

Adsorption of *p*-nitrophenol from aqueous solutions by Zr⁴⁺ activated carbon: Adsorption isotherm studies

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Received 28 April 2017; accepted 8 January 2018

The dynamic adsorptive separation of *p*-nitrophenol from aqueous solution by newly modified coconut shell based granular activated carbon impregnated with Zr⁴⁺ has been studied. The adsorption behaviour is described by isotherm models of Langmuir, Freundlich and Dubinin-Radushkevich equations. The isotherm parameter shows loading of activated carbon with zirconium ions during stages of activation significantly improve the adsorption potential of activated carbon towards *p*-nitrophenol. Pore structure characteristics of the newly prepared granular activated carbon GACZR 1273 and GACOZR 1273 have been determined by nitrogen (N₂) gas adsorption isotherms data at 77K. Study shows each carbon has its own specific characteristics such as porosity, pore structure and surface area compared to their respective starting carbon GAC and GACO. The surface characteristics of carbon are directly related to the adsorptive removal of *p*-nitrophenol from aqueous solution under dynamic and equilibrium condition.

Keywords: Adsorption, Granular activated carbon, Isotherms, *p*-Nitrophenol, Surface area

p-nitrophenol is a common organic pollutant; its maximum concentration level in the industrial effluent for safe discharge into surface water bodies is 1.0 mg/L¹. WHO recommends the permissible limit of phenolic compound is 0.001mg/L in potable waters². The main sources of *p*-nitrophenol which are released into the aquatic environment are the wastewater from industries such as coke ovens in steel plants, petroleum refineries, resin, petrochemical, fertilizer, pharmaceutical, chemical and dye industries³.

Adsorption is one of the most widely used methods for removing pollutants in the tertiary treatments and the activated carbons are most frequently employed. Activated carbons are important commercial adsorbents, with large specific surface area, high porosity, adequate pore size distributions and high mechanical strength⁴. They are widely employed in water and wastewater treatment processes for removing organic compounds such as phenol and its derivatives⁵⁻⁷. Surface treatment modifications of carbon adsorbent generate more adsorption sites on their solid surface for adsorption. Physical activation involves two steps, namely carbonization of the precursor in an inert atmosphere and subsequent activation of the resulting char in the presence of carbon gasification reactants (gaseous); such as carbon

dioxide, steam /air or a suitable combination of the above mentioned gaseous activating agents. In chemical activation process, activating agents has been extensively employed for the production of activated carbon with desired pore structure. It is usually done in a single step process for the preparation of activated carbon where carbonization of precursor/starting carbon occurs in the presence of chemical agents. Solid activating agents like alkali and alkaline earth metal containing substances or some acids (e.g.: KOH, NaOH, Li₂CO₃, Na₂CO₃, K₂CO₃, Rb₂CO₃, Cs₂CO₃, ZnCl₂, H₃PO₄) are commonly used.

The impregnation of metal ion or its salts modifies the porous structure of activated carbon. Increase in the adsorption efficiency was observed by impregnation of carbon with some metal ions for the removal of lead, arsenic, chromium, nickel etc⁸.

Zirconium and its ions are known to be quiet environmentally safe, having low biotoxicity and is relatively inexpensive. One of the most important characteristics of them are relatively good catalytic potential, high reactivity, large surface area, ease of separation, and accessibility of a large number of active sites for interaction with different contaminants^{9,10}. Adsorption performances of various types of activated carbon towards phenol and their derivative have been

reported in earlier studies. In this regards this study, report the adsorption efficiency enhancement of GAC by incorporating zirconium as ZrOCl₂ during stages of activation for generating extra porosity.

Subsequently, adsorption study is conducted with an aim to correlate the effect of these salts/ ions on carbon. Effects are taken to compare the efficiency of newly prepared carbons for the removal of *p*-nitrophenol from aqueous solution with porosity and surface area.

Adsorption isotherm explains the interaction between adsorbate and adsorbent and is critical for design of adsorption process. The Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms models are used to describe the equilibrium isotherm data of *p*-nitrophenol adsorption by the new carbons.

There are four carbons GAC 383, GACO 383, GACZR 1273 and GACOZR 1273 used in this study. GAC 383 is the native carbon based on coconut shell, GACO 383 is acid oxidised and others are Zr⁴⁺ impregnated activated carbons of GAC 383 (GACZR 1273) and GACO 383 (GACOZR 1273).

Experimental Section

The activated carbon purchased from Indo German carbon limited, Cochin, Kerala, India [Particle size (US mesh) 12 × 40, iodine No. 1100 mg/g, apparent density 0.50 g/cc, moisture 5%, ash 4 %] is used throughout the study and it was washed with 0.5 M NaOH and repeated with 0.5 M HCl. Sufficient bed volume of distilled water is passed through carbon bed until a neutral pH was noted for the eluted water. Then carbon is filled in a glass column for further washing. Washed carbon was dried in an air oven at 110°C, and it is represented as GAC 383.

Carbon oxidation was done in the reaction mixture containing 100 g acid washed activated carbon, 130 mL of 13% HNO₃ and 540 mL of distilled water, and it is refluxed for 3 hr. After oxidation, the samples was filtered and thoroughly washed with hot distilled water until the pH became neutral, then dried in an air oven for 24 hr at 383 K. The nitric acid treated activated carbon was represented as GACO 383.

Impregnation ratio of zirconium

Mixing 10 g carbon (GAC and GACO) and solution of 0.5 g zirconyl chloride in water with shaking at 80°C using magnetic stirrer and kept in water bath for drying. These impregnated carbons are activated under steam at 1273K is represented as GACZR 1273 and GACOZR 1273.

Samples characterization and analytical methods

Surface characterization of the newly prepared carbon was performed using FTIR (Thermo Nicolet, Avatar 370) spectroscopy for qualitatively analyzing the nature of surface functional groups. Boehm's titration used for the quantitative measurement of surface oxygen functional groups on the new Zr⁴⁺ based activated carbon. In this method, the number of acidic sites namely carboxylic, lactonic and phenolic can be distinguished by neutralization with bases of various basicity (NaHCO₃, Na₂CO₃, NaOH). Basic groups are determined by neutralization with dilute HCl as per the above method. An XRD analyzer (Bruker AXS D8 Advance) was used to measure powder X-ray diffraction patterns of the new GAC series. Scanning Electron Microscopy (JOEL Model JSM - 6390LV) is used for the study of surface morphology.

