Adsorption of *p*–nitrophenol on coconut shell granular activated carbon: Isotherms, kinetics and thermodynamics

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Adsorption of *p*-nitrophenol by modified granular activated carbons based on coconut shell from aqueous solutions has been studied under laboratory conditions. Four granular activated carbons GAC383 (native form), GACO383 (its nitric acid oxidised form), GACZC1073 (native form incorporated with Zn^{2+} ions and activated at 1073) and GACOZC1073 (oxidised form impregnated with $ZnCl_2$) have been used. Batch experiments have been carried out with variants being concentration, time, temperature and equilibrium conditions. Pseudo first, second order kinetic models, intraparticle diffusion models and Elovich kinetic model are applied to study the respective kinetics. Pseudo second order rate equations are found to be best suited for the adsorption systems. Equilibrium isotherm for concentration range (25-3000 mg/L) is analysed by Langmuir (L) and John - SivanandanAchari (J-SA) isotherm models. GACZC1073 has higher adsorption capacity (490.2 mg/g) than GACO383 (224.2 mg/g). The temperature on the adsorption of *p*- nitrophenol is studied at different temperatures. The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy are calculated using Van't Hoff equation. It is inferred that, the adsorption of *p*-nitrophenol on new modified carbons is endothermic and occurs through physisorption. This study reveals that Zn^{2+} ions impregnated activated carbon GACZC1073 has more adsorption efficiency evidenced by a high adsorption of rate α and surface diffusion K_{id1} promoted by extra adsorption sites generated during activation.

Keywords: Adsorption, Adsorption kinetics, Granular Activated Carbon, John–Sivanandan Achari (J–SA) Isotherm, *p*-nitrophenol

Adsorption kinetics, equilibrium isotherm and thermodynamic studies are very important for the optimization of adsorption process for the design of unit operation[1]. Adsorption kinetics involves the determination of the rate at which pollutants are removed from solution media onto carbon surface. Also it controls the residence time of the solute and hence its uptake at the solid-solution interfaces[2].

Studies on adsorption isotherms are essential to understand how adsorbate interact with carbon granules and are critical in optimizing the use of adsorbent[3]. To design an adsorption reactor system, heat change of adsorption process is also important. Hence, study of the prominent thermodynamic parameters of the adsorption process such as enthalpy, entropy and free energy change are mostly done in adsorption science[4]. In this regard, adosrption of *p*-nitrophenol by modified granular activated carbons based on coconut shell from aqueous solutions had been studied under laboratory conditions. Four granular activated carbons GAC383 (native form), GACO383 (its nitric acid oxidised form),

GACZC1073 (native form incorporated with Zn^{2+} ions and activated at 1073) and GACOZC1073 (oxidised form impregnated with Zn^{2+} ions) were used. Batch experiments were carried out as a function of concentration time, temperature and equilibrium conditions. The main objective of this work is to make an attempt to evaluate the relative adsorption potential of coconut shell based granular activated carbons (GAC383, GACO383, GACZC1073 and GACOZC1073) newly developed under a set of activation conditions using *p*-nitrophenol as adsorbate.

Experimental Section

Commercially available coconut shell based granular activated carbon (manufactured by Indo German Carbon Industry, Cochin, India) was used as the basic carbon source for the preparation of new carbon series[5]. One kilogram of this carbon washed with NaOH and HCl to remove impurities and neutralize to neutral *p*H 7.0 and dried at 110°C and marked as GAC383. This was then oxidised by 12.9% HNO_3 washed with distilled water and dried at 110°C

and labelled as GACO383. About 10 g of GAC383 mixed with 50 mL water containing 0.035 g $ZnCl_2$ (Zn^{2+} = 0.017g) and activated under steam at 1073K in a temperature controlled furnace. The carbon was then dried in oven and the product was designated as GACZC1073. The same procedure was followed for GACO383 and the sample was marked as GACOZC1073. These four carbons were further used for the study of adsorption kinetics, isotherm and thermodynamic studies.

