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Preparation of Activated Carbon from Phragmites Australis: Equilibrium Behaviour Study

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Abstract

Activated carbons were prepared from phragmites australis by chemical activation with K_2CO_3 (1:1w)(AC1), $ZnCl_2$ (1:1w)(AC2), NaOH (1:1w)(AC3), and 28.5% H_3PO_4 (AC4) followed by pyrolysis at 800°C in steam atmosphere. Different activated carbons have been used for the removal of methylene blue (MB) dye from aqueous solutions. The optimum condition for the production of colorless methylene blue aqueous was determined. The activated carbon prepared by chemical activation with K_2CO_3 attained a maximum value of 153 (mg/g) at a carbonization temperature of 800°C with activation duration of 30 min and at an impregnation ratio of 1.0. Porosities of activated carbons were characterized by cyclic voltametry and electrochemical impedance spectroscopic and SEM techniques.

Keywords: Activation methods, phragmites, adsorption methylene blue, porosity, electrochemical behavior.

Introduction

Activated carbon is well known as a porous material and has a large specific surface area. Therefore, such a material has desirable adsorption properties and has been used for purification and elimination of hazardous components in the gas and liquid phases. It is also valued as a catalyst and a catalyst support. Due to the current problems of environmental pollution, activated carbon is expected to play an important role in pollution abatement. Activated carbons can be produced either by physical or chemical methods. Chemical agents, such as zinc chloride, potassium hydroxide or phosphoric acid[1-4], may be mixed with the source material prior to carbonization so as to ensure the formation of porosity[5]. Activated carbon with high specific surface area is suitable for gas storage, gas purification, recovery of solvent vapor and manufacture of electric double layer capacitors[6-9]. Their properties depend on the pore surface area available for the adsorption of molecular species[10-14]. The porosity is a function of both the precursor as well as the type of the activation[15-17].

Precursors to activated carbons are organic materials that can be designed for adsorption of specific adsorbate, by using appropriate precursor[18-20], dehydrating agent and by optimizing the activation process conditions. Activated carbons (ACs) have been played the leading role in electric double layer capacitors (EDLCs), due to their properties of large inner surface resulting in a huge specific capacitance, high pore accessibility, satisfactory conductance of the solid, acceptable electro-chemical window and stability of the charged capacitor etc[21-23].

In this work, we attempted to prepare activated carbon from phragmites by chemical activation with K_2CO_3, $ZnCl_2$, NaOH and H_3PO_4 and compared their adsorption capacity to each other. However, alkali hydroxides are hazardous, expensive and corrosive and $ZnCl_2$ is unfriendly the environment and create waste disposal problem. Thus, a more benign chemical is desired; K_2CO_3 is not a hazardous chemical and not deleterious as it is frequently used for food additives. The influences of the pore structure (methylene blue number, specific surface area, SEM, cyclic voltametery and impedance) were further examined.

Material and Methods

Adsorbate: Some carbon has mesopore structure which adsorbs medium size molecules such as dye methylene blue. MB was chosen in this study because of its known strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material. MB has a molecular weight of 373.9×10^{-3} (Kg/mol) that supplied by Merck. A stock solution of MB (1000 mg/L) was prepared and suitably diluted to the required initial concentration. A calibration curve of absorbance vs. concentration was constructed using a UV spectrophotometer (CECILL model: UV 5501) at maximum wavelength of 664 nm.