Batch equilibrium adsorption study

For each batch adsorption study 0.025 g of this granular activated carbon was added to 25 mL *p*-nitrophenol solutions of known concentration [25, 50, 75, 100, 150, 200, 250, 350, 500, 750, 1000, 1250, 1500, 2000, 2500 and 3000 mg/L] prepared in aqueous media in a 250 mL Erlen Mayer flask and placed on a temperature-controlled LABLINE water bath shaker. The solutions were withdrawn from the shaker at the predetermined time interval and are filtered out using Whatmann No.1 filter paper. The residual concentration of *p*-nitrophenol in solution after adsorption is determined using UV-Visible spectrophotometer (CARY 50 Probe) at wavelength 317 nm. The amount adsorbed at time, q_t (mgg⁻¹) and at equilibrium condition, q_e (mgg⁻¹) was calculated according to the following Eq. (1) and Eq. (2).

$$q_t = \frac{V(C_0 - C_t)}{W} \quad \dots(1)$$

$$q_e = \frac{V(C_0 - C_e)}{W} \quad \dots(2)$$

where C_0 and C_e are initial and equilibrium adsorbate concentrations (mg l⁻¹) respectively. C_t is adsorbate concentration at time (mg l⁻¹). V is the volume of solution (L) and W is a mass of adsorbent

Batch kinetic study

Pre weighed amount of the adsorbents (0.05 g) were added to batch reactor flasks containing 50 mL of the aqueous solution of 250 mg/L *p*-nitrophenol. The

flasks were kept in a temperature controlled shaking water bath, at the end of time interval t (8h), the flask were withdrawn, their contents were filtered and the filtrates analysed for *p*-nitrophenol.

In order to investigate the kinetics of adsorption of *p*-nitrophenol on the adsorbents, various kinetic model like pseudo first order and pseudo second order, and intraparticle diffusion model were used.

Solid-Gas equilibria studies

The pore structure characteristic of the activated carbons was determined by N₂ adsorption-desorption isotherm at 77K volumetrically using Micromeritics TriStar 3000 V6.07 BET analyser. This isotherm data subjected to BET, I point, Langmuir, Freundlich and Dubinin-Radushkevich isotherms for the determination of pore volume and surface area.

Results and Discussion

Surface chemistry of impregnated carbons

FTIR spectra of new activated carbon series (Fig. 1) point out that relatively high intensity-peak was observed at 3460, 1640, and 1100 cm⁻¹ for HNO₃ modified carbons compared to that of nitric acid untreated carbons.

The peak at 3460 cm⁻¹ attributed to O-H stretching vibration due to the hydroxyl group and adsorbed H₂O. Peak at 1640 cm⁻¹ is a characteristic for carbon material and is probably ascribed to the carbonyl group which is highly conjugated in the graphene layers such as quinone structure C=O. And the band at 1100 cm⁻¹ is ascribed by the C-O stretching and O-H bending modes of alcoholic, phenolic, and carboxylic groups^{11,12}.

Surface oxygen group on carbon with acidic character namely carboxylic, phenolic, and lactonic groups are determined by neutralization with base of NaHCO₃, NaOH and Na₂CO₃ respectively. Whereas basic groups are determined by neutralization with HCl. For carbon GACZR 1273 and GAC 383, respectively there are 0.393 meq/g and 0.40 meq/g of carboxylic, 0.444 meq/g and 0.45 meq/g of phenolic, 0.202 meq/g and 0.18 meq/g lactonic, 0.62 meq/g and 0.5 meq/g basic functional groups. Whereas nitric acid modification of these carbons namely GACZR 1273 and GACO 383 shows 0.62 and 1.38 meq/g carboxylic, 1.52 and 2.1 meq/g phenolic, 0.9 and 1.34 meq/g lactonic, 0.38 and 0.2 meq/g basic functional groups respectively.

It indicates that, surface modification with nitric acid enhances the oxygenation of C-O acid functional groups on the surface of the carbon. Means that number

of acidic sites increases when carbon is reacted with oxidizing agent, on the other hand the number of basic sites are reduced. Nitric acid treatment of carbons incorporates larger amounts of oxygen functional groups on the carbon surface.

From the XRD spectrum (Fig. 2), the interlayer spacing d_{002} can be determined using the Bragg's equation.

$$d = \lambda / 2\sin \theta \quad \dots (3)$$

where λ is the x-ray wavelength and θ is the scattering angle for the peak position. The crystallite size along c axis, L_c , and the size of the layer planes, L_a are determined from the half-width of the diffraction peak using the Scherrer equation.

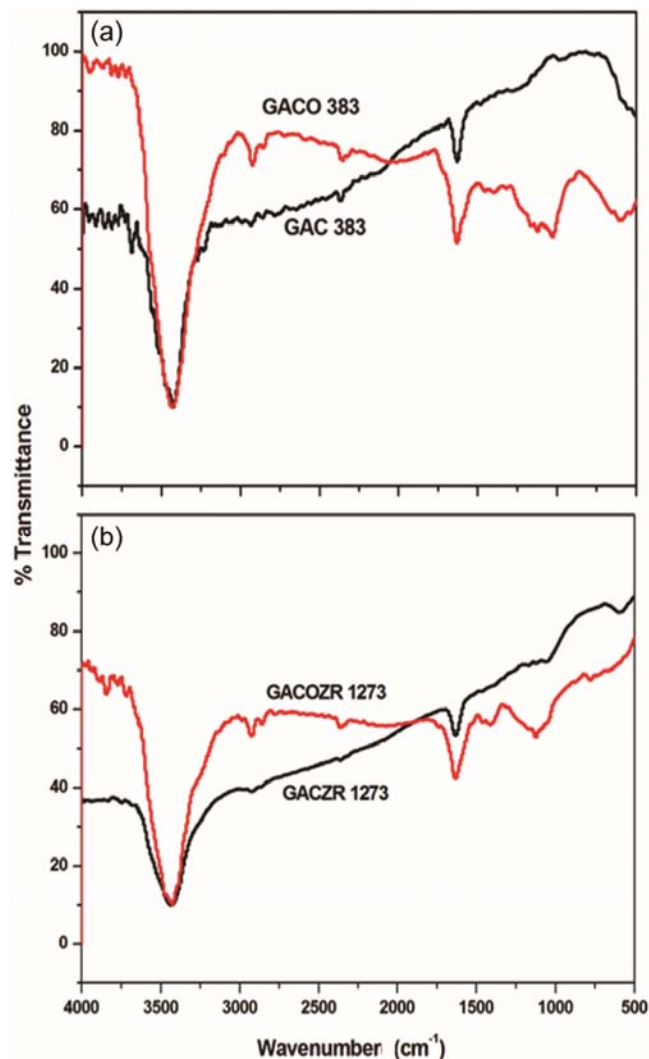


Fig. 1 — FTIR spectra of carbon (a) GAC 383 & GACO 383 (b) GACZR 1273 & GACOZR 1273

$$L = K \lambda / B \cos \theta \quad \dots (4)$$

where L is L_c or L_a , B is the half-width of the peak in radians, and K is the shape factor. The quantities L_c and L_a are named stack height and stack width, respectively. The (002) peaks are used to calculate L_c and L_a . The shape factor $K = 0.9$ and $K = 1.84$ are used for calculation of L_c and L_a , respectively¹³.

