John- Sivanandan Achari Isotherm Method for the Determination of Surface Area of Porous Materials: Analysis of Granular Activated Carbons

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Abstract

John – Sivanandan Achari isotherm equation log log $C_e = C + n \log q_e$ has many advantages for the structural characterization of porous materials. Linear plot of log logCe versus log q_e conform to a straight line and subsequent extrapolation of amount adsorbed (q_e) , to the xaxis. This way one can directly determine the monolayer $q_m(J-SA)$ and hence the specific surface area (SA m²/g) of the material. This can be analytically proved by applying the method in any type of solid-liquid equilibrium adsorption data. In this study, adsorption of methylene blue (MB) dye molecules on modified granular activated carbon (GAC) has been attempted to determine the porosity, and surface area by the new method. The solids are GAC 383 (native carbon- coconut shell based), GACO383 (native carbon oxidized) and a new carbon (GACOLaO1273). This carbon is prepared in the laboratory by steam activation after incorporating GAC383 with Lanthanum(La^{3+}) ions. Carbons are tested in batch reactors with fixed MB concentrations by adsorptive techniques. The isotherm model behavior of the carbons are hereby reported using John - Sivanandan Achari isotherm (J-SA) equation using specific adsorption data. Porous material category as IUPAC type, constants and parameters are further evaluated with Langmuir, Freundlich, Dubinin - Radushkevich isotherms. It is seen that the isotherm followed the features of micro porous materials on using John – Sivanandan Achari (J-SA) isotherm. Porosity and surface area determined are found to give agreeing results on comparing with other isotherm models. This research is intended to highlight the significance of John and John-Sivanandan Achari (J-SA) isotherms as a tool for material characterization studies- a model originated as Indian analytical scientific skill.

Keywords: John-Sivanandan Achari (J-SA) Isotherm; Activated carbon; Methylene Blue (MB); Adsorption isotherms; Specific surface area.

1. Introduction

John & John – Sivanandan Achari isotherm model methods are known are developed by Dr. P. T. John (Formerly Scientist, National Physical Laboratory, New Delhi) applied by Dr. V. Sivanandan Achari (School of Environmental Studies, Cochin University of Science &Technology, Cochin) to study textural behavior of carbons & porous materials. Porosity and surface area are the prominent structural parameters of any kind of porous materials used in industrial applications. These are most pertinent textural properties to report the adsorption efficiency of materials when used in separation and purification¹ process.

Langmuir² in 1918 proposed the monolayer coverage concept by assuming a monolayer formation on the homogeneous surface in which the reciprocal slope of the plot gives the monolayer volume. Brunauer–Emmett–Teller (BET)³ method is the widely used method for the determination of surface area of porous materials using the monolayer adsorption capacity (V_m) and molecular cross-sectional area (0.162 nm² or 0.162 x 10⁻¹⁸ m²). Calculations of Specific surface area (SSA) in BET equation method consider the C value as a constant for type I porous material behaviour. Further evaluation of micropore volume involves the use of many methods. By which the prominent one is the *t*-plot method ⁴ comprises an empirical comparison of an isotherm with a non-porous reference material of similar composition. In order to overwhelm the use of a standard multilayer thickness curve, later on α_s isotherm was introduced. In which the standard isotherm is plotted in a reduced form $(n/n_x)_s$. The plot $(n/n_x)_s$ versus relative pressure (p/p_0) where n_x is generally taken as the amount adsorbed at p/p_0 0.4. The micropore capacity was found by extrapolating the linear section of α_s plot. Another method for the determination of micropore volume was centered on Dubinin's pore volume filling theory ⁵ plotted with log q versus $log^2(p_0/p)$ provided the linear portion of the plot extrapolated to deliver the micropore volume. Later on, John isotherm ⁶⁻⁹ was introduced by a renowned Indian Scientist P.T. John, with proper scientific explanation for the phases in adsorption plots of porous materials. The isotherm displayed with distinct kinks corresponds to the pore filling mechanisms with amount adsorbed at each phase obtained by extrapolating each kink to abscissa. Constant n slope of the each phase is a measure of adsorption efficiency known as adsorbablity constant by John. Isotherm constants and parameters can reveal many features of materials. Constant C in BET isotherm later becomes known that which is actually not so. Hence, reported the introduction of I plot by Pomonis 2005 10 , considering a non-linear plot whose kink (point of inflection) will deliver the monolayer volume.

