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ADSORPTION OF *P*-NITROPHENOL ONTO La^{3+} INCORPORATED COCONUT SHELL BASED GRANULAR ACTIVATED CARBON: ISOTHERM AND KINETIC STUDY

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ABSTRACT

The present study discusses with the application of lanthanum incorporated coconut shell based granular activated carbon for the adsorption of *p*-Nitro phenol from aqueous solution. The native carbon used in the study has been designated as *GAC* and its HNO_3oxidized form was *GACO*. These carbons were modified using lanthanum ions (La^{3+}) and designated as *GACLa* and *GACOLa*. The basic and modified carbons were characterized using CHN, FTIR, XRD and SEM analysis. The new prepared carbons were subjected to batch adsorption study using p-nitro phenol as adsorbate. The adsorption isotherm data were further analyzed using adsorption isotherm models Langmuir, Freundlich and John-SivanandanAchari isotherm. The results showed that there has been an increased amount of *p*-nitrophenol adsorption by lanthanum modified *GACLa* and oxidized carbon *GACOLa* compared with the basic carbons *GAC* and *GACO*. Langmuir isotherm was found to be best fitted to explain the adsorption process based on the regression analysis (R^2). Application of John-SivanandanAchari isotherm (J-SA) revealed the phase change mechanism involved in the adsorption process. The adsorption data were again analyzed using the pseudo first and second order kinetic models and found that the adsorption process follows pseudo second order kinetics.

KEYWORDS: Activated Carbon, Lanthanum Ions, Adsorption Isotherm, Kinetics, John-SivanandanAchari Isotherm Plots.

Phenolic compounds and their dissolved derivatives in water are very much toxic to human health and to other living organisms, because of carcinogenic property (Achari *et al*., 2017) (Mohd *et al*., 2009).These compounds are widely produced from pharmaceutical, petrochemical and other chemical manufacturing industries (Achari *et al*., 1998) (Varank *et al*.,2012). Hence the water should be treated before being discharged into the natural environment water bodies. Activated carbon adsorption is a favorable method convincingly due to process efficiency, high adsorption capacity and lower operational cost for treating the waste water containing organic pollutants (Mohd *et al*.,2009). Apart from the high porosity and surface area of the activated carbon the surface functional groups also play a role in the adsorption process.The modification of activated carbon with lanthanum compounds is a new method of approach. Lanthanum compounds are getting increased attention because of its non-toxicand environmentally friendly nature (Zhang *et al*.,2011). Lanthanum compounds incorporated adsorbents are widely used for removing phosphate (Zhang *et al*., 2011) from aqueous solution. The present study deals with the removal of *p*-nitro phenol using the lanthanum ion incorporated coconut shell based granular activated carbon.

MATERIALS AND METHODS

Preparation of Carbons

The coconut shell based activated carbon (manufactured by Indo German Carbon Industry, Cochin, India) has been used as a carbon precursor material. It was washed till neutral pH, dried at 110^0C and marked as *GAC*. This was then oxidized with 12.9% HNO_3, washed till neutral pH, dried at 110^0C and marked as *GACO*. The new carbons *GACLa* and *GACOLa* was prepared by treating *GAC* and *GACO* with lanthanum oxide (La_2O_3). La_2O_3 prepared in the laboratory by a sol gel method already known (Wang *et al*; 2006). La_2O_3 has been get dissolved in 12.5mLof 12.9% HNO3 and then into which carbon dispersed. For this La2O3/carbon ratio of 0.03 has been kept for saturation. Then collected dried, filled in silica crucible and kept in a specially designed vessels made of steel. This container is placed in temperature programmed furnace. The container is activated at a higher temperature of 1073K in the presence of super-heated steam. The new carbons were designated as *GACLa* and *GACOLa*.