The diffraction profiles exhibited broad peaks at around 24 and 42° which are assigned to the reflection from (002) and (100) planes. The occurrence of broad

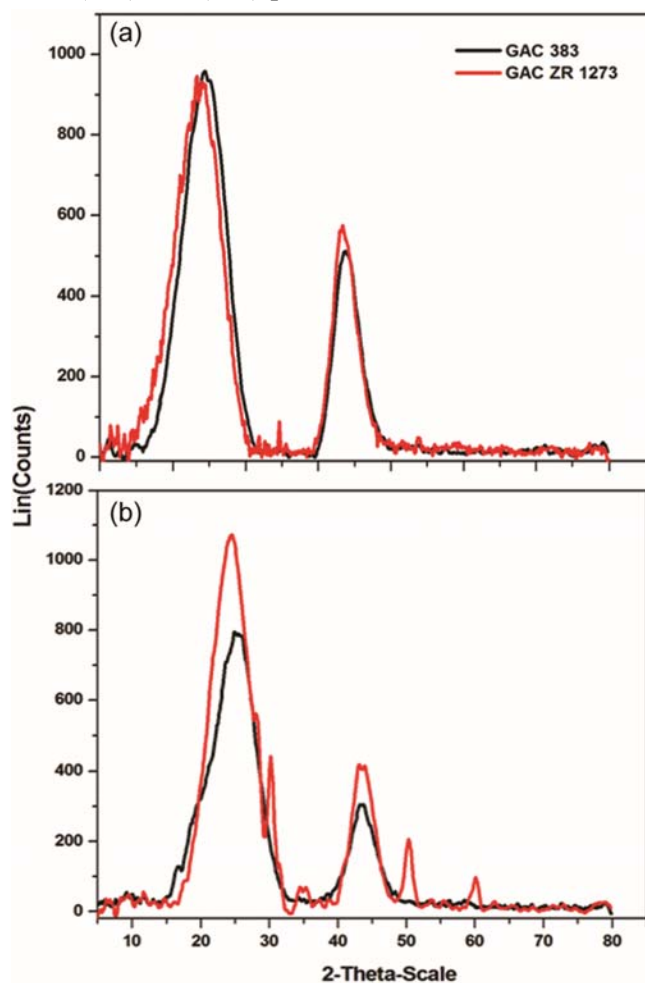


Fig. 2 — XRD spectra of carbon (a) GAC 383 & GACZR 1273 (b) GACO 383 & GACOZR 1273

peaks at these 2θ indicated a regularity of crystal structure and resulting in better layer alignment. The interlayer spacing values, d_{002} , summarized in Table 1 are in the range of 0.35 to 0.37 nm. This reveals that these are non graphitized carbons. Non graphitized carbon has well developed microporous structure that is preserved even during the high temperature treatment¹⁴.

Morphological observation by SEM photograph shows that wide ranges of pores are present on new granular activated carbon surface. Pores present in sample GACOZR 1273 are apparently more open compared to GACZR 1273 (Fig. 3). It indicates nitric acid modification can cause the widening of pores on GACOZR 1273. Since, an increase in the degree of activation makes the pore walls thinner which are more easily destroyed by the HNO₃ treatment - *this* results in a widening of the microporosity¹⁵.

Solid-liquid Adsorption isotherm study

Equilibrium adsorption isotherm results show that adsorption increases with increase in the *p*-nitrophenol concentration as in the case of Type I isotherms, given by microporous materials. Equilibrium adsorption data fitted to well-known isotherm models such as Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) equations. Adsorption characteristics of all carbons for the removal of *p*-nitrophenol (Fig. 4) shows that adsorptive capacity of new coconut shell based carbon enhanced by impregnating with zirconium ions. Among the carbons, oxidized carbon GACO 383 was found to have less adsorptive capacity than others. This is because of higher proportion of carbon-oxygen functional groups, they ionize in water to produce H⁺ ions. These are directed towards liquid phase leaving negative sites on the carbon surface and suppress the further adsorption of *p*-nitrophenol. Isotherm data fitted to well-known isotherms like Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models and adsorption parameters were determined (Table 2).

Langmuir isotherm

The Langmuir isotherm is generally applicable to

Table 1 — Surface oxygen functional groups by Boehm titration and crystalline parameters by XRD

Sample name	Surface functional group				XRD parameters		
	Carboxylic meq/g	Phenolic meq/g	Lactonic meq/g	Base meq/g	Lc (0.9)	La (1.84)	d_{002}
GAC383	0.400	0.450	0.180	0.500	1.14	2.28	0.364
GACO383	1.38	2.10	1.34	0.200	0.970	1.94	0.356
GACZR 1273	0.393	0.440	0.200	0.620	0.979	2.00	0.371
GACOZR 1273	0.620	1.52	0.900	0.380	1.31	2.68	0.362

homogeneous adsorption where the absorption of each adsorbate molecule onto the porous surface has equal adsorption activation energy and can be represented in the linear form as follows^{16,17}

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad \dots (5)$$

where C_e and q_e is the liquid phase adsorbate concentration and solid phase adsorbate concentration at equilibrium. The parameter q_m and K are calculated

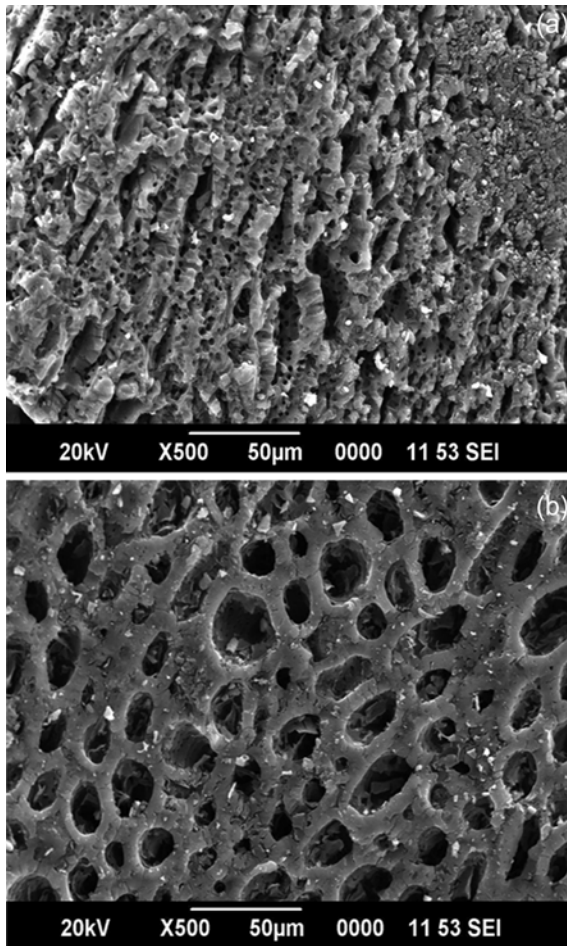


Fig. 3 — SEM images of carbon (a) GACZR 1273 and (b) its nitric acid modified form of carbon GACOZR 1273

by plotting C_e versus $\frac{C_e}{q_e}$ (Fig.5). Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the adsorbent surface.

