九州大学学術情報リポジトリ
Kyushu University Institutional Repository

Rice Husk derived Activated Carbon for the Adsorption of Scarlet RR an Anionic Disperse Dye

Kaur, Manpreet
Department of Applied Sciences, Punjab Engineering College

Mittal, Nisha
Department of Applied Sciences, Punjab Engineering College

Charak, Abhishek
Department of Industrial and Production, Punjab Engineering College

Amrit Pal Toor
University Institute of Chemical Engineering & Technology, Panjab University

他

https://doi.org/10.5109/6782146

出版情報：Evergreen. 10 (1), pp.438-443, 2023-03. 九州大学グリーンテクノロジー研究教育センター
バージョン：
権利関係：Creative Commons Attribution-NonCommercial 4.0 International

Rice Husk derived Activated Carbon for the Adsorption of Scarlet RR an Anionic Disperse Dye

Manpreet Kaur[1], Nisha Mittal[1], Abhishek Charak[2], Amrit Pal Toor[3], Vasundhara Singh[1,*]

[1]Department of Applied Sciences, Punjab Engineering College, Chandigarh, India

[2]Department of Industrial and Production, Punjab Engineering College, Chandigarh, India

[3]University Institute of Chemical Engineering & Technology, Panjab University, Chandigarh, India

*E-mail: vasun7@yahoo.co.in

(Received July 12, 2022; Revised January 24, 2023; accepted January 24, 2023).

Abstract: Bioinspired mesoporous activated carbon was synthesized using rice husks. SEM (scanning electron microscopy), XRD (X-ray powder diffraction), FTIR (fourier transform infrared spectroscopy), and BET(Brunauer–Emmett–Teller) were used to detrmine the textural qualities and physicochemical properties of the produced activated carbon .Monolayer and multilayer isotherm models were evaluated to examine the adsorption investigations on hydrophobic Scarlet RR. The Langmuir adsorption isotherm best explained the results because the monolayer's adsorption capacity was 996 mg/g at adsorbent dosage of 1.5 g/L. The results suggested that bio-inspired activated carbon would work well as an adsorbent for dye removal from polluted water.

Keywords：Activated Carbon, Rice Husk, Hydrophobic disperse dye, Scarlet RR.

1. Introduction

In order to prepare electrode materials, remove pollutants from industrial wastewater and provide catalytic assistance for the creation of supercapacitors, activated carbon is frequently used. Activated carbon as a highly porous material has potential applications in wastewater remediation as a result of its high thermal stability, large surface area, and stability under acidic and basic conditions. However, the high cost of processing and production is of great concern and therefore its production from agricultural waste will not only reduce its operating cost but also help in agricultural waste management. Worldwide, 571 million tons of rice are produced annually, resulting in nearly 140 million tons of rice husk waste.(1) Rice husks are a potential adsorbent material because they contain cellulose, hemicelluloses, and lignin along with various functional groups such as hydroxyl, carboxyl, aldehyde, etc., and ketone, etc.(2-5) As a result, rice husks are a plentiful, accessible, and economical source for the creation of inexpensive activated carbon.

The color of textile effluent is the most problematic and serious problem because it affects the transparency of water and also reduces the solubility of oxygen in natural water bodies. (6,7) Textile wastewater generally contains resistant dyes, dissolved solids, surfactants and high color that show toxic effects on aquatic and human life. To overcome this issue, a variety of techniques, including membrane treatment, coagulation, chemical oxidation, photocatalysis, membrane treatment, biological process, and adsorption using various adsorbents, have been used in recent years.(8-10) Among these adopted methodologies is adsorption using activated carbon an economically feasible and effective for removing dyes and other dissolved impurities.11-13) However, commercially available activated carbon is relatively expensive. Therefore, to develop a cost effective, eco-friendly and highly effective adsorbent from a cheaper precursor is the necessity of the hour.