Characterization of the Prepared Carbons

The newly prepared La loaded carbons were characterized using CHNOS, FTIR, XRD, and SEM analysis.The elemental analysis of the prepared carbon samples were done using Elementar Vario EL III. Fourier Transform Infrared Spectroscopy (FTIR) was used for the qualitative detection of surface functional groups on the prepared carbon samples. The IR spectrum was obtained by using Thermo Nicolet Avatar 370 over the frequency range of 4000-400 cm^{-1}. Crystallinity of the carbon samples were determined using the XRD analysis (Bruker AXS D8 Advance), the surface morphology was

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characterized using the scanning electron microscope (JEOL Model JSM - 6390LV).

Batch Adsorption Equilibrium and Kinetic Studies

Batch adsorption experiments were carried out by using *p*-nitrophenol solution of concentration 25-2000 mgL^{-1}(25,50,75,100,150,200,250,350,500,750,1000,1250,1500, 2000 mg/L) with an adsorbent dosage of 1g L^{-1} at a room temperature of 30 ± 1^0C. The Erlenmeyer bottles were agitated in a temperature controlled shaker at an equilibration time of 480 minutes. At the end of equilibrium period, the contents of the bottle were filtered through a Whatman No.1 filter paper and the supernatant were analyzed for residual concentration by a UV-Vis spectrophotometer (Systronics UV-Vis Double Beam Spectrophotometer) at a wavelength of 317 nm.

The effect of contact time was performed under the same batch condition at different time intervals using *p*-nitrophenol concentration of 250mgL^{-1}. The amount adsorbed at equilibrium (q_e) was calculated using the equation.

$$q_e = (C_0 - C_e)\ V/W \qquad (1)$$

$$q_t = (C_0 - C_t)\ V/W \qquad (2)$$

Where C_0 is the initial concentration mg L^{-1}, Ce is the concentration at equilibrium (mg L^{-1}), V is the volume of the solution and W is the mass of the carbon (mg).

RESULTS AND DISCUSSION

Activated carbon is unique carbonaceous material having enough porosity, surface area and surface functional groups. Apart from these the structure of carbon consists of heteroatoms like hydrogen, nitrogen, oxygen and sulphur. These heteroatoms can also influence the adsorption properties of the carbon mainly the presence of oxygen surface functional groups, which is mainly present in the edges of the graphene layer (Marsh and Rodriguez; 2006). The % composition of these heteroatoms has been estimated using the CHNO analysis.The elemental analysis of the carbons *GAC, GACO, GACLa* and *GACOLa* were done and given in Table 1. It is found that the carbon *GACLa* has high carbon content (81.36%) followed by *GACOLa* (C = 79.06%) compared with the basic carbons *GAC* (C = 78.15%) and *GACO* (C = 73.43%). This is due to the fact that these carbons when subjected to activate at a higher temperature of 1073K causes the elimination ofnon-carbon species like hydrogen, oxygen and nitrogen resulting in the enrichment of carbon (Sekirifa *et al*., 2013). Oxidation of the carbon GAC was done using 13% $HNO_3$to obtain GACO which enhanced the surface oxygen functional groups withthe higherfor of *GACO*with higher O content (22.01%).

Table 1: Elemental analysis results and elemental composition of carbons GAC, GACO, GACLa and GACOLa

Carbon	C%	H%	N%	O%
GAC	78.15	1.88	0.17	19.80
GACO	73.43	3.99	0.57	22.01
GACLa	81.36	1.63	0.61	16.4
GACOLa	79.06	1.98	0.80	18.16