Freundlich isotherm

Freundlich isotherm model commonly used to describe the adsorption characteristic of the heterogeneous surface, is applied to the new carbon. Figure 6 represents the isotherm plot of *p*-nitrophenol by a unit mass of solid adsorbent. The linear form of the equation applied is given as^{18, 19}

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots (6)$$

where C_e and q_e is the liquid phase *p*-nitrophenol adsorbate concentration (mg/L) and solid phase adsorbate concentration (mg/g) respectively at equilibrium. K_F is a function of energy of adsorption and is a measure of adsorptive capacity. $1/n$ is determined as the intensity of adsorption.

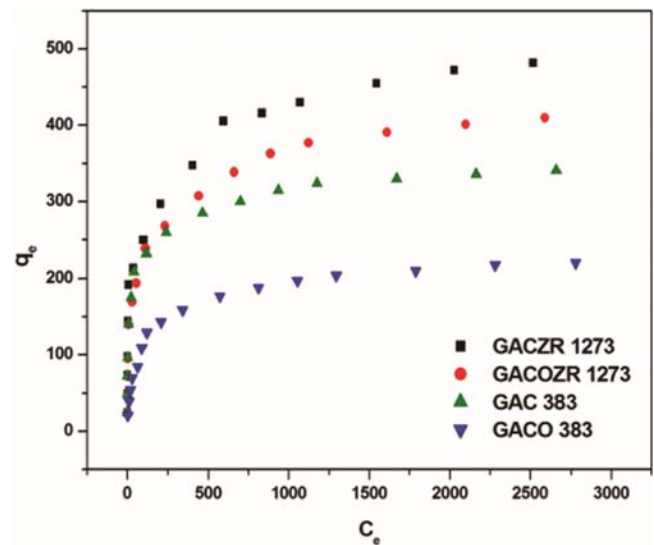


Fig. 4 — Adsorption isotherm of *p*-nitrophenol on carbon GAC 383, GACO 383, GACZR 1273 and GACOZR 1273

Table 2 — Adsorption parameters obtained from Langmuir, Freundlich and Dubinin-Radushkevich isotherm plot

Sample	Langmuir isotherm parameter			Freundlich isotherm parameter			D-R isotherm Parameter			
	q_m (mg/g)	K_L L/mg	R^2	n	K_F L/g	R^2	q_{mi} (mg/g)	β	R^2	E (Kj/mol)
GAC 383	334.45	10.6	0.999	4.05	60.73	0.944	78.19	0.1462	0.983	1.90
GACO 383	224.22	2.24	0.999	2.97	19.33	0.893	51.31	3.35	0.975	0.386
GACZR 1273	478.47	8.39	0.999	3.10	33.85	0.947	96.48	0.1286	0.989	1.97
GACOZR1273	409.84	6.68	0.998	3.42	50.52	0.944	78.73	0.141	0.943	1.88

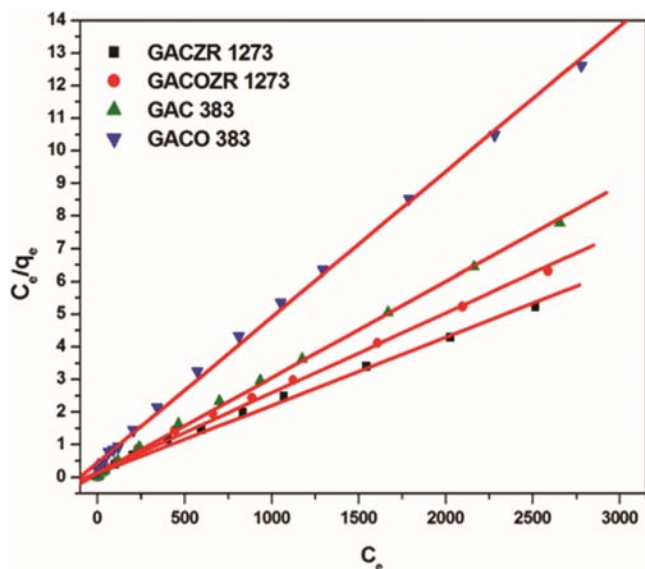


Fig. 5 — Langmuir adsorption isotherm of *p*-nitrophenol on carbon GAC 383, GACO 383, GACZR 1273 and GACOZR 1273.

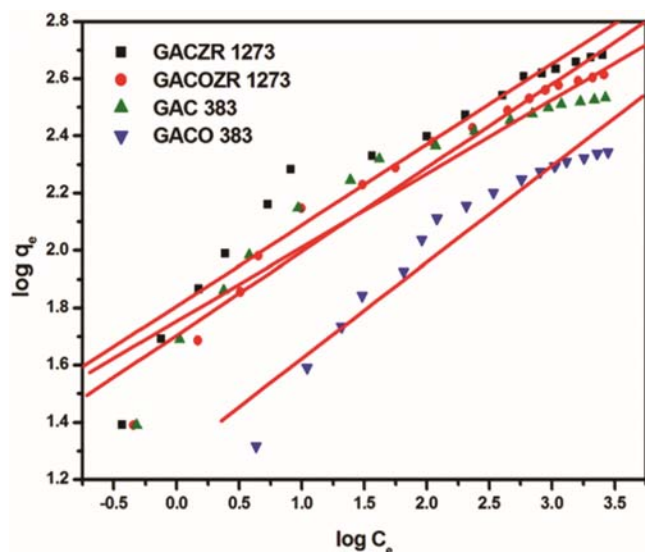


Fig. 6 — Freundlich adsorption isotherm of *p*-nitrophenol on carbon GAC 383, GACO 383, GACZR 1273 and GACOZR 1273

Dubinin Radushkevich (D-R) isotherm

The Dubinin-Radushkevich (D-R) isotherm generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface for gas-solid equilibria. In the case of liquid-phase adsorption, Dubinin-Radushkevich (D-R) equation assumes that the adsorption in micropores is limited to a monolayer. The linear form of D-R equation for aqueous phase is expressed as Eq. (7).

$$\ln q = \ln q_{mi} - \beta \varepsilon^2 \quad \dots (7)$$

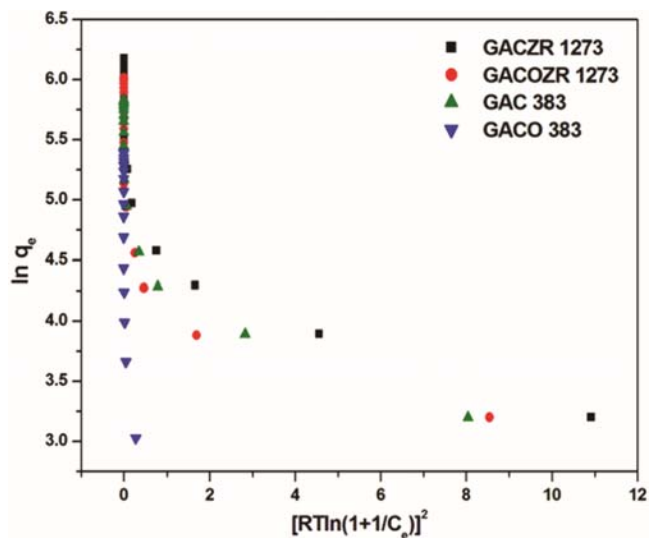


Fig. 7 — Dubinin-Radushkevich adsorption isotherm of *p*-nitrophenol on carbon GAC 383, GACO 383, GACZR 1273 and GACOZR 1273

β is a constant related to energy of adsorption, ε is the Dubinin - Radushkevich (D-R) isotherm constant and q_{mi} which is defined as adsorption due to micropores.

$$\text{where } \varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad \dots (8)$$

Eq. (7) is plotted as a function of logarithm of amount adsorbed ($\ln q$) versus ε^2 (Fig.7). Calculated the mean free energy per molecule of adsorbate from D-R isotherm constant β .