Material behavior is determined from equilibrium isotherm analysis of *solid* –*gas* or *solid*-*liquid* system using a set of model calculations and proper interpretation of parameters or constants. In adsorption methods, to ascertain monolayer volume (v_m) or monolayer quantity (q_m) adsorbed, we can apply different adsorption isotherm equations. John and John – Sivanandan Achari (J-SA) isotherm equations⁷ are well-established mathematical models, from which we can directly obtain the adsorptionmonolayer (v_m/q_m) for adsorption system follows Type I, II & IV features. It is found that, the method is successful for determining adsorption efficiency, porosity and surface area of many porous materials according to the category to which both *solid-gas* and *solid-liquid* adsorption systemsbelongs¹¹.

Recent literature in chemistry, material science, separation & purification cites many carbon porous materials are tested for their efficiency using the John & John –Sivanandan Achari (J-SA) isotherm methods. Known are coconut shell based granular activated carbon incorporated with cerium compounds reported¹² to have phenol 224.2mg/g adsorbed onto cerium nitrate incorporated carbon (GAC CN1273) activated at 1273K. For *p*-nitrophenol molecules, the amount adsorbed was found to be 653.6mg/g and for methylene blue molecules the amount was 299.40mg/g. Zn²⁺/nano ZnO¹³ loaded coconut shell based granular activated carbon incorporated with Zn²⁺ activated at 1073K (GACZC1073) has a higher adsorption capacity (490.2mg/g) than the basic carbon GAC383 (340.1mg/g) ¹⁴. Zr⁴⁺/nano ZrO₂¹⁵ incorporated coconut shell based granular activated at 3% more removal of *p*-nitrophenol (478.5mg/g) than the basic carbon GAC383 suggests that, Zr⁴⁺ generates more accessible pores for the *p*-nitrophenol molecules. Method is particularly useful to apply for the performance evaluation of any porous material applied in adsorption treatment reactor systems described in the following sections.

Methylene Blue (MB) dye bears many industrial & analytical applications. Hence, has been used for the adsorption study of many porous solids like granular activated carbon (GAC), charcoal, graphite and silica. It is used mostly as a prominent organic molecular adsorbate used in analytical chemistry as is one with known cross-sectional area $(1.20 \text{ nm}^2)^{16}$ applied in many adsorption studies. In this study, we make an attempt to explain how John – Sivanandan Achari (J-SA) isotherm method is suitably used to determine adsorption monolayer q_m and specific surface area $SA m^2/g$ of granular activated carbon (GAC) using methylene blue (MB) dye in liquid phase under equilibrium batch reactor conditions.

2. Experimental

Commercially available coconut shell based granular activated carbon (GAC) obtained from Indo-German Carbons Limited, Kochi, India of size 12x40 mesh size (0.9-1.1mm) was used as the starting material.Specifications of the starting material used in the present study as supplied by the manufacturerwere: iodine number (110mg/g), surface area (1150 m²/g), apparent density (0.50g/cc), moisture (5%), ash (4%) and pH 9-11. Before use, the GAC was washed with distilled water to remove impurities present on the surface and then dried at 383 K and marked as GAC383.

A portion of GAC383 was oxidized with 12.9% HNO₃and refluxed for 3 hours, thereafter filtered. The procedure was repeated by adding a fresh solution of HNO₃ and distilled water in the same ratio as the previous. A reaction time of 4 hours was then maintained. After oxidation, the samples were filtered and thoroughly washed with hot distilled water until the pH became neutral, then dried in an air oven for 24 hours at 383 K. The product obtained by the oxidation are labelled as GACO383. A portion (10g) of GACO383 carbons was taken in a conical flask and was impregnated within a dispersion of nano Lanthanumoxide (La₂O₃) and the content was then carbonized under steam activation at 1273 K in a specially designed temperature programmed furnace. The product was labelled as GACO1273.