Selection of granular activated carbon for the adsorption process is largely dependent due to favourable physico chemical characteristics such as porosity, surface area, surface functional groups, surface morphology, crystallinity etc. The textural properties of the carbon materials are given in Table 1. Evaluation of physical charateristics such as pore volume and surface area were undertaken by using nitrogen adsorption–desorption isotherm at liquid nitrogen 77K using Micromeritics (Tristar 3000 V6. 07A). Surface functional groups were quantitatively measured using Boehm titration method. The elemental composition [C, H, N & O] of the modified granular activated carbons were evaluated by using Elemental Vario EL III. The surface morphology was evaluated by using Scanning Electron Microscope (SEM) Jeol Model JSM-6390LV and High Resolution Transmission Electron Microscope (HRTEM) Jeol /JEM 2100.

The batch experiments of the adsorption kinetics and isotherms were conducted at a temperature of 30°C in a 100 mL screw cap conical flask. 1.0 g/L adsorbent dosage was weighed and placed in the flask containing 50 mL solution of p-nitrophenol of a desired concentration ranging from 25-3000 mg/L and temperature ranging from 10 to 50°C. The adsorption kinetics were studied using initial concentration of p-nitrophenol 250 mg/L in a temperature controlled bath shaker. For isotherm study shaking time was fixed as 480 minute based on preliminary studies conducted for the determination of equilibration time. After shaking, the suspension was filtered using Whatmann No.1 filter paper. The concentration of the filtrate was measured using a UV-Visible Spectrophotometer at 317 nm.

Adsorption kinetic studies were undertaken using p-nitrophenol and the time dependent data were used to test different kinetic models such as pseudo first, Ho second, intraparticle diffusion and Elovich models[6]. Equilibrium data were applied to different isotherm models such as Langmuir isotherm and John – Sivanandan Achari (J- SA)[7-9] isotherm to calculate the adsorption capacity and other structural constants. The thermodynamic parameters such as enthalpy, entropy and Gibbs free energy (ΔH, ΔS and ΔG) were calculated from the Langmuir isotherms parameter (K_L) by using the Van't Hoff Equation[10].

Results and Discussion
Characterisation of modified GACs

The physico chemical characteristics of modified granular activated carbons (GAC383, GACO383, GACZC1073 and GACOZC1073) are listed in Table 1. The granular activated carbon impregnated with Zn^{2+} ions and activated at high temperature shows high basic groups, high carbon content, large micropore volume and surface area compared to other carbons. Granular carbons having very high carbon content is expected to have high surface area. It is known that the Zn^{2+} ions incorporated into the interior of GAC inhibits the expected contraction during activation temperature, which implies that Zn^{2+} may act as a template for creation of micro porosity[11]. In this, carbon GACZC1073 has higher micropore volume and micro porous surface area. GACOZC1073 shows higher BET surface area and

Table 1 — Physico – chemical characterization of modified granular activated carbon (GAC) based on coconut shell

Carbon	Carboxylic(meq/g)	Lactones(meq/g)	Phenolic(meq/g)	Base (meq/g)	C%	H%	N%	O%	V_t ($Cm^3 g^{-1}$)	V_{mic} ($Cm^3 g^{-1}$)	SA_{BET} (m^2/g)	SA_{mi} (m^2/g)
GAC383	0.40	0.17	0.45	0.50	89.43	0.60	0.36	9.6	0.573	0.351	996.8	588.7
GACO383	1.38	1.34	2.10	0.20	65.10	2.61	0.58	31.7	0.526	0.297	974.3	540.6
GACZC1073	0.39	0.10	0.20	0.90	94.47	0.09	0.31	5.1	0.569	0.378	1083.6	767.0
GACOZC1073	0.23	0.94	0.17	0.43	84.07	0.52	0.59	14.8	0.604	0.221	1101.8	349.4

lower micro pore volume and micro pore surface area that is because oxidation/ activation enlarge the pore structure. Granular activated carbon oxidized with nitric acid (GACO383) shows high oxygen content, less percentage of carbon and enhances the acidic functional groups. The SEM (Fig. 1) and TEM (Fig. 2) images showed that GACZC1073 is highly microporous evidenced by the porosity (0.378 cm^3/g) and surface area (767 m^2/g) value determined by N$_2$ gas adsorption at 77K.