Activated carbon preparation: Stems of phragmites Australis were collected from babol lake, Iran. The precursor was first washed with distilled water to remove surface adhered dirt, filth and water soluble materials and then dried. The dried P. australis was crushed in a laboratory mill and sieved to obtain particles ranging 1 – 2 mm. The raw materials were subjected to four types of chemical activation: Chemical treatment followed by pyrolysis. The activation were carried out by using K_2CO_3, NaOH, $ZnCl_2$ and H_3PO_4 solutions, where part of the sample was soaked in K_2CO_3, NaOH, $ZnCl_2$ at impregnation ratio of

1:1, and the other in H_3PO_4 solution (28% concentration) for 24 h. After decantation, the samples were pyrolysed in a muffle furnace in steam atmosphere at 800°C for 30 min. Adsorbent obtained by chemical activation with K_2CO_3, $ZnCl_2$ and NaOH are termed activated carbon-1,2,3 (AC1), (AC2), (AC3), while those with 28% H_3PO_4 are termed activated carbon-4, (AC4). The activated product was then cooled to room temperature and washed with deionized water to remove remaining chemical. Generally, HCl 0.1 N was more efficient in removing Zn from the activated carbon than distilled water. Subsequently the samples were transferred to a beaker containing a 250 ml solution of hydrochloric acid (about 0.1 mol/L), stirred for 60 min, and then washed with hot deionized water until the pH of the washing solution reached 6 – 7 and dried at 120^0C. The final activated carbon products were ground and sieved to particle sizes of 125 µm before being employed in liquid-phase adsorption. Textural characterization was carried out by Scanning electron microscopy (Phillips X_l 130).

Adsorption studies: Batch adsorption experiments were carried out at room temperature (25°C). Exactly 50 mL of reactive dye solution of known initial concentration (100 – 400 mg/L) was shaken at the constant agitation speed (200 rpm) with a required dose of adsorbents (0.01 - 0.05 g) for a specific period of contact time (30 – 180 min) in a mechanical shaker, after noting down the initial pH of the solution to the optimum pH. The pH of the solutions was adjusted to the required value by adding either 1M HCl or 1M NaOH solution. After equilibrium, the final concentration (C_e) was measured. The percentage removal of dye and adsorption capacity (q_e) were calculated using the following relationship equations (1,2):

$$\% \text{ Re } moval = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

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

In this equation C_0 and C_e (mg/L) are the liquid-phase concentrations of dye initially and at equilibrium, respectively. V is the volume of the solution and W is the mass of dry adsorbent used (g).

Relationship between MB Adsorption and surface area: In order to further characterize the adsorptive nature of locally sorted activated carbon in technologically deficient laboratories, we utilize application of methylene blue adsorption to estimate surface area (S_{MB}) and activated carbon performance. Principles: The Langmuir equation was used to calculate the specific surface area of the adsorbents[24]. The general form of Langmuir isotherm is as equation (3):

$$Y = \frac{KC}{1 + KC} \quad (3)$$

In this equation Y is the fraction of adsorbent surface covered by adsorbed methylene blue molecules, K is a constant, and C is the equilibrium methylene blue solution concentration. In this research, equation (4): $Y = N / N_m$ (4)

In this equation N represents the number of moles of methylene blue adsorbed per gram adsorbent at equilibrium concentration, C, and N_m is the number of moles of methylene blue per gram of adsorbent required to form a monolayer. After making the substitution and rearranging equation (5), we obtain:

$$C / N = C / N_M + 1 / KN_M \quad (5)$$

The plot of C/N vs C for all adsorption isotherms of methylene blue gives a straight line with slope equal to $1/N_m$, and intercept equal to $1/KN_m$. Therefore, the Langmuir isotherm is an adequate description of the adsorption of the methylene blue onto adsorbents. The specific surface area was calculated by equation (6)[25]: $S_{MB} = (N_g \times a_{MB} \times N \times 10^{-20}) / M$ (6)

In this equation S_{MB} is the specific surface area in 10^{-3} (Km^2/Kg^{-1}), N_g is the amount of methylene blue adsorbed at the monolayer of adsorbents in (Kg/Kg). (In this research we defined experimental q_e as N_m, which is the amount methylene blue adsorbed at the monolayer of adsorbents in (mg/g) or 10^{-3} (Kg/Kg), a_{MB} is the occupied surface area of one molecule of methylene blue =197.2 Å² [26], N is Avogadro's number, 6.02×10^{23} (mol^{-1}); and M is the molecular weight of methylene blue, 373.9×10^{-3} (Kg/mol).