The mean free energy, E (kJ/mol) per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) computed by the relationship^{20,21}.

$$E = \frac{1}{\sqrt{2\beta}} \quad \dots (9)$$

Isotherm parameter obtained from the adsorption of *p*-nitrophenol on GAC 383, GACO 383, GACZR 1273 and GACOZR 1273 are given in the Table 2.

Linear regression is used to describe the best fitting of the *p*-nitrophenol isotherm. The equilibrium data for *p*-nitrophenol adsorption were well fitted to the Langmuir equation ($R^2=0.99$) with maximum monolayer adsorption capacity 478.5 mg/g, 409.8 mg/g, 334.5 mg/g, and 224.2 mg/g respectively for GACZR 1273, GACOZR 1273, GAC 383 and GACO 383. These results indicate that large proportion of *p*-nitrophenol molecule gets adsorbed on the surface of Zr⁴⁺ modified carbons compared to basic carbons

(GAC 383 & GACO 383). This is evidenced by monolayer volume of GACZR 1273 (478.5 mg/g) shows 43% enhancement compared to GAC 383 (334.5 mg/g) whereas GACOZR 1273 (409.8 mg/g) shows 83% enhancement compared to GACO 383 (224.2 mg/g). This suggests that impregnation of zirconium on GAC 383 and GACO 383 generates more accessible sites for *p*-nitrophenol molecule.

Adsorption of *p*-nitrophenol with respect to Freundlich model indicate that constant K_F (which is considered as adsorption binding constant) is in the range of 19.33-60.73 Lg^{-1} , and n values are greater than unity, and occurs in the range of 2.97-4.05 (means adsorption is favorable as it bear between the value of 1-10).

Dubinin-Radushkevich (D-R) parameters q_m and β were determined from intercept and slope of isotherm plot and are given in the Table 2. The adsorption due to micropore obtained from the intercept of the D-R isotherm plot are 96.48 mg/g (GACZR 1273), 78.73mg/g (GACOZR 1273), 78.19 mg/g (GAC 383) and 51.31 mg/g (GACO 383). It indicate more number of micropores are newly developed on GAC during activation after impregnation with Zr^{4+} i.e carbon have an extra porosity due to Zr^{4+} activation which in turn leads to its higher adsorption efficiency towards *p*-nitrophenol molecules. In liquid phase, the mean free energy E of carbons observed is in the range of 0.386-1.97 kJ/mol, shows the prevalence of physisorption process. This means adsorbate bound to the surface of carbon by relatively weak Van der waals forces.

Furthermore Table 2 shows that nitric acid-modified carbon has low *monolayer* values (q_m and q_{mi}) compared to non oxidised carbons i.e. GAC 383 > GACO 383 and GACZR 1273 > GACOZR 1273. This is because acidic surface groups were reported to be unfavourable for the adsorption of aromatic compounds as they reduces the electron density from the basal plane of the carbon; thus reducing the $\pi - \pi$ * interaction between the aromatic ring and basal plane of the carbon. Also surface acidic functional groups ionises to become negative sites on the surface of carbon. They repels the approaching phenoxide ion, thus reducing the donor-acceptor interaction between the phenolic group and carbon surface²².

Study of adsorption kinetics will give more insight into the fundamental properties of these carbons.

Adsorption kinetic study

Three kinetic models, pseudo first order kinetics²³, pseudo second order kinetics²⁴, and intra particle

diffusion models²⁵ were used to investigate the adsorption of phenol on carbon GAC 383, GACO 383, GACZR 1273 and GACOZR 1273 are discussed in the following sections.

Pseudo first order kinetics

Pseudo first order equation of Lagergren²³ is one of the most widely used for the adsorption of solute from solution. The rate of adsorption was assumed to be proportional to the difference between the maximum capacity q_e , at equilibrium and the capacity (q) at time, t . The linear form of the equation is given below

$$\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \dots (10)$$

Where q_e and q_t are the amounts of the *p*-nitrophenol adsorbed on respective carbon at equilibrium and at time t (mg g^{-1}), and K_1 is the first order rate constant (min^{-1}).

The plot of the linearized form of the first order model $\log (q_e - q_t)$ versus t for the adsorption of *p*-nitrophenol concentration $C_0 = 250mg/l$ at 30°C (Fig. 8) depicts that the adsorption data do not fit this kinetic equation. Suggests that adsorption on GAC 383, GACO 383, GACZR 1273 and GACOZR 1273 does not follow first order reaction.

Pseudo second order kinetics

It is assumed that the adsorption capacity is proportional to the number of active sites occupied on the new carbon adsorbent. Accordingly, the linearised form of pseudo second order kinetic equation is rewritten as²⁴.

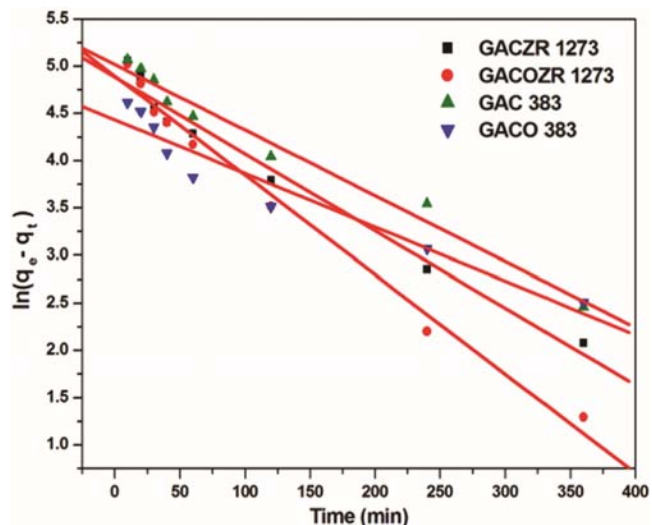


Fig. 8 — Pseudo first order kinetic model for new carbon GAC series

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \dots (11)$$

Where q_e is the maximum adsorption capacity (mg g⁻¹) for the pseudo-second-order adsorption, K_2 is the equilibrium rate constant for the pseudo second order adsorption (g mg⁻¹ min⁻¹). Values of K_2 and q_e were calculated from the plot of t/q_t against t (Fig. 9). The kinetic data for the adsorption of *p*-nitrophenol onto activated carbon under various conditions were calculated from the respective plots and were given in Table 3.