Functional groups present in the carbon surface were qualitatively valued using the FTIR analysis given in Figure1. The broad sharp peak in the range of 3500-3200 cm^{-1} corresponds to the O-H stretching vibrations of hydroxyl groups.The peaks in the range of 1585-1600 cm^{-1} indicates the aromatic C=C stretching of the carbon graphitic planes.The peaks at the range of ~1190 cm^{-1} relates to the C-O stretching vibrations of the functional groups developed during the modification process (Figueiredo *et al*., 1999). XRD analysis of the carbon samples was shown in Figure2 and the result shows two broad peaks at 2θ = 20-25^0 and 2θ = ~ 45^0. Peak at 2θ = 20-25^0 corresponds to (002) reflection of carbon due to the stacking structure of aromatic layers. The broadening of the 002 peak was inferred in terms of the small dimensions of crystallites perpendicular to aromatic layers (Yoshizawa *et al*., 2000). The peak at ~ 42^0 relates to the (100) plane of the graphite structure (Rajendran *et al*., 2015). The decrease in the intensity of the XRD peaks relates to the decrease in crystallinity and the increase inthe amorphous nature of the carbon which is a beneficial property for adsorbents (Das *et al*., 2015). SEM analysis of the carbons *GAC, GACO, GACLa* and *GACOLa* in Figure3 shows the clear porous structure of the carbons *GAC*, *GACO*, *GACLa* and *GACOLa*. It is inferred that the material have a uniform distribution of pores interconnected by graphene layers.

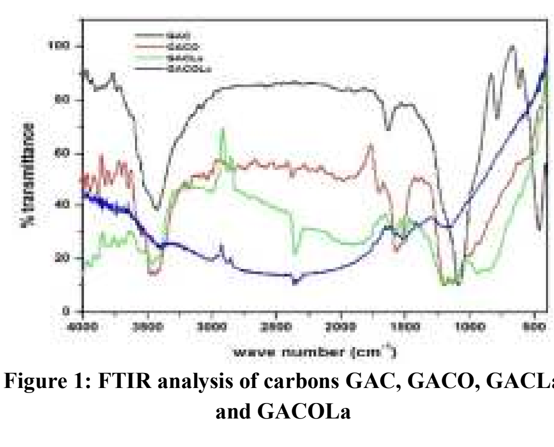

Figure 1: FTIR analysis of carbons GAC, GACO, GACLa and GACOLa

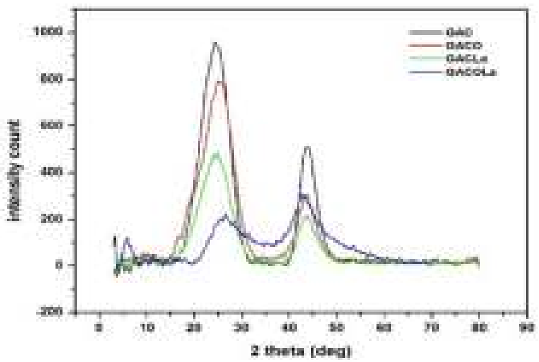

Figure 2: XRD analysis of carbons GAC, GACO, GACLa and GACOLa

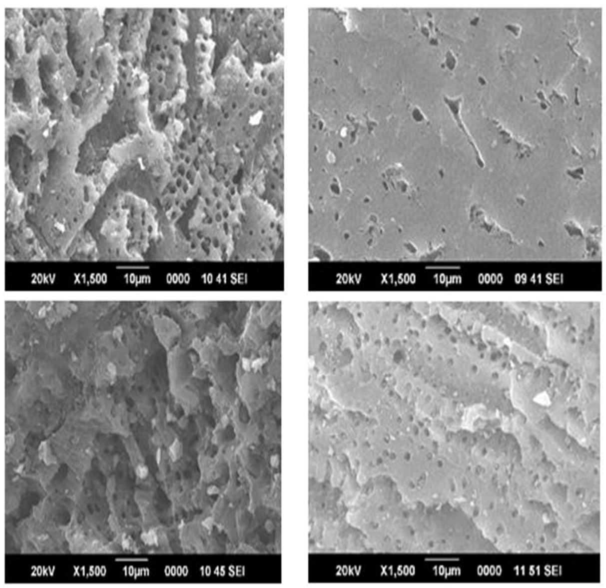

Figure 3: Scanning electron micrograph analysis of carbons GAC, GACO, GACLa and GACOLa.

Adsorption Isotherm

Adsorption efficiency of new carbon produced and their native forms are evaluated by applying isotherm models. Adsorption isotherms relate the amount of solute adsorbed at constant temperature and its concentration in equilibrium solution.Application of adsorption isotherm models is very much essential for explaining the adsorption process. Langmuir and Freundlich isotherm models were applied to the adsorption data and the parameters obtained from these models explain the monolayer adsorption capacity, adsorption efficiency of the carbon and the favorability of the adsorption process.