SEM: Morphologies of forms molded and carbonized were observed under scanning electron microscope (Philips XL30) before and after using of methylene blue. It is useful to determine the particle shape, porosity and appropriate size distribution of the adsorbent.

Results and Discussion

Investigation of adsorption parameters: Effect of initial concentration of dye: The effect of initial concentration of dye on the removal of MB dye (in terms of percentage removal) on various adsorbents was studied as shown in figure 1. The percentage removal of the dye was found to decrease with the increase in initial dye concentration. This indicates that there exist reductions in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of methylene blue (MB). Similar results have been reported in literature[27]. The results show that the percentage removal of dye decreases from 76 to 34, 44 to 18, 60 to 19 and 40 to 16 as the initial dye concentration increases from 100 up to 400 ppm for 0.03 g/L of AC1, AC2, AC3 and AC4 respectively.

Effect of dose of adsorbent: The effect of dose of adsorbent on the percentage removal of MB dye is shown in figure 2. The percentage removal of MB increased with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent[27,28].

Effect of contact time: The effect of contact time on the percentage removal of MB dye was investigated at initial dye concentration (100 - 400 mg/L) as shown in figure 3, the percentage removal of dye by different mass of activated carbon was rapid in the beginning but it gradually decreased with time until it reached equilibrium. The pattern of graphs was almost same for different dye concentrations. The plots reveal that

maximum percent removal of the dye after about 120 min of shaking. The rate of removal is higher in the beginning due to larger surface area available of adsorbent. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles.

Effect of pH: The effect of initial pH of dye solution on the percentage removal of MB was studied by varying the initial pH under constant process parameters. The results are shown in figure 4. The pH of the solution increase as the dye adsorbed increases considerably. The optimum pH was attained at pH of 6-7.

Adsorption isotherms: In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations for the equilibrium data for each system. Two isotherm models have been tested in the present study; Langmuir and Freundlich models. The applicability of the isotherm equations is compared by judging the correlation coefficient, R^2.

Langmuir model: Langmuir theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorbed layer was unimolecular. The theory can be represented by the following linear form equation (7):

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (7)$$

In this equation C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plots of C_e/q_e vs C_e show that the adsorption obeys Langmuir isotherm model for all adsorbents. The values of Q_0 and b were determined for all adsorbents from intercept and slopes of the linear plots of C_e/q_e vs C_e (table 1). The good fit of the experimental data and the correlation coefficients (R^2) higher than 0.94 indicated the applicability of the Langmuir isotherm model. The essential characteristics of Langmuir dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by the following equation, equation (8):[29]

$$R_L = \frac{1}{1 + bc_o} \quad (8)$$

In this equation C_0 is the initial dye concentration, (mg/L). The value of separation factor R_L, indicates the nature of the adsorption process as given below: i. For favorable sorption 1 $>R_L >0$, ii. For unfavorable sorption $R_L >1$, iii. For linear sorption $R_L = 1$, iv. For irreversible sorption $R_L = 0$.

In the present study, the values of R_L (table 2) are observed to be in the range 0 – 1, indicating that the adsorption process is favorable for all types of prepared activated carbons.

Freundlich Isotherm: Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage[29]. The well-known logarithmic form of the Freundlich isotherm is given by the following equation, equation (9):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_F and n are Freundlich constants with n giving an indication of how favourable the adsorption process. K_F ([mg/L]$^{1/n}$) is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero[30]. A value for $1/n$ below one indicates a normal freundlich isotherm while $1/n$ above one is indicative of cooperative adsorption[31]. A plot of log (q_e) vs log (C_e) is shown in figure 6, where the values of K_F and $1/n$ are determined from the intercept and slope of the linear regressions (table 1).