Methylene Blue (MB) (C₆H₁₈N₃SCl.3H₂O, MW: 319.85)of analar grade (Merck) of purity 99.9% was used to prepare different concentrations of MB ranging from 25-1500mg/L with GAC adsorbent dosage of 1.0g/L for the equilibrium batch adsorption tests. The amount adsorbed at equilibrium (q_e) was calculated using the equation (1).

where C_0 is the initial concentration in mg/L, C_e is the concentration at equilibrium (mg/L), V is the volume of the solution and W is the mass of the carbon (g).The quantity adsorbed was measured using spectrophotometer (Systronics) at 665 nm.The adsorption equilibrium data was used to fit John - Sivanandan Achari isotherm (J-SA) equation to evaluate the monolayer adsorption capacity, adsorption efficiency, porosity and surfacearea. From the monolayer adsorption capacityobtained $q_m(g/g)$,the surface area can becalculated¹⁷as

Where q_m is the monolayer adsorption capacity, 1.20 nm^2 is the cross-sectional area of MB, and 319.85(g/mol) is the molecular weight of methylene blue. Isotherm methods based on Langmuir, Freundlichand Dubinin-Radushkevich (D-R) isotherm methods are also used to

determine respective monolayer adsorption capacities. Hence, the surface area of the granular activated carbon under study were critically evaluated and agreement of test results are enumerated.

2. Results and Discussion

John (J) isotherm and *John–Sivanandan Achari (J-SA)* isotherm ¹⁸are mathematical models, to test adsorption potential of porous materials from solid-gas and solid–liquid adsorption systems respectively. Though the research on *John* isotherm model had been live from early sixties onwards, more rigorous analysis of isotherm data by various adsorption systems in *solid-liquid*equilibria is a focus of recent research to promote Indian scientific analytical skills.Testing of this isotherm model for new carbonaceous materials which are either activated under a set of conditions, or commerciallyprocured productsor using the data from published literature for the study of the model are common practices of evaluation. In all studies, the same isotherm data is subjected to regression analysis using the John isotherm models and further compared to the other known isotherms.

Comparison of the isotherm constants and analyses of the adsorption phases on the linearization procedures and evaluation of pore volume and subsequent surface area determination are the common steps followed. Mathematical expressions of the new isotherms are shown as linear form in equations (3) and (5). Pore filling phenomena occurring on a porous material is very distinct in this isotherm plots as straight lines joined at kinks with lines with definite slopes, hence the method is otherwise called phase change method (Fig.1).

2.1. John Isotherm for (Solid-Gas) Systems

$\log \log P =$	$C + n \log V$	(3)	
		······································	

Where;	$P = p/p_0 \times 10^N$	 4))

and 'V' is the amount adsorbed (cm^3/g) STP at relative pressure (p/p_0) .

2.2. John-Sivanandan Achari (J-SA) Isotherm for (Solid-Liquid) Systems

John–Sivanandan Achari (*J-SA*) Isotherm for (solid-liquid) equilibrium adsorption systems are given by

 $\log \log C_e = C + n \log q_e \tag{5}$

Where;
$$C_e = C_e \times 10^N$$
(6)

 q_e is the amount of MB adsorbed (mg/g) and C_e is the concentration of adsorbate (mg/L) is known to be an ideal isotherm model to describe solid-liquid adsorption reactor systems and characterization of porous materials. N is an integer usually in between 3 to 8 so as to make $log C_e$ positive and $log log C_e$ can be made. Here N is taken as 4.

The John isotherm models are originated based on Polanyi potential theory. Many wellknown adsorption equations like Langmuir equation, Dubinin-Radushkevich equation, Henry's equation, de Boer-Swikkers equation, Frenkel-Halsey-Hill equation and Temkin equation can be derived from John Isotherm equation with minor approximations. John and Achari (2002)⁷ enumerated the advantages of John isotherm model on comparison to other conventional isotherm models.

Logarithm of monolayer capacity of any adsorbent material is related to equation by

$$\log q_e = \frac{(\log \log C_e - C)}{n}$$
(7)

where C and n are the intercept and slope respectively for the plots are drawn. If there are cases where equilibrium constants does not give a possible value in its log form, C_e is multiplied by an integer, that is $C_e = C_e \times 10^N$ where N is an integer so chosen that lowest log log C_e of the data is positive. The value of log q_e corresponding to the highest log log C_e on the extrapolated line is taken, whose antilogarithm gives the monolayer capacity $q_m(J-SA)$ for the isotherm with one adsorption phase (for Type I isotherms as per IUPAC-2015 classification¹⁹, given by most microporous materials).