Langmuir isotherm assumes that adsorption take place on specific homogeneous sites with uniform distribution of energy levels without the transmigration of particles from one site to another (Langmuir. 1918). Based on these assumptions Langmuir developed the equation as

$$C_e/q_e = 1/K_L + (a_L/K_L)\ C_e \qquad (3)$$

Where $C_e$is the equilibrium concentration (mgL^{-1}), 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. The Langmuir isotherm is plotted (Figure 4&5) with C_e/q_ein *y* axis and C_e in *x* axis with slope a_L/K_L and intercept $1/K_L$.

The Freundlich isotherm (Freundlich. 1906) equation is an empirical equation used to describe a heterogeneous system. The linear form of the equation is

$$\log q_e = \log K_F + 1/n \log C_e \qquad (4)$$

Where $C_e$is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), *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^{-1}) is the adsorption capacity of the adsorbent. The Freundlich isotherm plot was plotted (Figure6) with*log* q_e in *y* axis and *log* C_e in *x* axis whose slope and intercept are *1/n* and *log* K_F respectively. The monolayer adsorption capacity (*b*) and the isotherm constants obtained are given in Table 2.

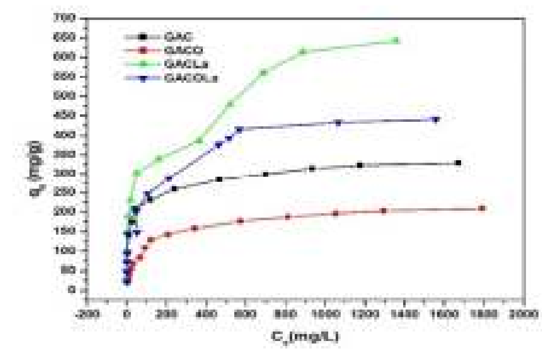

Figure 4: Isothermplots C_e vs q_e for *p*-nitrophenol on carbons GAC, GACO, GACLa and GACOLa (C_0=25-2000mg/L).

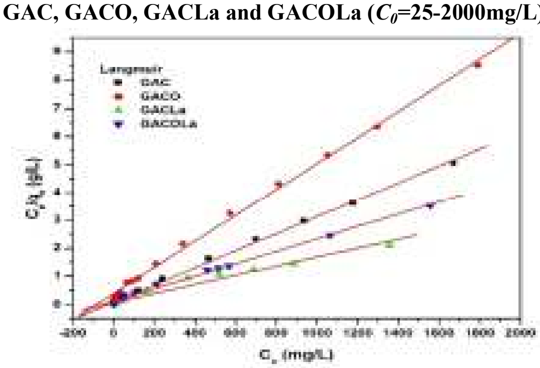

Figure 5: Langmuirisotherm plot for *p*-nitrophenol onto GAC, GACO, GACLa and GACOLa (C_0=25-2000mg/L).

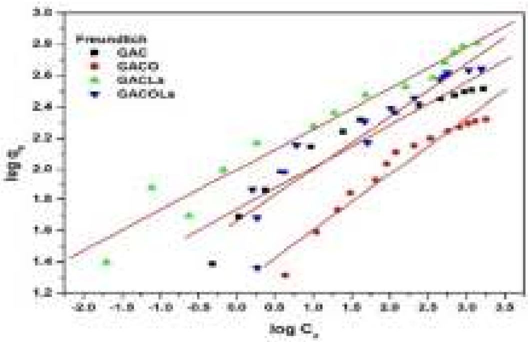

Figure 6: Freundlichisotherm plot for *p*-nitrophenol onto GAC, GACO, GACLa and GACOLa (C_0=25-2000mg/L).