Disperse dyes are widely used in the textile industry for dyeing mainly polyester, synthetic fabrics, acrylic and polyamide materials, etc.(14-17) Degradation of these dyes is quite challenging because these dyes contain a non-ionic end, which makes them hydrophobic in nature.(18-20) Due to the solubility problem, disperse dyes are poor candidates for mechanistic studies. Even a small amount of disperse dye (concentration in $\mu g\ L^{-1}$) can be dangerous because these dyes are carcinogenic and mutagenic.(21-23)

Thus, to meet the discharge standard set by the government and to effectively remove dyes to eliminate environmental problems, adsorption study with biomass-derived activated carbon could be beneficial to the environment.(24, 25)

In the current study, mesoporous activated carbon was synthesised utilising agricultural waste, namely rice

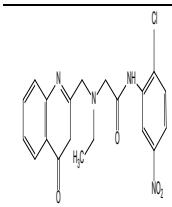
husks, and was then examined using SEM, XRD, FTIR, and BET techniques. Adsorption studies were performed on the hydrophobic dispersion dye Scarlet RR and the experimental data were examined by fitting the Langmuir and Freundlich models.

2. Materials and Methods

2.1 Materials

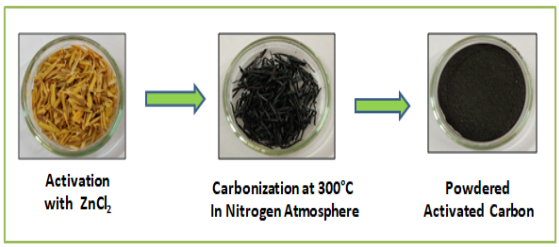
The synthesis and adsorption investigations were employed by using analytical-grade chemicals only. Rice husk was collected from the Punjab province's Faridkot district. Table 1 demonstrates the chemical properties of the disperse dye Scarlet RR that Arora Textiles, Ludhiana, Punjab, provided as a gift. All studies involved adjusting the pH of the dye using diluted NaOH and HCl. The removal percentage were evaluated using a UV-visible spectrophotometer from Perkin Elmer, by recording the absorbance of Scarlet RR after particular interval of time.

Table 1. Chemical properties and characteristics of Scarlet RR

Chemical structure	Dye name	Colour index	λ_{max}	Chemical formula
	Scarlet RR	Disperse Red 54	530nm	$C_{20}H_{18}N_4O_4$

2.2 Synthesis of Rice Husk Derived Activated Carbon

According to Scheme 1, activated carbon was created by a single activation step. To remove undesired pollutants and other contaminants from their surface, rice husks was washed numerous times. The cleaned sample was activated by soaking in $ZnCl_2$ solution for a whole night before being dried at 80 °C to eliminate any remaining water. The rice husk was then carbonised by being heated in a muffle furnace for four hours at 300 °C at a temperature rice of 5 °C per minute while being exposed to a nitrogen environment. The obtained sample then powdered using mortar and pestle.



Scheme. 1- Synthesis of Activated Carbon from Rice Husk

2.3 Adsorption experiments

Adsorption isotherms were studied using Scarlet RR at different dye concentrations (10, 20, 30, 40 and 50 ppm) to perform adsorption experiments. The aqueous solution was kept in the dark for 240 min with varying amounts of catalyst (1 g/L, 1.5 g/L, and 2 g/L) at room temperature. An aliquot of 5 ml was taken every thirty minutes and analyzed spectrophotometrically. The amount of adsorbate adsorbed at equilibrium, at equilibrium, q_e (mg/g) was evaluated by subtracting (C_e)equilibrium concentration and(C_o) initial dye concentration (C_o) as depicted in equation 1.[7]

$$q_e = \frac{(C_o - C_e)V}{W} (1)$$

Here, volume of the solution is V and mass of activated carbon used is depicted as W (g).

3. Results and Discussion

3.1 Characterization of synthesized adsorbent

XRD analysis of the synthesized activated carbon shows the presence of a single broad peak from 20° to 30° indicating the formation of the 002 phase of graphitic carbon. As depicted in Fig. 1, the activated carbon obtained is amorphous in nature and the absence of any other peak confirms the purity of the synthesized material.

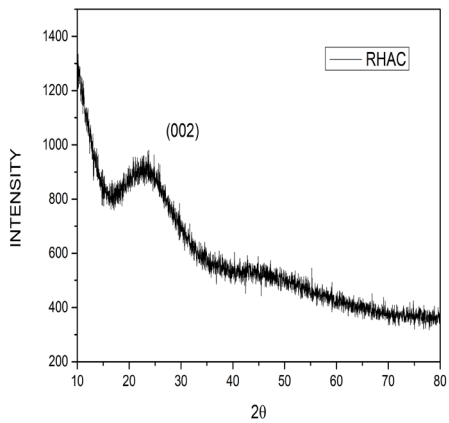


Fig. 1. XRD of synthesized activated carbon

The SEM images of the synthesized activated carbon are illustrated in Figure 2. From the obtained images, it can be concluded that synthesized mesoporous activated carbon features fully irregular cracks, pores, and and crevices. Evaporation of the zinc chloride activator led to pores, which further leads to a large surface area.