Adsorption kinetic study

The adsorption kinetic study of *p*-nitrophenol on four carbons (GAC383, GACO383, GACZC1073 and GACOZC1073) was undertaken using initial concentration (250 mg/L) at a temperature 30°C. Figure 3 shows the *p*-nitrophenol uptake behaviour as a function of time. Among these four carbons Zn^{2+}

impregnated granular activated carbon activated at 1073K (GACZC1073) shows maximum adsorption capacity (229.5 mg/g) for an initial concentration of 250 mg/L *p*-nitrophenol used for kinetic study (Table 2). These time dependent data are applied in
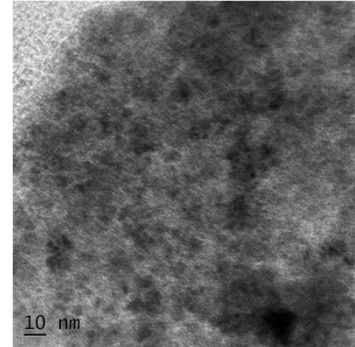

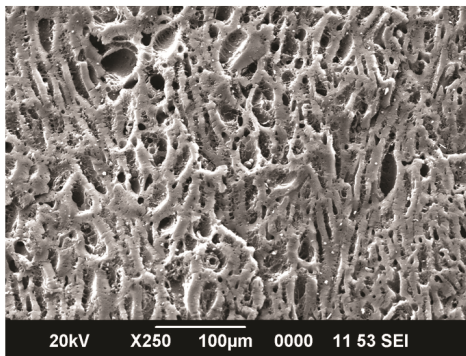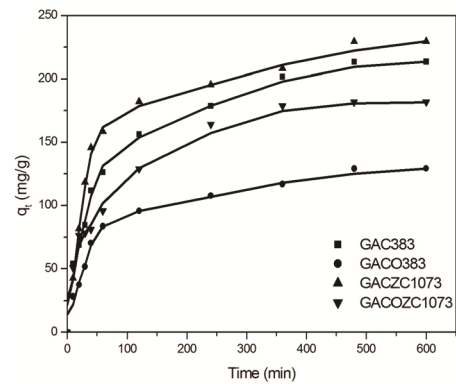Fig. 2 — Transmission electron microscopy of GACZC1073

Fig. 3 — Effect of contact time on the adsorption of *p*-nitrophenol on granular activated carbon (GAC) based on coconut shell

Fig. 1 — Scanning electron microgrpahs of GACZC1073 at 100μm magnification

Table 2 — Kinetic Parameters for the adsorption of *p*–nitrophenol on granular activated carbon (GAC) based on coconut shell

Kinetic Models	Parameters	Carbon			
		GAC383	GACO383	GACZC1073	GACOZC1073
Experimental value	$q_e exp$ (mg/g)	213.4	129.3	229.5	181.6
Pseudo first order	$q_e cal$ (mg/g)	151.3	84.2	129.3	151.5
	K_1 (min^{-1})	0.007	0.006	0.006	0.0103
	R^2	0.98	0.93	0.87	0.98
Pseudo second order	$q_e cal$ (mg/g)	228.8	136.8	258.6	199.2
	K_2*10^5 (gmg^{-1}min^{-1})	9.20	15.6	11.30	10.40
	R^2	0.99	0.99	0.99	0.99
Intraparticle diffusion Model	K_{id1} (mgg^{-1}min$^{-1/2}$)	16.80	12.89	26.56	8.77
	C_1	-2.21	-15.83	-35.02	28.67
	R^2	0.97	0.97	0.95	0.89
	K_{id2} (mgg^{-1}min$^{-1/2}$)	5.34	2.99	4.18	4.91
	C_2	97.64	62.04	133.47	80.75
	R^2	0.99	0.99	0.96	0.95
Elovich Kinetic Model	α (mgg^{-1}min^{-1})	12.76	10.75	18.24	11.64
	β (gmg^{-1})	0.0233	0.0397	0.0226	0.0276
	R^2	0.99	0.97	0.94	0.97
	E_a(kcal/mol)	0.2267	0.1792	0.4943	0.1926

different kinetic models such as Pseudo first order, Ho second order, Weber intra particle diffusion model and Elovich model to identify the mechanism of adsorption on modified carbons.