Correlation coefficient is closer to unity for pseudo second order kinetic model and q_e calculated is found to be closer to experimental q_e than pseudo first order model. Therefore, the adsorption reaction can be approximated more favourably by the pseudo second order kinetic model for all carbon prepared and studied.

The first order and pseudo second order kinetic models cannot identify the diffusion mechanism and

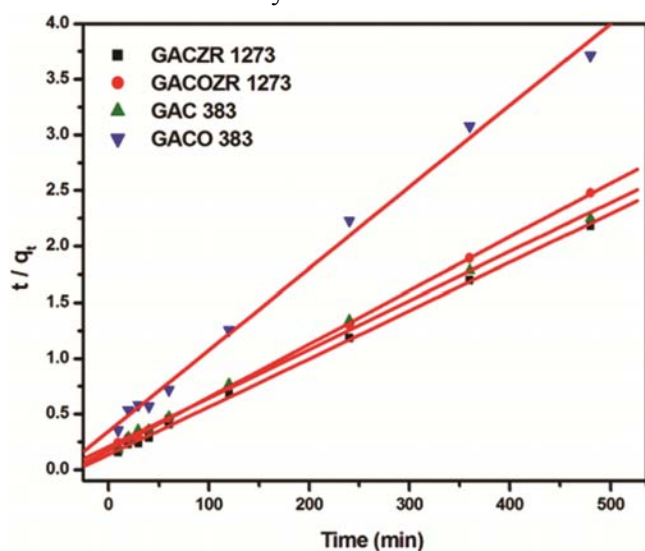


Fig. 9 — Pseudosecond order kinetic model for new carbon GAC series

the kinetic results are then analyzed by using the intraparticle diffusion model.

Intra particle diffusion study

Generally a process is regarded as diffusion controlled, if its reaction rate is dependent upon the rate at which component diffuse towards one another. The possibility of intra particle diffusion was explored by using the intra particle diffusion model^{25, 26}.

$$q_t = K_{id} t^{1/2} + C \quad \dots (12)$$

where K_{id} is the intra particle diffusion rate constant (mg/g min^{1/2}) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer i.e larger the value of C , the greater is the boundary layer effect²⁷. When intra particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of q_t versus $t^{1/2}$ yields straight line passing through origin and the slope gives the rate constant K_{id} .

The deviation of straight lines from the origin (Fig. 10) may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the initial parts are attributed to boundary layer diffusion effects or external mass transfer effects and second linear portion indicate the intraparticle diffusion. Among the carbon, comparatively high C value of GACZR 1273 indicates larger boundary layer effect.

When GAC 383, GACO 383, GACZR 1273 and GACOZR 1273 are fed into an aqueous solution of *p*-nitrophenol, all the carbons attained their maximum (equilibrium) adsorption capacities near to 8 h. In all cases, the adsorption kinetics has been satisfactorily fitted by a pseudo second order kinetics. Multi linear

Table 3 — Determined kinetic parameter for the adsorption of *p*-nitrophenol on GAC 383, GACO 383, GACZR1273, GACOZR 1273 soaked into aqueous solution of initial concentration 250mg/l.

Sample	Exp q_e	Pseudo first order			Pseudo second order			Intra particle diffusion		E_a (kJ/mole)	
		q_e cal (mg/g)	$K_1 \times 10^4$ Min ⁻¹	R^2	q_e cal (mg/g)	$K_2 \times 10^5$ gm g ⁻¹ min ⁻¹	R^2	K_{id} (mg/g min ⁻¹)	C		R
GAC 383	213	151.3	69.4	0.978	228.8	9	0.996	16.8	-2.2	0.984	7.71
GACO 383	129	84.25	57	0.931	136.8	16	0.994	12.9	-15.8	0.985	10.33
GACZR 1273	220	132.6	81.3	0.978	232	14	0.998	19.8	4.024	0.964	15.1
GACOZR 1273	194	134.0	105	0.986	209.2	13	0.998	19.6	-15.4	0.979	9.44

plot of intra particle diffusion model assume that, adsorption on carbons influences two steps. First stage assumes the external resistance to mass transfer by surrounding particles and second stage assumes controlling intra particle diffusion. The high concentration of adsorbate molecule on the surface of the carbon adsorbent pushes the adsorbed *p*-nitrophenol molecule from the carbon surface through the pores (intraparticle diffusion) to the internal sites of the carbon.

The magnitude of activation energy gives an idea of type of adsorption involved in the new adsorption system, which is mainly physical or chemical in nature. The temperature effect on the rate constant has been found practically in all cases and well represented by the Arrhenius equation.²⁸

$$\ln K_2 = \ln A - \frac{E_a}{RT} \quad \dots (13)$$

Where K_2 is the rate constant obtained from pseudo second order kinetics, A is the frequency of adsorption (min^{-1}), E_a the activation energy of the reaction (J mol^{-1}), R the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature.

For all four carbons, a plot of $\ln K_2$ against the reciprocal of absolute temperature, $1/T$ (Fig. 11) gives a straight line, and the corresponding A and E_a are determined from the intercept and the slope respectively of each regression line. A is temperature-independent and becomes small for adsorption of large molecular weight molecules like *p*-nitrophenol and is found to be in the range of 0.1995×10^{-2} to 5.22×10^{-2} . The E_a values were small ($<10 \text{ kJmol}^{-1}$) indicates that

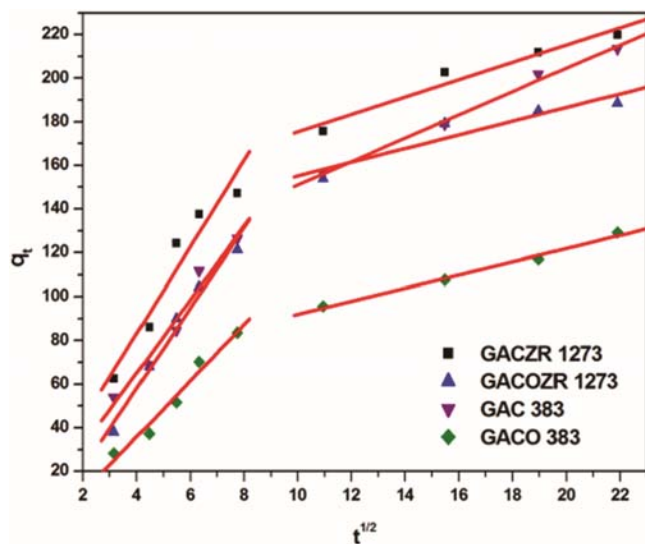


Fig. 10 — Intra particle diffusion model for new carbon GAC series

adsorption of *p*-nitrophenol onto GAC are physisorption in nature.

Thermodynamic parameters

The thermodynamic parameters obtained from Langmuir constant (K_L) is given by Eq. (14). The ΔH and ΔS parameters for *p*-nitrophenol on GAC 383, GACO 383, GACZR 1273 and GACOZR 1273 carbons are calculated from the slope and intercepts of the plot of $\ln K_L$ versus $1/T$ (Fig. 12), are given in Table 4.