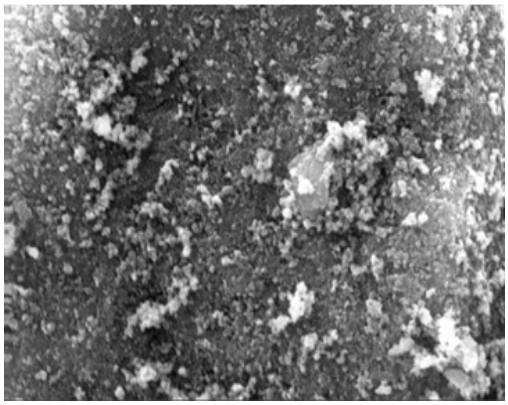


Fig. 2. SEM of synthesized activated carbon

Fig. 3 explains the synthetic activated carbon's FTIR spectrum. The existence of hydroxyl groups was confirmed by the O-H stretching peak at 3391 cm^{-1}. due to water adsorption on the surface, of hydroxyl groups. Aliphatic carbon is responsible for the peak at 1718 and the stretching vibration of the C-H bond obtained at 1960 cm^{-1}. At 1596 cm^{-1}, there was a peak that was attributable to the carboxyl group's C=O vibration. It was determined that the peaks at 1239 and 1057 cm^{-1} were caused by the ring vibration of the aromatic skeleton, which is primarily seen in carbonaceous material.

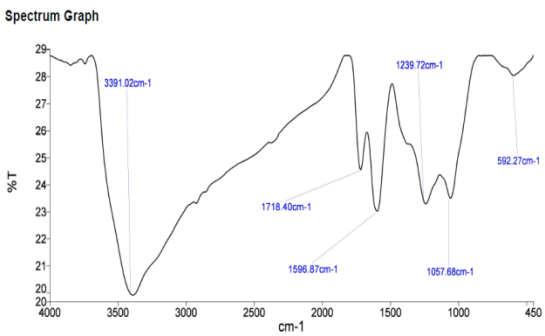


Fig. 3. FTIR spectra of synthesized activated carbon

The N_2 adsorption-desorption isotherm was employed to investigate the Brunauer-Emmett-Teller (BET) of the synthesised carbon, as shown in Fig. 4. The bioinspired synthetic material displayed a type IV isotherm with H4 hysteresis, supporting the properties of a mesoporous material. According to Table 2, the produced activated carbon has an average diameter of 3.54 nm and a specific surface area of 218 (m^2/g).

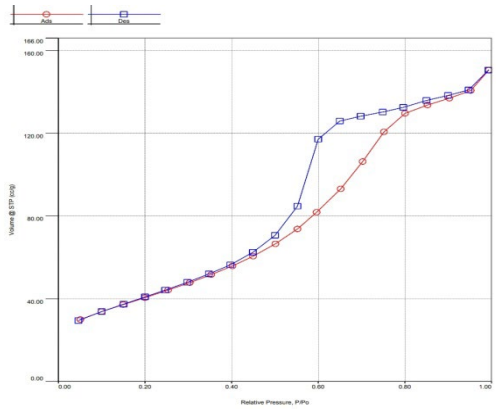


Fig. 4. N_2 adsorption–desorption isotherms of synthesized activated carbon

Table 2. The pore parameters of rice husk derived activated carbon

$S_{BET}(m^2/g)$	Total pore volume (V_m cm^3 /g)	Pore volume Dp(nm)
218	0.436	3.54

3.2 Adsorption behaviour of Scarlet RR bioinspired activated carbon

Adsorption studies were performed in a 100 ml flasks using 50 ml of Scarlet RR standard solution in a range of concentrations (10 ppm to 50 ppm), and the mixture was agitated at 300 rpm in the dark using a magnetic stirrer. Adsorbent concentrations ranged from 1 to 2 g/l. As depicted in Fig. 5, the UV absorbance spectra of the Scarlet RR solution were recorede for 240 minutes.