Pseudo first order model

Among the common kinetic models known to study adsorption,

Lagergen model is the simplest one followed for solute adsorption. This model is expressed in a linear form[12].

$$ln(q_e - q_t) = lnq_e - K_1 t \qquad \dots (1)$$

where K_1 (min^{-1}) is the pseudo-first order rate constant, t (min) the contact time, q_t and q_e are the amount of nitrophenol adsorbed at any time t and at equilibrium respectively for the granular activated carbon under study. The constants are given in Table 2.

Ho second order kinetic model

Ho presented a sorption based pseudo-second order rate law expression for the reaction rate dependence on the adsorption capacity on solid phase but not the concentration of adsorbate. The model is represented in the following form[13].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad \dots (2)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), t is the reaction time (min), q_t is the amount of adsorbate adsorbed at time t (mg/g), K_2 is the equilibrium rate constant of pseudo second order adsorption (g/mgmin). This model is used to express the kinetics of p-nitrophenol adsorption on the new carbons and the graph shown in Fig. 4.
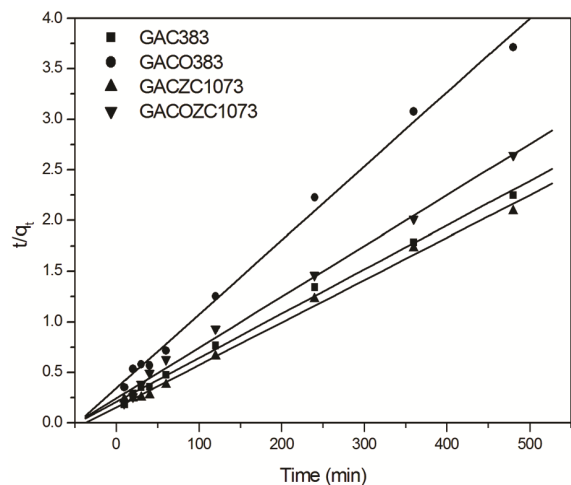

Fig. 4 — Pseudo second order kinetic model for the adsorption of p-nitrophenol on granular activated carbon (GAC) based on coconut shell

Intraparticle diffusion model

Weber and Morris[14] used intraparticle diffusion model to predict the rate controlling step of an adsorption process. When mass transfer is the controlling step, it is important to identify the diffusion mechanism. According to intraparticle diffusion model, the initial rate of diffusion is given by the following Equation:

$$q_t = K_{id} t^{0.5} + C \qquad \dots (3)$$

where q_t (mg/g) is the amount of p-nitrophenol adsorbed at any time t (min), K_{id} (mgg^{-1}min$^{-1/2}$) is the intra particle diffusion constant and C is the boundary layer thickness from the slope and intercept respectively, the plot of q_t $vs.$ square root of time in min shown in Fig. 5, for the new granular activated carbons.

Elovich kinetic model

The simplest form of Elovich model[15] is represented by

$$q_t = \frac{1}{\beta}(ln\,\alpha\beta) + \frac{1}{\beta} ln\,t \qquad \dots (4)$$

The α (mg g^{-1} min^{-1}) is the initial rate constant and β (g mg^{-1}) is related to the extent of surface coverage and activation energy of adsorption, can be determined respectively from the intercept and slope of the plot q_t vs. lnt. Activation energy (E_a) for the adsorption of p-nitrophenol on these modified carbons is obtained using Arrhenius equation based on Elovich constant (β), from a linear plot of log β against $1/T$ for the temperature ranges from 283 to 323K.