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \dots (14)$$

The values of ΔH and ΔS were computed from the slopes and intercept of the plot. From these, we can

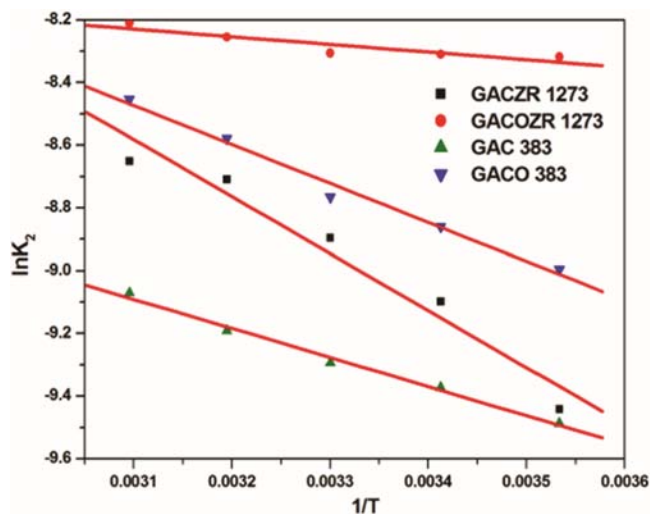


Fig. 11 — Plot of $\ln K_2$ versus $1/T$

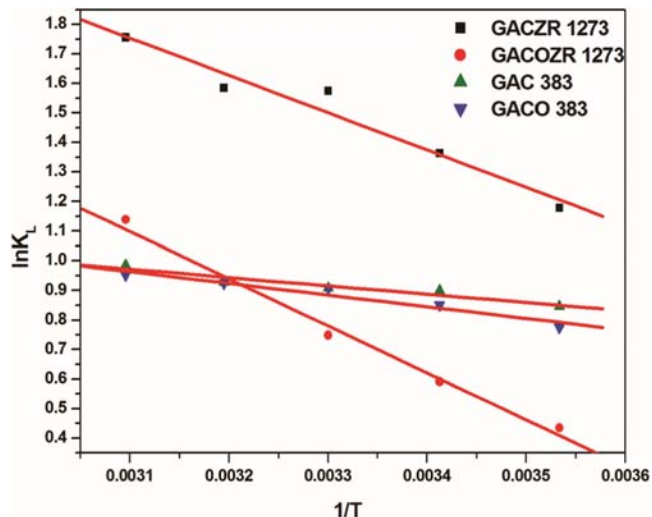


Fig. 12 — Plot of $\ln K_L$ versus $1/T$

Table 4 — Thermodynamic parameters for *p*-nitrophenol adsorption on GAC 383, GACO 383, GACZR 1273 and GACOZR 1273.

Sample	ΔH KJ/mol	ΔS J/mol.K	ΔG (KJ/mol)				
			283K	293K	303K	313K	323K
GAC 383	6.04	38.2	-4.77	-5.15	-5.53	-5.92	-6.30
GACO383	2.94	16.4	-1.70	-1.87	-2.03	-2.19	-2.36
GACZR 1273	21.6	89.3	-3.67	-4.56	-5.46	-6.35	-7.24
GACOZR 1273	9.53	46.98	-3.77	-4.24	-4.71	-5.18	-5.65

calculate the change in free energy using the following Eq. (15).

$$\Delta G = \Delta H - T\Delta S \quad \dots (15)$$

The positive value ΔH of all adsorbents indicates endothermic nature of adsorption i.e the adsorption of *p*-nitrophenol is favoured at higher temperatures. The positive value of ΔS suggests the randomness of the adsorption process, also indicated greater stability of adsorption process with no structural changes at the solid-liquid interface.

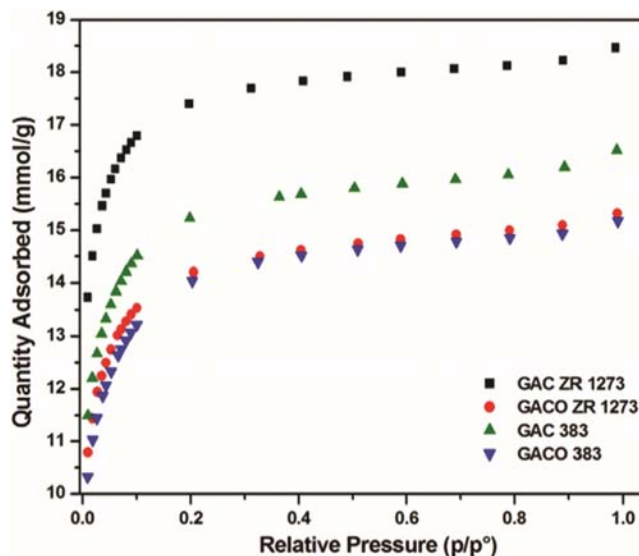
Negative value of ΔG shows spontaneous adsorption and the degree of spontaneity of the reaction. The more negative value of ΔG with temperatures suggests increase in feasibility of adsorption at higher temperatures. This is due to the rise in number of adsorption sites generated as a result of breaking of some internal bonds near edge of active surface sites of adsorbent²⁹.

Solid-Gas Adsorption Isotherms

Adsorption isotherm characteristics of the GAC are studied using N₂ adsorption at 77 K. Porosity and surface area has much significance in the study of adsorption.

The N₂ adsorption isotherms of the activated carbons show Type I isotherm as per the IUPAC classification. All the four members of GAC series reported in this study shows higher porosity properties with rise of activation temperature up to 1273K. All isotherms have a steep rise in the initial stage of adsorption at lower p/p_0 range (Fig. 13). Thereafter progressed well to attain saturation at high pressure range. Pores are preferably filled at $p/p_0 < 0.2$ as evidenced by steep adsorption front. This reveals very high adsorption efficiency of the carbon within narrow micropore range³⁰.

The adsorption capacity and the respective specific surface area of each carbon are also evaluated to study the features of isotherms of BET, *I* plot, Langmuir, Freundlich and D-R using N₂ adsorption data at 77K. The BET isotherm method based upon theory of multilayer adsorption was applied on these carbons using the Eq. (16).


 Fig. 13 — N₂ adsorption isotherm plot for the new carbons at 77K

$$\frac{1}{V(p/p_0 - 1)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left(\frac{p}{p_0} \right) \quad \dots (16)$$

The linear plot, which is extended usually in the range $0.05 < P < 0.3$. From the graph, adsorbed volume V_m for the formation of monolayer as well as *C*- constant are determined³¹.

Table 5 shows the result of BET analysis. Some discrepancy due to lack of a positive *C* character for BET equation for the region $p/p_0 > 0.1$ or $p/p_0 = 0.3$. But *C* value become positive and is greater than 150 for p/p_0 upto 0.1.