John – SivanandanAchari (*J-SA*) isotherm (John and Achari; 2002) for the solid - liquid systemcan be referred to as a phase change method. The finer micropore filling, sub micropore filling, monolayer completion are distinct with definite slope (n) regarded as phases for adsorption on microporous carbon. The John–SivanandanAchari *(J-SA)* equation is given as

$$\log\log C_e = C + n \log q_e \qquad (5)$$

$C_e = C_e \times 10^N$ where N is an integer, properly chosen to make log log Ce positive for constructing J-SA model plots. Where $C_e$is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), $C$and n are *J-SA* constants. n is the slope referred to as adsorb ability constant, a measure of adsorption efficiency. The *J-SA* isotherm plot is plotted (Figure7-10) with $\log\log C_e$ in y axis and $\log q_e$ in x axis with slope n and intercept C. Amount of *p*-nitrophenol adsorbed to each phase of adsorption is obtained by extrapolating the highest point to the x axis.

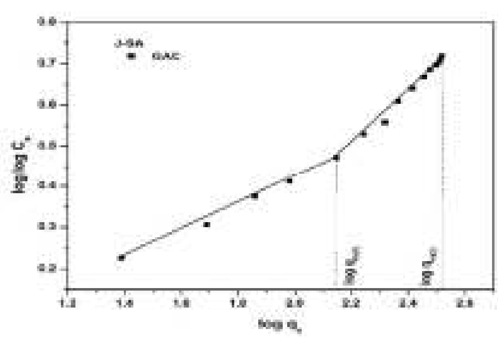

Figure 7: John-SivanandanAchari isotherm plot for *p*-nitrophenol on carbon GAC.

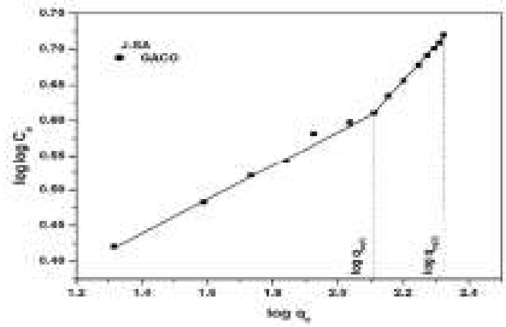

Figure 8: John-SivanandanAchari isotherm plot for *p*-nitrophenol on carbon GACO.

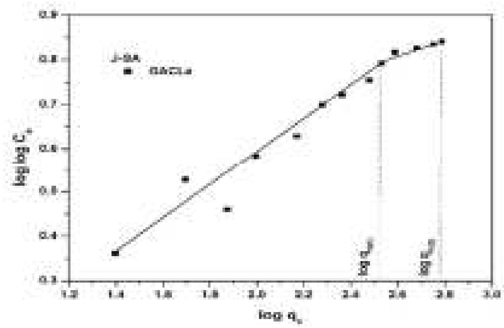

Figure 9: John-SivanandanAchari isotherm plot for *p*-nitrophenol on carbon GACLa.

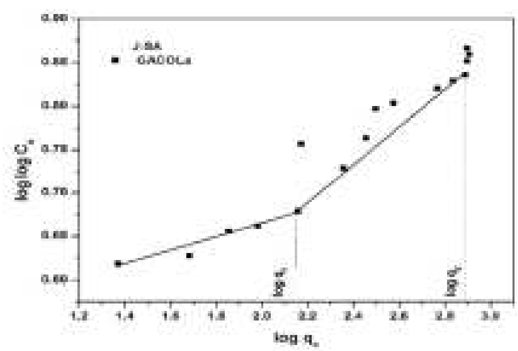

Figure 10: John-SivanandanAchari isotherm plot for *p*-nitrophenol on carbon GACOLa.

The results are shown in Table 2 revealed that the *p*-nitrophenol adsorption for lanthanum incorporated granular activated carbon (GACLa) 625 mg/g as evidenced by the higher monolayer adsorption capacity*b* (mg/g) obtained from the Langmuir adsorption isotherm constants. This confirms that there are homogeneous active sites present on the surface of carbon (Bulut and Aydin; 2006).The best fit of regression analysis (R^2=0.99) confirms the applicability of Langmuir isotherm. The Freundlich constant K_F is also high for *GACLa* (99.19) revealed the higher adsorption capacity of *GACLa* and the value *1/n* less than 1 showed the favorability of adsorption process.