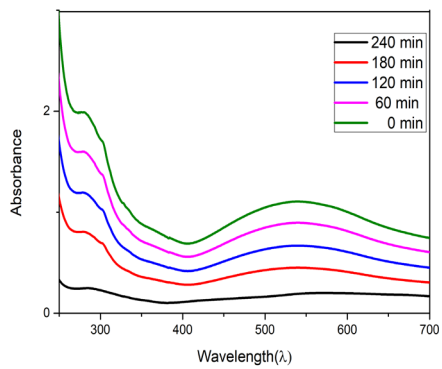


Fig. 5 UV spectra of Scarlet RR adsorbed and effect of adsorbent dose on dye adsorption

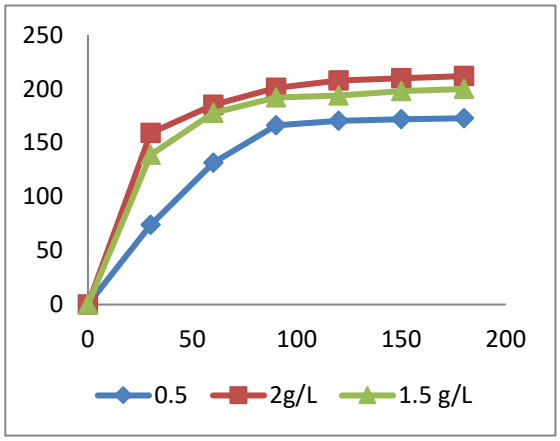


Fig. 6q_e vs time plot by varying adsorbent dose

To explain the equilibrium state attained following the adsorption process, isothermal models were used to forecast the distribution of adsorbate and solid-liquid phases of molecules. The plot of qe vs. time used to determine the adsorbent's affinities and capacity is displayed in Fig. 6. The dye removal efficiency of the synthesised activated carbon on Scarlet RR at various adsorbent loadings was examined using Langmuir and Freundlich isotherms. The Freundlich isotherm well described multilayer adsorption happening on heterogeneous surfaces and is expressed by Equations 2 and 3. The Langmuir isotherm model operates under the presumption that a homogenous adsorbent surface supports only monolayer adsorption.

$$q_e = \frac{q_{max} K_a C_e}{1+K_a C_e} \qquad (2)$$

Where q_{max} is the maximum capacity for adsorption in mg/g, Ka is the adsorption constant in L/mg, Ce is the equilibrium dye concentration in mg/L, and qe is the quantity of dye absorbed per unit weight of the adsorbent in mg/g. [7]

$$q_e = K_f C_e^{1/n} \qquad (3)$$

Here, K_f is the relative adsorption capacity in mg/g and $L/mg^{1/n}$ and adsorption intensity depicted as 1/n. The nonlinear plots of the isotherms models as depicted in Equation. (1) and (2) are shown in Fig. 6, Based on other isotherm parameters recorded and high R^2 values given in Table 3, the better fit is provided by the Langmuir isotherm model indicating the adsorbent showed homogeneous monolayer adsorption**.**

Adsorption intensity is shown as 1/n, and K_f is the relative adsorption capacity in mg/g and $L/mg^{1/n}$. Fig. 6 displays the nonlinear graphs of the isotherms models provided in Equations (1) and (2). The Langmuir isotherm model offers a better fit based on other isotherm parameters measured and high R^2 values shown in Table 3, showing the adsorbent displayed uniform monolayer adsorption.

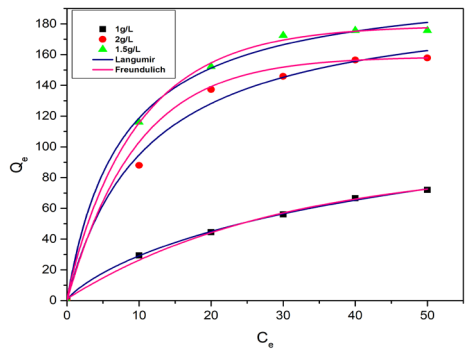


Fig. 7.$C_e$vsQ_e plot of Langmuir and Freundlich isotherm

Table 3. Adsorption isotherm parameters of Scarlet RR adsorption

Type of isotherm	Parameter	Adsorbent Dose		
		1g/L	1.5 g/L	2g/L
Langmuir	q_m (mg/g)	167	996	198
	Ka (L/mg)	0.03	7.03	1.96
	R^2	0.999		
Freundlich	K_f(mg/g)$(L/mg)^{1/n}$	0.86	4.13	1.89
	N	0.804	1.46	0.964
	R^2	0.986		