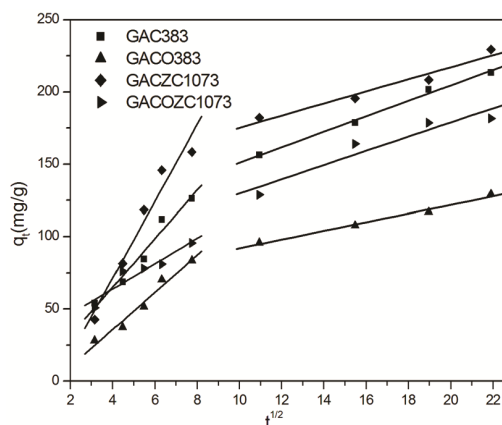The kinetic parameters for the adsorption of p-nitrophenol on modified granular activated

Fig. 5 — Intrapartcile diffusion model for the adsorption of p-nitrophenol on granular activated carbon (GAC) based on coconut shell

carbons are calculated and listed in Table 2. The amount adsorbed ($q_e exp$) determined from the batch kinetic study is more comparable with q_e calculated ($q_e cal$) obtained from the pseudo second order kinetic model whose correlation coefficient ($R^2=0.99$) was found to be high compared to the first order model applied (R^2 ranges 0.87-0.98). This means the adsorption of *p*-nitrophenol on these modified GAC follows Ho second order kinetic model[16] which implies adsorption is controlled by the square of unoccupied sites on granular activated carbons. To determine the adsorption mechanism, the intraparticle diffusion model by Weber is applied on this time dependent adsorption data. Figure 5 shows two straight line portions on plotting the data. The first stage is attributed to surface diffusion and the second stage is due to pore diffusion. The K_{id1} (ranges 8.77-26.56 mgg^{-1}min$^{-1/2}$) is higher than the K_{id2} (ranges 2.99-5.34 mgg^{-1}min$^{-1/2}$) for all carbons indicating that pore diffusion is a slow step (Table 2). This reveals that the adsorption mechanism of *p*–nitrophenol on the new carbons also follow intraparticle diffusion model. As regards to Elovich model tested, GACZC1073 shows higher initial adsorption rate (α) compared to other carbons. The activation energy (E_a) calculated ranges 0.17-0.49 kcal/mol (is less than 4.0 kcal/mol) indicate that the surface diffusion[17] has a major role on adsorption. Zn^{2+} ions impregnation increases adsorption sites on the surface of granular activated carbon. Hence, enhances the overall adsorption efficiency.

Adsorption Isotherm and thermodynamic study

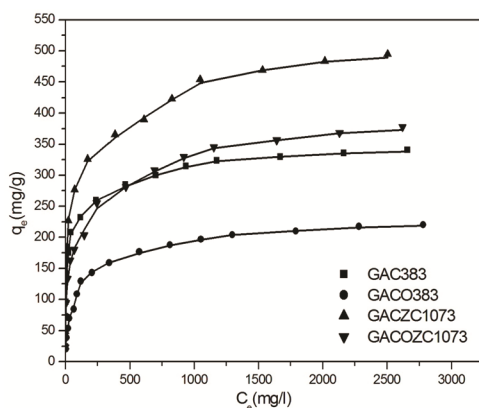Figure 6 depicts the isotherm plot for *p*- nitrophenol over the new GAC's, in which the amount of *p*- nitrophenol adsorbed per gram of adsorbent *(q_e)* is plotted against the equilibration concentration *(C_e)*. The isotherm has a steep phase in the beginning followed by saturation at higher initial concentration typical for type I microporous materials as per IUPAC (2015) classification[18]. The equilibrium data are further processed to fit the standard adsorption isotherm models of Langmuir and John – Sivanandan Achari *(J-SA)* Isotherm models.

Langmuir isotherm is a mathematical construct to evaluate the adsorption efficiency of activated carbon (Fig. 7). The form of the model is[19]

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad \cdots (5)$$

K_L (Lmg^{-1}) is adsorption energy and q_{max} (mg/g) is monolayer adsorption capacity.

John – Sivanandan Achari (J-SA) Isotherm is an emperical isotherm[20-22] and the equation can be expressed as

$$log\ log\ C_e = C + n\ log\ q_e \qquad \cdots (6)$$

C and *n* are the *J-SA* isotherm constants; *n* is referred as adsorbability constants and is a measure of adsorption efficiency.