The John – SivanandanAchari (*J-SA*) isotherm of the basic carbons *GAC* and *GACO* shows two straight lines-first line attributed to the presence of surface functional groups and second phase tomicropore filling(Mercy Thomas, 2016). The amount of *p*-nitrophenol adsorbed at each phases of adsorption is given in Table 2. The lesser adsorption shown by *GACO* in first phase (128.94mg/g) and second phase (84.11 mg/g) corresponds to the presence of excess surface functional groups generated during HNO_3 oxidation. According to Mattson *et al* (*1969*) the adsorption of aromatic adsorbates like *p*-nitrophenol proceeds through a donor- acceptor complex mechanism .The aromatic graphene layers of the carbon surface acting as electron donors and the electron deficient aromatic ring of *p*-nitrophenol molecules act as electron acceptors. The presence of surface functional groups on the carbon, with their deactivating role due to oxygen containing groups reduces the π electron density in the basal plane of the carbon.Thus weakening the π- π dispersive interaction thereby declines the adsorption capacity (Li *et al*.,2009).The higher amount of adsorption by *GACLa* and *GACOLa* compared to the basic carbons *GAC* and *GACO* ,is due the presence of lanthanum ions (La^{3+}) creating an electrostatic force of attraction between the carbon surface and *p*-nitrophenol molecules. The higher amount of adsorption in first phase for *GACLa* confirms the role of lanthanum ions in adsorption with higher *n* value to (0.36). *GACOLa* has three distinct phases due to surface functional groups, microporous structure due to the presence of lanthanum ions and monolayer completion. The higher carbon content of the *GACLa*, which well agrees with the CHNOS test result presented in Table 1 (81.36%) created during the steam activation at higher temperature (1073K)along with lanthanum ions confirms a higher adsorption capacity towards *p*-nitrophenol molecules.

Table 2: Asorption isotherm parameters for of *p*- nitrophenol onto carbons GAC, GACO, GACLa, GACOLa.

Carbon	Langmuir Isotherm			Freundlich isotherm			John-SivanandanAchari isotherm				
	b (mg/g)	K_L	R^2	K_F (L/g)	n	R^2	n_1	n_2	q_{m1} (mg/g)	q_{m2} (mg/g)	q_T (mg/g)
GAC	328.94	11.81	0.99	54.70	3.7	0.90	0.32	0.66	140.60	188.47	329.07
GACO	215.51	2.57	0.99	17.55	2.7	0.94	0.24	0.49	128.94	84.11	213.05
GACLa	625.00	12.78	0.97	99.19	3.8	0.96	0.36	0.17	371.53	245.06	682.33
GACOLa	450.45	8.62	0.99	46.17	3.0	0.87	-0.04	0.63	138.99	636.28	776.24

Adsorption Kinetics

In order to optimize the adsorption process on new carbons, the time dependent data was applied to kinetic models like Lagergren's pseudo first order (Lagergren; 1898) and Ho's pseudo second order kinetic models (Ho and Mckay; 1999).The linear equation for pseudo first order equation applied is given by

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

Where q_e and q_t are the amount of adsorbate adsorbed at equilibrium and at time t (mg g^{-1}) respectively, k_1 is the pseudo first order rate constant and t is the time in minutes. The linear plots of $ln\ (q_e$-$q_t)$Vst is given in Figure (11). The pseudo second order kinetic rate equation used is given as

$$t/q_t = 1/(k_2 q_e^2) + t/q \qquad (7)$$

Where k_2 is the pseudo-second-order rate constant, q_e and $q_t$are the amount of phenol adsorbed at equilibrium and at time t (mg g^{-1}) respectively and t is the time in minutes. The linear plots of t/q_t vs t is given in Figure (12). The q_e value obtained from the pseudo second order equation shows a good agreement between experimental and calculated q_e values. The correlation coefficients for the pseudo second order kinetic equation (R^2 =0.99) indicating the applicability of pseudo second order kinetic equation to explain the adsorption process.