Table 3 and Fig. 7 show that the maximum adsorption was attained at 1.5 g/L of activated carbon loading with adsorption capacity of 218 mg/g due to the wide specific surface area of prepared activated carbon. The Langmuir adsorption isotherm on the mesoporous carbon was best fitted, showing that the adsorption on the activated carbon was a monolayer.

4. Conclusion

The current study embarked on the synthesis of bio-inspired activated carbon obtained from agricultural waste via economically viable and experimentally feasible method. The current study demonstrates that the activated carbon that was formed was mesoporous in nature with a large specific surface area. Scarlet RR anionic disperse dye was significantly removed from synthetic wastewater by the developed adsorbent. The results demonstrated that a monolayer adsorption using the Langumire isotherm supported an optimum adsorbent loading of 1.5 g/L.

References

1) N.K. Soliman, A.F.Moustafa, A.A. Aboud, and K.S.A.Halim,"Effective utilization of Moringa seeds waste as a new green environmental adsorbent for removal of industrial toxic dyes," *Journal of Materials Research and Technology* 8., no. 2,1798-1808(2019).https://doi.org/10.1016/j.jmrt.2018.12.010.
2) D.Datta, Ö.K.Kuyumcu, Ş.S.Bayazit, and M. A.

Salam, "Adsorptive removal of malachite green and Rhodamine B dyes onFe3O4/activatedcarbon composite," *Journal of Dispersion Science and Technology* 38., no. 11, 1556-1562(2017).https://doi.org/10.1080/01932691.2016.1262776.