Monolayer adsorption capacity increases according to the order GACZC1073 (490.2 mg/g) > GACOZC1073 (377.4 mg/g) > GAC383 (340.1 mg/g) > GACO383 (224.2 mg/g), that indicates granular activated carbon incorporated with Zn^{2+} ions and activated / carbonized at 1073K has the highest adsorption efficiency among the group selected for isotherm study. The J-SA plot Fig. 8 shows a straight line with single phase adsorption and the q_m *(J-SA)* and monolayer adsorption capacity $q_{max}(L)$ of

Fig. 6 — General isotherm plot for the adsorption of *p*-nitrophenol on granular activated carbons based on coconut shell
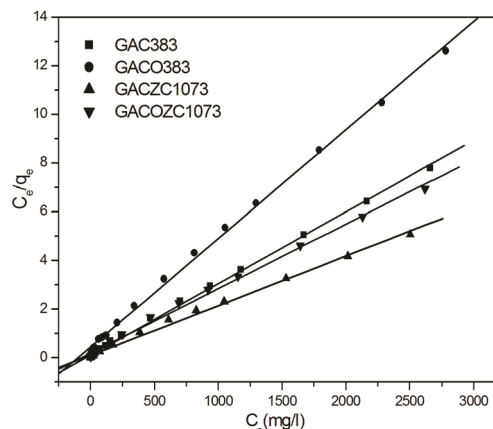

Fig. 7 — Langmuir isotherm for the adsorption of *p*-nitrophenol on granular activated carbons based on coconut shell

Langmuir model (Fig. 7) are comparable for all GAC's as listed in Table 3 indicating that these modified carbon are microporous and belongs to type I category according to classification by John and Achari (2002)[23].

Thermodynamic parameters

The mechanism of adsorption of *p*- nitrophenol on the above carbon is elucidated by different thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). These parameters were calculated from the Langmuir isotherm constants (K_L) adopting the Van't Hoff's Equation (7 and 8). The temperature effect on the adsorption of *p*- nitrophenol was studied at 5 different temperatures (10, 20, 30, 40 and 50°C) as shown in Figs 9 and 10.

$$\Delta G = -RT \ln K_L \qquad \qquad \ldots(7)$$

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \ldots (8)$$

The values of ΔS and ΔH are calculated from the intercept and slope of the plot *ln* K_L versus *1/T* for *p*-nitrophenol adsorption on different GAC and are given in Table 4. The positive value of *ΔH* indicates that adsorption of *p*- nitrophenol on GAC were

Fig. 9 — Plot of $\ln K_L$ versus 1/T for the estimation of thermodynamic parameters for the adsorption of *p*-nitrophenol on GACO383 based on coconut shell
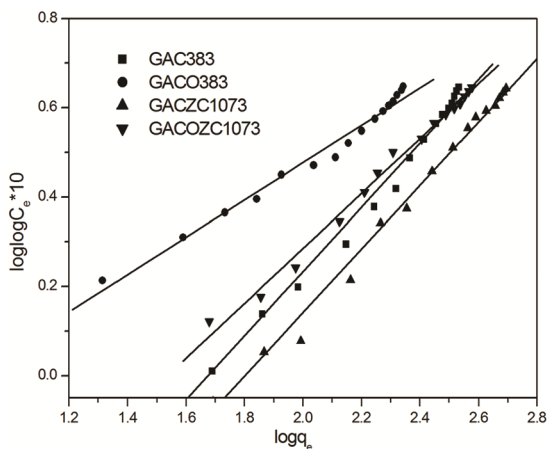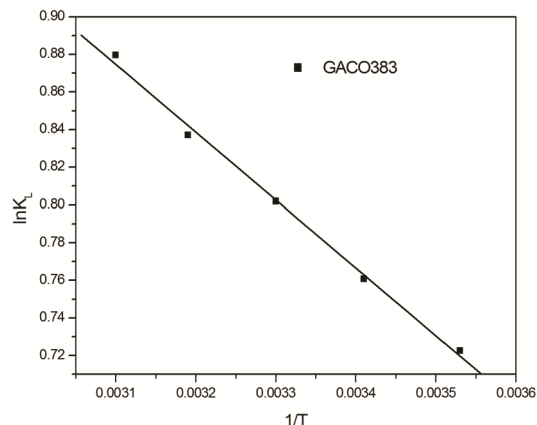