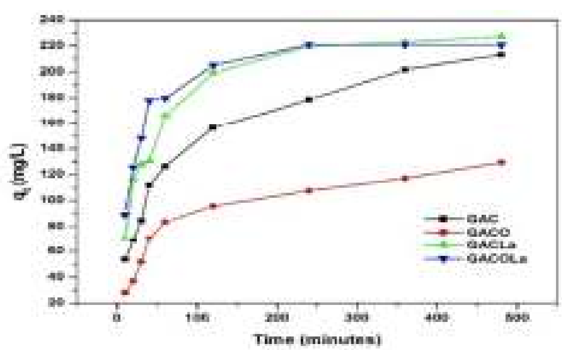

Figure 11: Effect of contact time for the removal of *p*-nitrophenol onto GAC, GACO, GACLa and GACOLa (C_0= 250mg/L).

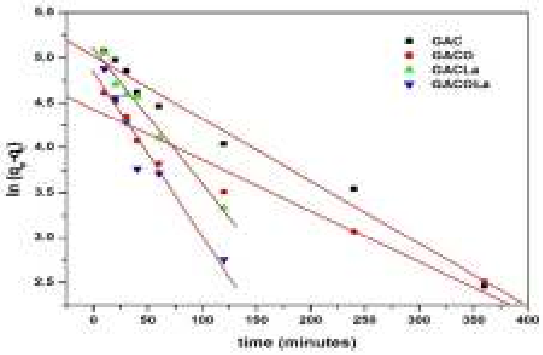

Figure 12: Pseudo first order kinetic model for *p*-nitrophenol onto GAC, GACO, GACLa and GACOLa(C_0= 250mg/L)

The kinetic parameters are shown in the Table 3. The results showed that the calculated q_e agree very well with the experimental q_{exp} and pseudo second order kinetic model shows a regression of 0.99 which confirms that the adsorption process follows a pseudo second order reaction mechanism. The activation of coconut shell based carbon with lanthanum ions provide excellent adsorption capacity towards *p*-nitrophenol, as the La^{3+} ions generate accessible features on carbon surface to attract organic molecules. The mechanism of adsorption follows a pseudo second order phenomena. Isotherm features are best descended by John-SivanandanAchari isotherm as they provides distinct adsorption phases occurring on carbon surfaces.

Table 3: Kinetic parameters of granular activated carbon GAC, GACO, GACLa and GACOLa.

Carbon	$q_{e\,exp}$ [mg g^{-1}]	Pseudo second order			Pseudo first order		
		$q_{e\,cal}$ [mg g^{-1}]	k_2 [mgh]	R^2	q_{cal} [mg g^{-1}]	k_1 [h^{-1}]	R^2
GAC	213.4	228.8	0.92 x10^{-4}	0.99	151.2	0.0069	0.98
GACO	129.2	136.7	1.55 x10^{-4}	0.99	84.2	0.0056	0.93
GACLa	227.3	239.8	1.62 x10^{-4}	0.99	163.4	0.0149	0.98
GACOLa	220.8	228.8	3.00 x10^{-4}	0.99	127.5	0.0183	0.93

CONCLUSION

In the present study coconut nut shell based activated carbons were modified with lanthanum ions were prepared and its adsorption efficiency towards *p*-nitrophenol solution were studied. The newly prepared carbon samples were characterized by CHNOS, SEM, FTIR and XRD. The effective removal of *p*-nitrophenol followed well known isotherms like Langmuir, Freundlich and John-SivanandanAchari isotherms. Among the carbons, *GACLa* and *GACOLa* shows higher adsorption efficiency towards *p*-nitrophenol confirmed by the highest monolayer adsorption capacity from Langmuir adsorption isotherm. Applying the John-SivanandanAchari isotherm reveals the phase change mechanism involved in the adsorption process. Higher amount of adsorption is shown by La^{3+} incorporated granular activated carbons *GACLa* and *GACOLa* compared with the *GAC* and *GACO*. Kinetic study indicates that the adsorption process follows pseudo second order kinetic model controlled by the factors (i) substrate *p*-nitrophenol concentration (ii) availability of active vacant sites on new carbon surfaces.