3) M. Kaur, S. Sandhu, A. P. Toor, and V. Singh. "Time-dependent mechanistic insight into photo-degradation of mixed hydrophobic disperse dyes by magnetically separable nitrogen iron codoped titania under visible light using process variable optimization." *Journal of Cleaner Production* 342 (2022):.https://doi.org/10.1016/j.jclepro.2022.130940
4) G.Crini, "Non-conventional low-cost adsorbents for dye removal: a review," *Bioresource technology* 97., no. 9, 1061-1085(2006).https://doi.org/10.1016/j.biortech.2005.05.001.
5) L. Dong, W. Liu, Y.Yu, P.Gu, and G. Chen, "Preparation, characterization, and application of macroporous activated carbon (MAC) suitable for the BAC water treatment process," *Science of the total environment.*, *647*, 1359-1367 (2019).https://doi.org/10.1016/j.scitotenv.2018.07.280.
6) L.K.Shrestha,M. Thapa, R. G. Shrestha, S. Maji, R.R.Pradhananga, and K.Ariga, "Rice husk-derived high surface area nanoporous carbon materials with excellent iodine and methylene blue adsorption properties," *C* 5., no. 1,10(2019).https://doi.org/10.3390/c5010010.
7) N. Mittal, M. Kaur, and V. Singh. "Adsorption studies on hydrophobic disperse dye using cellulose derived mesoporous activated carbon." *Materials Today: Proceedings* (2022).https://doi.org/10.1016/j.matpr.2022.04.765
8) S.Jeevanantham, A. Saravanan, R. V. Hemavathy, P.S. Kumar, P. R. Yaashikaa, and D. Yuvaraj, "Removal of toxic pollutants from water environment by phytoremediation: a survey on application and future prospects," *Environmental technology & innovation* 13., 264-276(2019).https://doi.org/10.1016/j.eti.2018.12.007.
9) M. Valarmathi, and P.R. Gogate, "Degradation of Acid Scarlet 3R dye using oxidation strategies involving photocatalysis based on Fe doped TiO2 photocatalyst, ultrasound and hydrogen peroxide," *Separation and Purification Technology* 274.,119011(2021).https://doi.org/10.1016/j.seppur.2021.119011.
10) J. Miyawaki, J. Yeh, H. S. Kil, J. K. Lee, K. Nakabayashi, I. Mochida, and S. H. Yoon, "Influence of pore size and surface functionality of activated carbons on adsorption behaviors of indole and amylase," *Evergreen.*, *3*(2) 17-24 (2016). https://doi.org/10.5109/1800868.
11) R. Muhammad, and S. Adityosulindro, "Biosorption of Brilliant Green Dye from Synthetic Wastewater by Modified Wild Algae Biomass," *Evergreen.*,133-140 (2022).https://doi.org/10.5109/4774228.
12) M. Sultan, I. I. El-Sharkawy, T. Miyazaki, B. B. Saha, and S. Koyama, "Experimental study on carbon-based adsorbents for greenhouse dehumidification," *Evergr. Jt. J. Nov. Carbon Resour. Sci. Green Asia Strat* 1., (2014).https://doi.org/10.5109/1495157.
13) K. Thu, T. Miyazaki, K. Nakabayashi, J. Miyawaki, and F. Rahmawati, "Highly Microporous Activated Carbon from Acorn Nutshells and its Performance in Water Vapor Adsorption," *Evergreen.*, 249-254 (2021).https://doi.org/10.5109/4372285.
14) A.F. Ridassepri, F.Rahmawati, K. R. Heliani, J. Miyawaki, and A. T. Wijayanta, "Activated carbon from bagasse and its application for water vapor adsorption," *Evergr. Jt. J. Nov. Carbon Resour. Green Asia Strateg.,* 7, 409-416 (2020).http://hdl.handle.net/2324/4068621.
15) Y. Wibisono, A. Amanah, A. Sukoyo, F. Anugroho, and E. Kurniati, "Activated Carbon Loaded Mixed Matrix Membranes Extracted from Oil Palm Empty Fruit Bunches for Vehicle Exhaust Gas Adsorbers," *Evergreen.*,593-600 (2021).https://doi.org/10.5109/4491651.
16) J. Miyawaki,I. Mochida, and S.H.Yoon,"Investigation on H2S Removal Factors of Activated Carbons Derived from Waste Palm Trunk," *Journal of Novel Carbon Resource Sciences* 7., 7-11(2013).
17) R.A. Rouf, M.A.H. Khan, K.M.A. Kabir, and B.B.Saha, "Energy management and heat storage for solar adsorption cooling," *EVERGREEN Joint Journal of Novel Carbon Resource Sciences & Green Asia Strategy* 3., no. 2 1-10(2016).https://doi.org/10.5109/1800866.
18) F.Jerai, T. Miyazaki, B.B.Saha, and S. Koyama, "Overview of adsorption cooling system based on activated carbon–Alcohol Pair," *Joint Journal of Novel carbon resources Sciences & green Asia Stratgy.,* 30-40(2015).https://doi.org/10.5109/1500425.
19) S.M.Ali,and A. Chakraborty, "Performance Study of Adsorption Cooling Cycle for Automotive Air-onditioning,"*Evergreen.*,12-22(2015).https://doi.org/10.5109/1500423.
20) R. Muhammad, and S.Adityosulindro, "Biosorption of Brilliant Green Dye from Synthetic Wastewater by Modified Wild Algae Biomass,"*Evergreen.*,133-140(2022).https://doi.org/10.5109/4774228
21) Al-Othman, Z. Ali, R. Ali, and Mu Naushad. "Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies." *Chemical engineering*

journal,238-247(2012)https://doi.org/10.1016/j.cej.2012.01.048

22) J.L. Sotelo, , G Ovejero, A. Rodríguez, S. Á. José Galán, and G. Juan. "Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon." *Chemical engineering journal* 443-453(2014):https://doi.org/10.1016/j.cej.2013.11.094
23) A. Rossner, S.A. Snyder, D.R.U. Knappe."Removal of emerging contaminants of concern by alternative adsorbents"*Water Res.,* 3787-3796(2009)https://doi.org/10.1016/j.watres.2009.06.009
24) Z. Aksu, F. Gonen. "Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves."*ProcessBiochem*., 39,599-613:(2004).https://doi.org/10.1016/S0032-9592(03)00132-8
25) D. Mohan and S. Chander. "Single component and multi-component adsorption of phenols by activated carbons"*Colloids Surf. A: Physicochem. Eng. Aspects,* 177,183-196(2001),https://doi.org/10.1016/S0927-7757(00)00670-1