

Thermodynamics: Thermodynamic studies have been undertaken to establish whether the process is spontaneous or not. Experimental results were used to calculate the thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0).

The Gibbs free energy change of the sorption reaction is given by:

$$\Delta G^o = -RT lnk \quad (11)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (12)$$

where k is the equilibrium constant obtained from Langmuir isotherm at different temperature. R is the universal gas constant and T is absolute temperature. ΔH^o and ΔS^o were obtained from the slope and intercept of the plot of Gibbs free energy change versus temperature (Fig. 13). The calculated results are reported in table 5. The adsorption of perchlorate onto MRH shows a spontaneous nature according to the negative values of ΔG^o. The positive values of ΔH^o and ΔS^o indicated the endothermic nature and the increase in randomness during the adsorption of perchlorate on MRH respectively.[5]

Heat of adsorption: Heat of adsorption (ΔH_X) calculated for a particular amount of adsorbate is required for the characterisation of adsorption process and for equipment design. Heat of adsorption (q_e =10 mg/g) was calculated using Clausius Clapeyron[5] equation expressed as:

$$\frac{d(\ln C_e)}{dT} = -\frac{\Delta H_X}{RT^2} \quad (13)$$

Equilibrium concentration (C_e) was obtained from the Langmuir isotherm data at different temperature. ΔH_X obtained from the slope of the plot of ln Ce Versus 1/T (Fig.14) is 101.4 kJ/mol. The ΔH_X value obtained in the present study varies between 80 and 400 kJ/mol indicating that the adsorption of perchlorate to MRH is on account of chemisorption.

Conclusion

The study deduces that the cationic surfactant modified rice husk (MRH) powder can be used as a very low-cost adsorbent for the removal of perchlorate from aqueous solutions. The adsorption of perchlorate on MRH is influenced by several factors. The process is pH dependent and it was found that maximum percentage of adsorption takes place at pH between 4 and 6.

Among the isotherm models, Langmuir model showed a better fit of the experimental data compared to the Freundlich model. The maximum adsorption capacity of 50 mg/g at 313 K obtained in the present study is relatively large. The adsorption data showed good agreement with the pseudo second order kinetic model for different sorbent concentrations. The values of activation energy of 106.4 kJ/mol estimated using Arrhenius equation indicates that the adsorption of perchlorate onto MRH was activated chemical sorption.

Table 4
Kinetic Parameters for Elovich model for the adsorption of Perchlorate onto modified rice husk at 40^{0}C

C_o(mg/L)	Elovich Model		
	α (mg/g min)	β(g/mg)	R^2
50	4.76	0.084	0.99
100	9.27	0.067	0.98
200	24.12	0.030	0.96

Table 5
Thermodynamic parameters for the adsorption of perchlorate on MRH (Volume 50ml, Weight of adsorbent = 0.1g, Contact time= 60 min, pH = 4, agitation speed =100 rpm)

S.N.	Temperature (^{o}C)	ΔG (kJmol^{-1})	ΔH (kJ/mol)	ΔS (J/mol/K)	R^2
1	20	-1.91	93.5	327	0.94
2	30	-6.66			
3	40	-8.48			