Fig. 8 — John – Sivanandan Achari isotherm for the adsorption of *p*-nitrophenol on granular activated carbons based on coconut shell
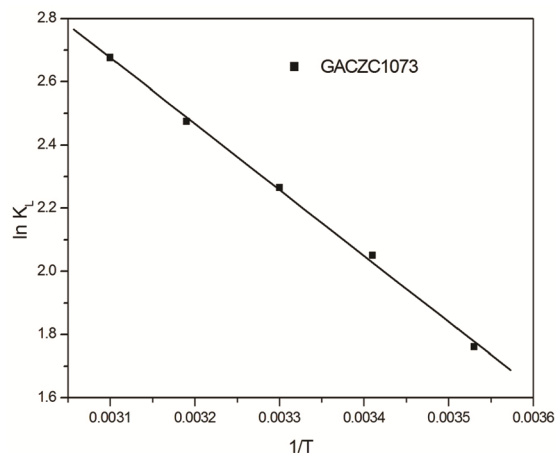

Fig. 10 — Plot of $\ln K_L$ versus 1/T for the estimation of thermodynamic parameters for the adsorption of *p*-nitrophenol on GACZC1073based on coconut shell

Table 3 — Equilibrium adsorption isotherm parameters for the adsorption of *p*-nitrophenol on granular activated carbon (GAC) based on coconut shell

Isotherm Models	Parameters	Granular Activated Carbon (GAC)			
		GAC383	GACO383	GACZC1073	GACOZC1073
Langmuir Model	$q_{max}(L)$ (mg/g)	340.1	224.2	490.2	377.3
	K_L (L/mg^1)	9.0	2.2	9.7	5.2
	a_L(L/mg^1)	0.026	0.010	0.019	0.014
	R^2	0.99	0.99	0.99	0.99
John SivanandanAchari (J-SA) isotherm	q_m(J-SA)(mg/g)	349.95	238.78	509.45	389.13
	C	1.20	0.3580	1.28	0.945
	n	0.718	0.417	0.711	0.615
	R^2	0.99	0.98	0.99	0.99

Table 4 — Thermodynamic Parameters for the adsorption of *p*-nitrophenol on granular activated carbon (GAC) based on coconut shell

Carbon	ΔG (KJmol^{-1})					ΔH (KJmol^{-1})	ΔS (Jmol^{-1}K^{-1})
	283	293	303	313	323		
GAC383	-4.78	-5.17	-5.54	-5.83	-6.36	6.02	38.18
GACO383	-1.70	-1.85	-2.02	-2.18	-2.36	2.96	16.45
GACZC1073	-4.14	-4.99	-5.71	-6.44	-7.19	17.16	75.44
GACOZC1073	-3.31	-3.72	-4.20	-4.68	-5.52	11.85	53.26

endothermic in nature. The adsorption occurs by endothermic process. Increasing temperature enhances the rate of diffusion of the adsorbate molecule across the external boundary layer and in the internal pores of the adsorbate particle, due to the decrease in the viscosity of the solution[24]. The magnitude of the standard enthalpy change, gives an idea for adsorption is physical or chemical in nature on carbon surfaces. The *ΔH* for all the new GAC is less than 20 KJ/mol which indicates that adsorption of *p*-nitrophenol on new modified GAC follows physisorption mechanism. The positive value of entropy change (Δ*S*) reflects good affinity towards the GAC and the increasing randomness at the solid-solution interface during the adsorption reaction. The negative Δ*G* confirms the feasibility and spontaneity of the adsorption process. From these data, we ascertain that the adsorption process is more favourable at higher temperature (323K), due to endothermic nature of the adsorption system.

Conclusion

Zinc ions impregnated activated carbon (GACZC1073) based on Indian coconut shell shows higher adsorption efficiency to remove *p*-nitrophenol compared to other granular activated carbons. Kinetic studies showed that adsorption of *p*-nitrophenol followed pseudo-second order model. Two phases in the intraparticle diffusion suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion, the particle diffusion is a slow step. Adsorption of *p*-nitrophenol on GAC shows good agreement between Langmuir and John-Sivanandan Achari isotherm plot and it indicate the development of microporosity during Zn^{2+} activation. The adsorption capacity of the carbon studied for the present communication can be arranged in the following order GACZC1073 (490.2 mg/g) > GACOZC1073 (377.4 mg/g) > GAC383 (340.1 mg/g) > GACO383 (224.2 mg/g). Thermodynamic parameters such as enthalpy change, free energy change and entropy change

showed that the adsorption process of *p*–nitrophenol is endothermic and spontaneous.