The isotherms of carbonaceous microporous materials, GAC383, GACO383 and GACOLaO1273 (Fig.2) have a steep rise in the initial stage of adsorption at lower concentration ranges, progressed well to attain saturation at higher ranges. The steep rise is because of micropores. These pores are preferentially filled fast as evidenced by a steep adsorption front. After this, the sub-monolayers were filled as these higher energy sites are unoccupied. At equilibrium concentration every carbon undergoes selective pore filling, and mesopores were filled leading towards the formation of a narrow hysterias loop in their solid-gas equilibrium isotherms particularly adsorbed with N_2 at 77K.

Methylene blue (MB) isotherm of GAC383, GACO383 and GACOLaO1273 was constructed and showsGACOLaO1273 has a strong affinity to MB than that of GAC383 and GACO383 attains saturation at higher concentration ranges.

2.3. John - Sivanandan Achari (J-SA) Isotherm Model Evaluation

The J-SA equation is very much useful in determining the monolayer adsorption capacity of the adsorbent in liquid phase⁸. The J-SA isotherm plot is given by the equation

$$\log \log C_e = C + n \log q_e \tag{4}$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), C_e is the Concentration of adsorbate is the liquid phase obtained from the equilibrium adsorption isotherm study and 'n' is the adsorption constant known as John adsorption capacity, is a measure of adsorption efficiency of the material. John-Sivanandan Achari isotherm plot with *log log C_e* against *log* q_e shown in the Fig.3 gives a single phase corresponds to the micro porous Type I compounds [7]. The end point of the plot when extrapolated to the x axis gives the monolayer volume $q_m(J-SA)228.3 \text{ mg/g}$ (GACOLaO1273), 176.1mg/g (GAC383), 138.2 mg/g (GACO383).

2.4. Langmuir Isotherm Equation

Langmuir Isotherm assumes a monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface². The linear form of Langmuir Isotherm is given by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{5}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium(mg/g), K_L and a_L are Langmuir constants which are related to the energy of adsorption, $K_L/a_L = b$, is the monolayer adsorption capacity. When $C_{e'}q_e$ was plotted against C_e , straight line with slope a_L/K_L and intercept $1/K_L$ was obtained and the constants a_L and K_L were calculated from the isotherm plotted (Fig.4) and their values are given in Table I. Langmuir isotherm shows a best fit among the isotherms used and the Langmuir isotherm parameters of the prepared carbons, GACOLaO1273, GAC383and GACO383 (Table 1). Among the series, GACOLaO1273 has the highest monolayer capacity b value of 229.4 mg/g followed by GAC383 (178.6mg/g) and GACO383 (131.8 mg/g). Langmuir isotherm fits best based on the regression analysis as the isotherm plot shows a higher regression of R² = 0.99.

2.5. Freundlich IsothermEquation

The well-known linear logarithmic form of Freundlich model used to study adsorption isotherm behavior from liquid phase is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

Freundlich models assumes heterogeneous surface energies. C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium(mg/g), n is the Freundlich constant related to the intensity of adsorption and whose value greater than 1 shows the favorability of the adsorption process and K_F (mg/g) is the adsorption capacity of the adsorbent²⁰. The slope $\frac{1}{n}$ ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero²¹.

The plot of *log* q_e *Vs log* C_e gives a straight line with slope ${}^{1}/{}_{n}$ (Fig.5) and intercept *log* $K_{F.}$ The Freundlich isotherm parameter are given in Table 1.The Freundlich constant K_F is higher for GACOLaO1273 (K_F =58.5 L/g) confirms the higher adsorption capacity for MB dye than that of GAC383 (K_F =45.0L/g) and GACO383 (K_F =39.6L/g).The value of n is greater than 1 confirms the favorability of adsorption²².

2.6. Dubinin-Radushkevich Isotherm Equation

To calculate the micro porevolume,Dubinin- Radushkevichmodel was used. Dubinin-Radushkevichlinear form can be applied on both homogenous and heterogeneous surfaces²³.

$$\ln q_e = \ln q_s - \beta \varepsilon^2 \tag{4}$$

Where q_e is the amount adsorbed at equilibrium (mg/g), q_s is the micro porevolume, and β is a constant related to mean free energy of adsorption mol²/KJ².

$$\varepsilon = [RT \ln(1 + 1/C_e)] \tag{5}$$

Where *R* is the universal gas constant J/mol/K, *T* is the absolute temperature (K). The plot lnq_e *Vs* \mathcal{E}^2 gives a straight line, which helps us to determine the q_s and β from the intercept and slope respectively. The D-R plot is given in Fig. 6(a-c), the micro pore volume from the D-R plot is obtained by linear fitting the lowest values of the isotherm plot. The intercept of the plot gives the micro pore volume (q_mD -R).D-R micro pore volume of GACOLaO1273K $q_m(D-R$ was obtained as 93.5 mg/g and micro pore surface area of 211.3 m²/g which is higher than GAC383 (136.3 m²/g) and GACO383(131.1 m²/g).