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REFERENCES

Achari V.S., Jayasree S., Rajalakshmi A.S., 2017. Adsorption of P – Nitrophenol on Coconut Shell Granular Activated Carbon : Isotherms, Kinetics and Thermodynamics. Indian Journal of Chemical Technology, **24**:471–478.

Achari V.S., 1998. Ph.D. Thesis. Modified Carbons and wood dust: Evaluation of Adsorption Properties. Department of Chemistry, University of Kerala, Kariavattom, Thiruvananthapuram.

Li B., Lei Z. and Z.H., 2009. Surface-Treated Activated Carbon for Removal of Aromatic Compounds from Water. Chem. Eng. and Techn., **32**(5):763–770.

Bulut Y. and Ayd H., 2006. A Kinetics and Thermodynamics Study of Methylene Blue Adsorption on Wheat Shells. Desalination, **194**:259–267.

Das D., Samal D.P. and Meikap B.C, 2015. Preparation of Activated Carbon from Green Coconut Shell and Its Chemical Engineering & Process Technology. Chem.Eng. & Pro. Techn., **6**(5):1–7.

Din A.T.M., Hameed B.H. and Ahmad A.L., 2009. Batch Adsorption of Phenol onto Physiochemical-Activated Coconut Shell. J. Hazar. Mater., **161**:1522–1529.

Figueiredo J.L., Pereira M.F.R., Freitas M.M.A. and Orfao J.J.M., 1999. Modification of the Surface Chemistry of Activated Carbons. Carbon, **37**:1379–1389.

Freundlich H.M.F., 1906, Over the Adsorption in Solution, Journal of Physical Chemistry, **57**:385.

Ho Y.S. and Mckay G., 1999. Pseudo-Second Order Model for Sorption Processes. Process Biochemistry, **34**:451.

John P.T., Achari V.S., 2002. Characterisation of Structural Parameters of Finely Divided and Porous Materials by a New Adsorption Isotherm. J. Mater. Sci., **37**(4):885–893.

Lagergren S., 1898. Zurtheorie der sogenannten adsorption geloesterstoffe. KungligaSvenskaVetenskapsakad, Handlingar, **24**: 1.

Langmuir I., 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum,J. Am.Chem. Soc., **345**: 1361.

Marsh and Rodriguez, 2006. Activated carbon, CPI Antony Rowe, Eastbourne, Great Britian, **22**:182.

Mattson J.A., Jr. H.B.M., Malbin M.D., Jr. W.J.W. and Crittenden J.C., 1969. Surface chemistry of active carbon: Specific adsorption of phenols. Journal of Colloid and Interface Science, **31**:116-130.

Mattson J.A., Jr. H.B.M., Malbin M.D., Jr. W.J.W. and Crittenden J.C., 1969. Surface chemistry of active carbon: Specific adsorption of phenols. -Appl. Pyrol., **99**:155–160.

Varank G., Demir A., Yetilmezsoy K., Top S., Sekman E. and Bilgili M.S., 2012. Removal of 4-Nitrophenol from Aqueous Solution by Natural Low-Cost Adsorbents. Ind. J. Chem. Techn., **19**:7–25.

Wang X., Wang M., Song H. and Ding B., 2006. A Simple Sol-Gel Technique for Preparing Lanthanum Oxide Nanopowders. Mater. Lett., **60**:2261–2265.

Zhang L., Wan L., Chang N., Liu J., Duan C., Zhou Q., Li X. and Wang X., 2011. Removal of Phosphate from Water by Activated Carbon Fiber Loaded with Lanthanum Oxide. J. Hazar. Mater., **190**:848–855.