SEM analyses: SEM images of the raw phragmites figure 5(a) the surface is relatively organized without any pores except for some occasional cracks and its char as well as some selected activated carbon (AC1) are shown in figure 5(b). Hydrolysis at 800 °C for 30 min produced a char with undulating surface. It is also noticed that there is a clear shrinkage and disintegration of the big grains to small ones after carbonization. The SEM images of the activated carbons show that the external surfaces for these carbons are full of cavities and quite irregular as a result of activation. It appears that there are many macropores of width > 250 nm that might be ink-bottle shaped on the surface of this carbon, indicating the aggressive attack of the reagent with the phragmires during impregnation. Those pores resulted from the evaporation of the chemical reagent (K_2CO_3) during carbonization, leaving the space previously occupied by the reagents. It is clear that, activated carbon appears to have numbers of pores where, there is a good possibility for dye to be trapped and adsorbed into these pores. Better information may be obtained from the image of MB are also observed on the surface or inside the pores of the AC1 figure 5(c).

Table-1
Langmuir and Freundlich Adsorption Constants for Different Adsorbent Materials

Dye concentration	The value of R_L			
	AC1	**AC2**	**AC3**	**AC4**
100	0.3333	0.5000	0.0625	0.0434
200	0.2000	0.3333	0.0322	0.0222
300	0.1428	0.2500	0.0217	0.0149
400	0.1111	0.2000	0.0163	0.0112

Table-2
Separation Parameter, (R_L) at Different Initial Dye Concentration

Adsorbent	Langmuir constants			Freundlich constants		
	Q_0 (mg/g)	B (L/g)	R^2	K_F	1/n	R^2
AC1	153	0.02	0.982	2.54	0.91	0.934
AC2	80	0.01	0.970	15.41	0.25	0.913
AC3	74	0.15	0.926	46.23	0.07	0.179
AC4	54	0.22	0.982	24	0.14	0.423

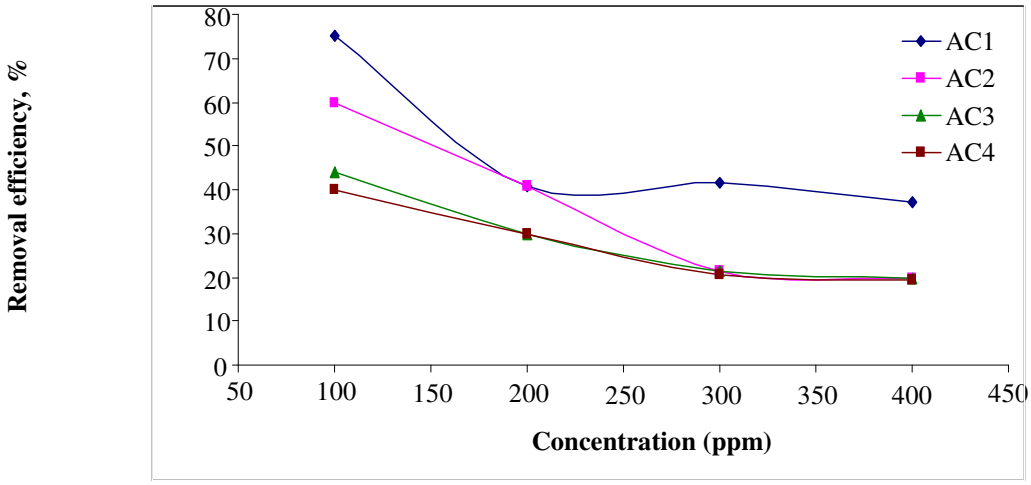

Figure-1
Effect of Adsorbent Concentration on Dye Removal at pH = 7 Contacted with 0.03 g/50mL of Different Adsorbents for 30 min