2. 7 Isotherm Model Analysis

John-Sivanandan Achari isotherm plot analysis, constants and parameters are given in Table (1). Reveals that, among the series, GACOLaO1273 has the highest monolayer capacity q_m

(J-SA) value of 228.3 mg/g (with specific surface area, SSA of 515.9 m^2/g). This carbon has plot with three distinct phases with slope *n* absorbability constants with $n_1(0.21)$, $n_2(0.71)$ & Followed by GAC383 has q_m 176.1mg/g (SSA of 397.9 m²/g) with n₁ (0.39). n₃ (0.36). Carbon GACO383 has two distinct phases with q_m 138.2 mg/g (SSA of 312.3 m²/g) with n₁((0.49), n_2 (0.41). It is seen that basic carbon GAC383 has a single phase (line plot without kink). GACO383 has a two phases with two lines in the graph with a kink in the J- SA plots. This confirms the microporous behavior with one type of homogenous porous structure with universal Type I character as per IUPAC (2015) guidelines for the basic carbon GAC383. Dr. P. T. John & V. S. Achari (2002)7 classified this type of porous materials are with monodisperse pores. There arises a question why the carbon GACO383 has a less qm and SSA regards to GAC383. We know that, GACO383 is an oxidized prodigy of GAC383 using HNO₃. This modification could widen the existing inherent micropores and leads to loss of porosity. Hence, monolayer capacity q_m is substantially reduced. This recorded a lower surface area. But both John-Sivanandan Achari & Langmuir isotherm fits best based on the regression analysis. Both isotherm plots show a higher regression of $R^2 = 0.99$, for the materials. This reveals that the homogeneity of the pores are retained even after the surface chemical treatment. This observation is further supported by the Dubinin- Radushkevich (D-R) model analysis. It is seen that in D-R plots, the three carbons have retained the microporosity with straight line plots. GAC383 with qm (D-R) 60.3 mg/g has micropore specific surface area (mSSA;136.3 m²/g) and GACO383 qm (D-R) 58.0 mg/g (mSSA; 131.1 m^2/g). Surface oxidation altered the dimension of micropores into width widening subsequently for a noticed reduction of micropore uptake capacity. As regards to GACOLaO1273K, $q_m(D-R)$ obtained is 93.5 mg/g with a micro pore surface area, mSAA of 211.3 m²/g. Here, the thermo chemical activation after doping with LaO at 1273 K, nearly double the micropore quantity adsorbed. Straight line plots indicate that the homogeneity of pores existed is retained during activation. New activation strategy generated more micropores on the native carbon surface.

John-Sivanandan Achari analysis of the plots of GACOLaO1273K gives very significant features. Plots are marked by three phases of adsorption separated by distinct kinks with definite slope (n) values. Each phase is controlled by a separate adsorption mechanism as the uptake occurs only in one type of pores restricted by pore geometry. These stages are finer pore filling/ uptake, micropore filling (uptake), monolayer coverage (adsorption). Each stages, the intensity of adsorption is decided by the dimension and availability of selective pores decided by their relative proportions. However, the monolayer adsorption is obtained at

the point of saturation in the case of micro and mesoporous materials. LaO doping and heat treatment followed at 10000C for the GACOLaO1273K, generated more proportion of micropores with good contribution by finer and wider micropores in addition to the existing micropores. This pore generation due chemo- thermal treatment is well reflected in the form and shape of John-Sivanandan Achari isotherm plots. The model evaluated GACOLaO1273 that treatment sufficiently tuned the material enough to attain a highest monolayer capacity qm (J-SA) 228.3 mg/g with SSA of 515.9

3. Conclusions

The adsorption parameters of the newly prepared carbon were evaluated by applying John-Sivanandan Achari Isotherm Equation and other standard adsorption isotherms. The monolayer capacity obtained from John-Sivanandan Achari Isotherm Equation was used to calculate the specific surface area of the adsorbent, which was very much comparable with Langmuir monolayer capacity and Surface area. The high porosity developed for the Carbon prepared by the chemical activation with La₂O₃ followed by the thermal activation at 1273K,increased the thermal degradation and volatilization process which leads to the development of pores with increase in surface area. These findings are a step forward to establish that, LaO activation at 1000°C can insitu generate more micropores on the surface of a basic carbon through a set of proper surface tuning procedures. Porous materials with any type of porous structure can be texturally characterized by John & John-Sivanandan Achari Isotherm model methods.