References

1   Arabi S, Sohrabi M R & Khosravi M, *Indian J Chem Technol*, 20 (2013) 173.
2   Jayasree S & Sivanandan Achari V, (Central Marine Fisheries Research Institute, Cochin), 2016.
3   Altenor S, Carene B, Emmanuel E, Lambert J, Ehrhardt J J & Gaspard S, *J Hazard Mater*, 165 (2009) 1029.
4   Singh K & Chandra B, *Indian J Chem Technol*, 22 (2015) 11.
5   Sivanandan Achari V & Jayasree S, Adsorption of *p*- nitrophenol on Zn^{2+} impregnated activated carbons, *Proceedings, 24th Swadeshi Science Congress*, (Thunchath Eezhuthachan Malayalam University, Tirur, Malappuram) 2014.
6   Jayasree S & SivanandanAchari V, Adsorption of *p*- nitrophenol on ZnO Incorporated Activated Carbons: Isotherms, Kinetics and Surface Area, *Proceedings, International Conference, MATCON*, Department of Applied Chemistry, CUSAT, 2016.
7   SivanandanAchari V, *Modified Carbons and Wood Dust: Evaluation of Adsorption Properties*, Ph.D. Thesis, University of Kerala, Trivandrm, 1998.
8   John P T & Bohra J N, *Indian J Chem Technol*, 1 (1963) 437.
9   Mercy T, *Adsorption Isotherm Characterisation of Porous Materials Using John Isotherm*, Ph.D. Thesis, School of Environmental Studies, Cochin University of Science and Technology, Cochin, Kerala, 2016.
10   Argun M E, Dursun S, Ozdemir C & Karatas M, *J Hazard Mater*, 141 (2007) 77.
11   Gonzalez-Serrano E, Cordero T, Rodríguez-Mirasol J & Rodríguez J J, *Ind Eng Chem Res*, 36 (1997) 4832.
12   Lagergren S, *K Sven Vetenskapsakad Handl*, 24 (1898) 6.
13   McKay G & Ho Y S, *Process Biochem*, 34 (1999) 451.
14   Weber W J & Morris J C J, *Sanit Eng Div Am Soc Civil Eng*, 89 (1963) 31.
15   Varank G, Demir A, Yetil Mezsoy K & Top S, *Indian J Chem Technol*, 19 (2012) 7.

16 Singh H & Choden S, *Indian J Chem Technol*, 21 (2014) 359.

17 Juang R S, Chen M L, *Ind Eng Chem Res*, 36 (1997) 813.

18 Thommes M, Kaneko K, Neimark A V, Olivier J P, Rodriguez – reinoso F, Rouquerol J & Sing K S W, *Pure Appl Chem*, 87 (2015) 1051.

19 Mckay G, Geundi M E L & Nassar M M, *Wat Res*, 21 (1987) 1513.

20 Sivanandan Achari V, Isotherm for Liquid Phase adsorption: Comparison with Langmuir and Freundlich models: *Proceedings, International Carbon Conference, Carbon,* (Robert Gordon University, Aberdeen, Scotland, UK), 2006.

21 Jayasree S, Rajalakshmi A S & SivananadanAchari V, Determination of Surface Area of Activated Carbons using John- SivanandanAchari Isotherm Plots, *Proceedings, 26ᵗʰ Kerala Science Congress*, (Veterinary and animal sciences University, Pookode, Wayanadu), 2014.

22 Rakhi, P, *John Isotherm Model – Evaluation of adsorption parameters*, M.Tech Thesis, Department of Civil Engineering, Government Engineering College, Thrissur, Kerala, 2010.

23 John P T & Achari V S, *J Mater Sci*, 37 (2002) 885.

24 Wang S & Zhu Z H, *Dyes Pigm*, 75 (2007) 306.