The rearrangement of BET equation in Scatchard type form will provide the line with slope equal to $(C-1)$ at any *P* (p/p_0) and *V* values. This plot is known as BET-Scatchard (B-S) plot³².

$$\left[V \left(1 - \frac{p}{p_0} \right) \right] / \frac{p}{p_0} = C V_m - (C - 1) \left[V \left(1 - \frac{p}{p_0} \right) \right] \quad \dots (17)$$

The graph gives an inclined *V* shape curve (\curvearrowright) with an inversion point termed *I* point. The extrapolation of this point towards x-axis is being marked as V_m i.e $[V(1-P)]_{I \text{ point}} = V_m$ (monolayer volume of *I* plot method). Specific surface area was calculated using Eq. (18).

$$SA = 4.356V_m \quad \dots (18)$$

So the *I* point method provides an alternate way to determine a unique value for the surface area of new carbon without any ambiguities. The surface areas of all GAC materials obtained from BET with positive C value ($p/p_0=0.1$) are comparable to that obtained from *I*-plot.

The variation of monolayer volume and surface area of GACZR 1273 from basic GAC 383 indicates that the impregnation of zirconium and activation with steam at 1273K enhances 15% monolayer adsorption capacity and surface area of GAC 383.

Porosity parameters obtained from N₂ adsorption data by applying various isotherm models are given in Table 6.

Langmuir equation (Eq. 19) is applied to the new carbons to study isotherm behaviour. The general form used to plot N₂ isotherm at 77K is

$$\frac{P}{V} = \frac{1}{bV_m} + \frac{P}{V_m} \quad \dots (19)$$

Langmuir isotherm indicate that GACZR 1273 has 15% more increment in the surface area and monolayer volume compared to basic carbon GAC 383. Nitric acid oxidised carbons, GACZR 1273 and GAC 383 shows relatively lower value compared to non oxidised carbons.

Freundlich isotherm plots are constructed as per Eq. 20 shows perfect linearity (0.999) with an evidence for high existence of microporosity and relatively high surface area³³.

$$\log V = \log K_F + \frac{1}{n} \log P \quad \dots (20)$$

Freundlich parameter K_F is measure of adsorption capacity, Higher K_F value suggests that tendency of N₂

molecule to occur on GACZR 1273 has comparatively greater than other carbons.

Dubinin-Radushkevich (D-R) equation³⁴ is used to determine micropore volume of the new carbon series from the N₂ adsorption isotherm at 77K.

$$\log W = \log W_0 - D \log^2 \left(\frac{P}{p_0} \right) \quad \dots (21)$$

W₀ is the mmol of N₂ adsorbate filling micropore of carbons. The parameters characterisation energy *E*₀, pore width *L* and surface area (S_{D-R}) were calculated using Eq. (22) and Eq. (23) and are given in the Table 6.

$$L = \frac{10.8}{(E_0 - 11.4)} \text{ nm} \quad \dots (22)$$

$$SA_{D-R} = \frac{2 \times 10^3 \times W_0 (\text{cm}^3/\text{g})}{L} \quad \dots (23)$$

The carbon prepared by incorporating Zr⁴⁺ have *L* value (average pore width) of 1.92 nm for GACZR 1273 whereas GAC 383 shows 2.56 nm i.e the micropore surface area was contributed by pores less than 2 nm are very much generated by chemical activation by incorporating with Zr⁴⁺ ions.

Dubinin-Radushkevich (D-R) isotherm analysis shows that GACZR 1273 has much higher micropore surface area (S_{D-R}) as compared to that of basic carbon GAC 383. The presence of zirconium in GAC enhances the porosity and surface area as seen in the Table 6 and the energy of adsorption (*E*₀) is 15-17 kJ/mol for the adsorption in pores having width < 2nm.

More *p*-nitrophenol molecules are attracted into these micropores on GACZR 1273 by intra particle diffusion mechanism; increasing the adsorption efficiency of GACZR 1273 towards *p*-nitrophenol.

Table 5 — Surface area and Porosity parameters calculated from nitrogen adsorption isotherms using BET and I plot methods

Sample	BET Analysis(p/p ₀ upto 0.3)			I plot		BET Analysis (p/p ₀ upto 0.1)		
	SA _{BET} m ² /g	V _m cm ³ /g	C _{BET}	S _I m ² /g	V _m =V _I	SA _{BET} m ² /g	V _m cm ³ /g	C _{BET}
GAC 383	996.8	229	-81.6	1275.4	293	1298.5	298.3	524
GACO 383	974.3	224	-119	1164.6	267.5	1186.5	272.5	439
GACZR 1273	1217.2	280	-104	1482.1	340.5	1497.3	343.9	873
GACZR 1273	976.2	224	-103	1193.2	274.1	1212.2	278.5	563

Table 6 — Porosity parameters of calculated from nitrogen adsorption isotherms using Langmuir, Freundlich, & D-R

Sample	Langmuir			Freundlich			D-R				
	SA _L m ² /g	V _m STP	R ²	n	K _F	R ²	SA _{D-R} m ² /g	W ₀ cm ³ /g	L nm	E ₀ kJ/mol	R ²
GAC 383	1465	337	0.999	9.4	210	0.999	474.8	392.7	2.56	15.6	0.986
GACO 383	1326	304	0.999	9.4	184	0.999	334.1	322.8	2.99	15.0	0.978
GACZR 1273	1687	388	0.999	11.5	259	0.999	647.9	401.7	1.92	17.0	0.995
GACZR 1273	1367	314	0.999	10.1	196	0.999	409.4	327.8	2.48	15.8	0.991

Conclusion

Removal of *p*-nitrophenol from aqueous solution using zirconium impregnated granular activated carbon shows better efficiency compared to the respective basic carbons. Langmuir models give fairly good fits to the adsorption data indicating a monolayer adsorption of *p*-nitrophenol onto these carbons. The adsorption process could be best described by the pseudo second order kinetic model and intraparticle diffusion kinetic model. The increase in negative value of ΔG with temperature suggests high feasibility of adsorption at higher temperatures. The adsorption efficiency of the GAC found to be significantly improved by the addition of Zr⁴⁺ since it increases the surface area and porosity of the granular activated carbon. The BET surface area and pore volume are important factors for determining the adsorptive capacity of activated carbons. Pore volume and surface area of zirconium modified carbons are significantly higher than the basic carbons. This confirms the carbons have extra porosity due to Zr⁴⁺ activation. All the experimental data show that zirconium impregnated granular activated carbons GACZR 1273 and GACOZR 1273 are most effective for the removal of *p*-nitrophenol than respective basic carbons GAC 383 and GACO 383 because of its large surface area and porosity, which are developed during the process of activation with zirconium.

Acknowledgement

The first author is thankful to University Grants Commission (UGC), Government of India, New Delhi for the financial support by awarding the project UGC – SAP- DRS Phase II as per the order No: F4 - 14/2015/DRS-II (SAP-II) Dated 19/12/2015 and the second author is thankful to UGC-BSR for the financial assistance in the form of Senior Research Fellowship.

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