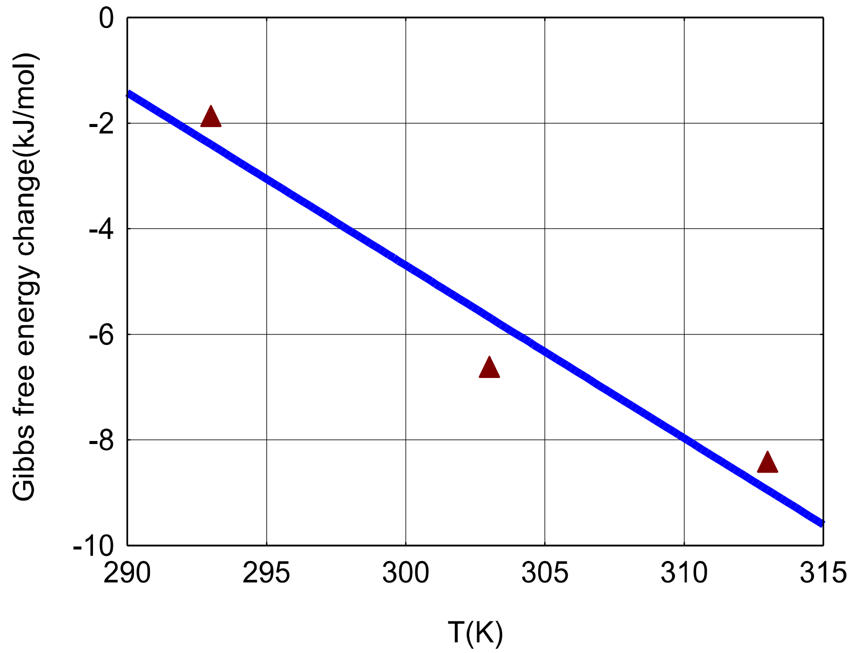

Fig. 13: Gibbs free energy variation with temperature

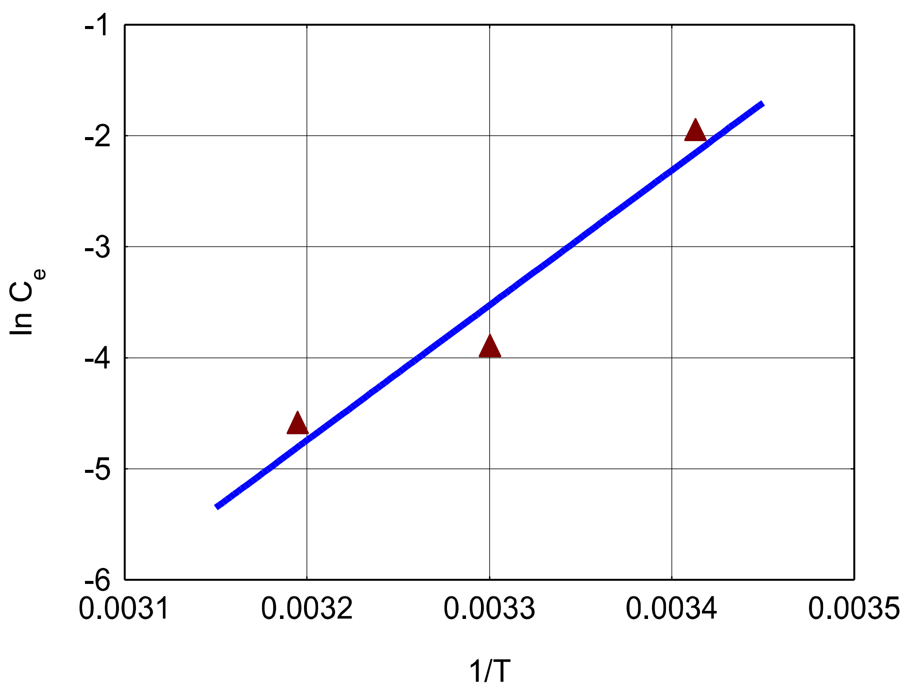

Fig. 14: Plot of ln Ce against 1/T for the adsorption of perchlorate on MRH

The heat of adsorption determined using Clausius Clapeyron equation also shows that adsorption of perchlorate on to rice husk is on account of chemisorption. The thermodynamic parameters ΔG°, ΔH^{o}, ΔS^{o} were also calculated and the results showed a feasible spontaneous endothermic adsorption process. The present study showed that MRH is an adsorbent that offers greater potential for the removal of perchlorate from water and waste water than other adsorbents reported in the literature. But further experiments concerning the continuous column experiment and desorption experiment should be conducted to understand further potential of MRH and its applications of perchlorate adsorption.

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