Figures

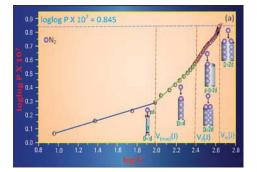


Fig 1: John isotherm plot for N₂ at 77K on micro porous carbon GC using equation log log $P = C + n \log V$). Phases of adsorption are distinct with kink and slope (n) to identify process of pore filling.

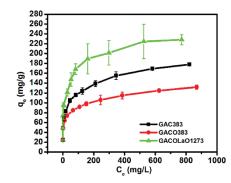


Fig 2: General Isotherm of GAC383, GACO383 and GACOLaO1273

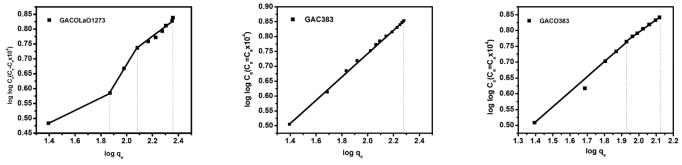


Fig. 3: John-Sivanandan Achari isotherm of GACOLaO1273, GAC383, GACO383

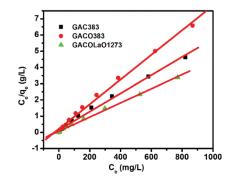


Fig 4 : Langmuir Isotherm of GAC383, GACO383, and GACOLaO1273

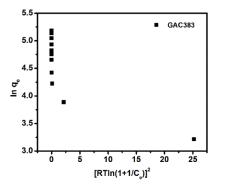


Fig. 6(a): Dubinin-Radushkevich isotherm plot for the adsorption of methylene blue onto carbon GAC383 at 303K. (C₀=25-1000mg/L, dosage=1g/L, equilibration period-10h)

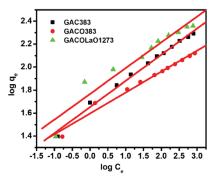


Fig 5 : Freundlich Isotherm of GAC383, GACO383 and GACOLaO1273

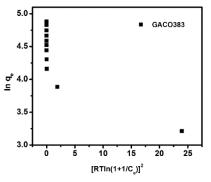


Fig. 6(b): Dubinin-Radushkevich isotherm plot for the adsorption of methylene blue onto carbon GACO383 at 303K. ($C_0=25-1000$ mg/L, dosage=1g/L, equilibration period-10h)

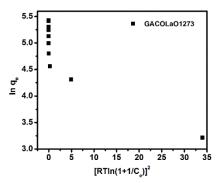


Fig.6(c): Dubinin-Radushkevich isotherm plot for the adsorption of methylene blue onto carbon GACOLaO1273 at 303K. ($C_0=25-1000$ mg/L, dosage=1g/L, equilibration period-10h)

Table:

Table 1. John- Sivanandan Achari (J-SA) isotherm parameters, monolayer adsorption $q_m(J-SA)$ and specific surface area (SA) of the granular activated carbons studied along with Langmuir Isotherm, Freundlich and Dubinin-Radushkevich (D-R) isotherm constants.

Carbon samples	Langmuir Isotherm			Freundlich isotherm		Dubinin-Radushkevich (D-R) isotherm		John–Sivanandan Achari Isotherm (J-SA)			
	b (mg/g)	K _L (L/g)	SA (m²/g)	R ²	K _F (L/g)	1/n	R ²	$q_{m(D-R)} \pmod{(\mathrm{mg/g})}$	$SA_{micro} (m^2/g)$	$q_m(J-SA)$ (mg/g)	SA (m²/g)
GAC383 GACO383 GACOLaO1273	178.6 131.8 229.4	6.24 4.57 13.6	403.6 297.8 518.4	0.999 0.993 0.996	45.0 39.6 58.5	0.227 0.181 0.224	0.992 0.980 0.931	60.3 58.0 93.5	136.3 131.1 211.3	176.1 138.2 228.3	397.9 312.3 515.9

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