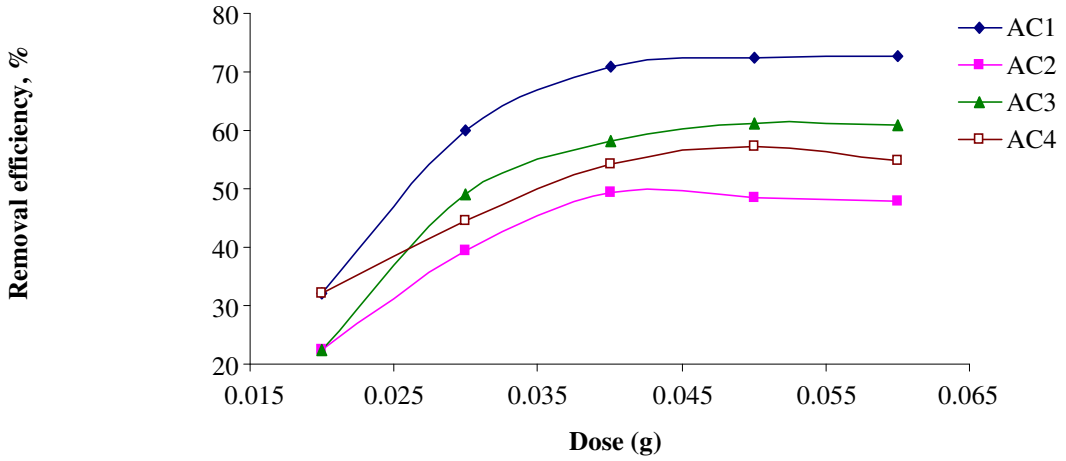

Figure-2
Effect of Dose of Adsorbent on the Removal of Dye at pH =7, C_0 = 50 mg L^{-1}, and Contact time = 30 min

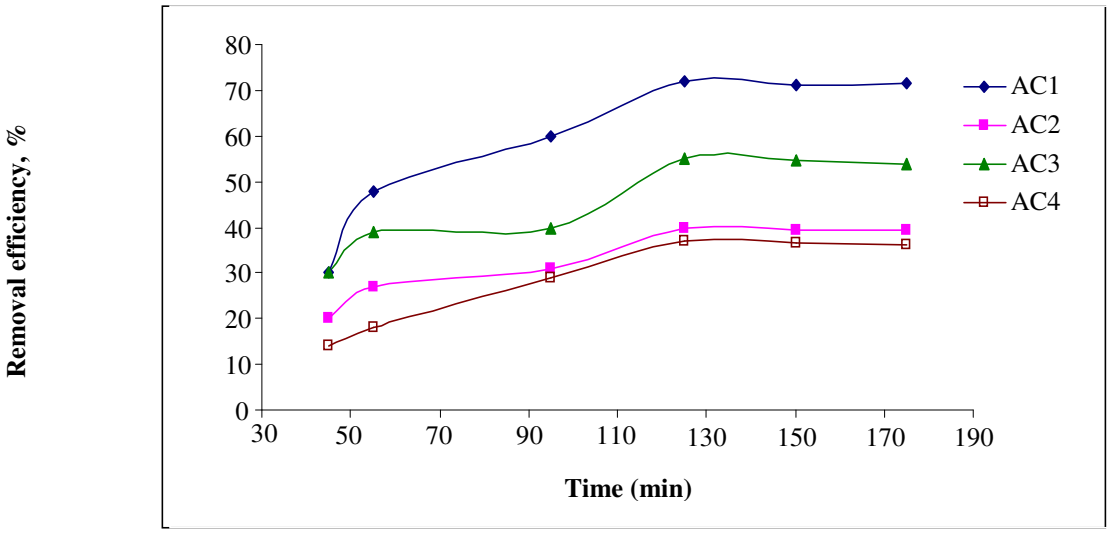

Figure-3
Effect of Contact Time on the Removal of MB Dye by Different ACs at pH =7, Dose of Adsorbent 0.03 g/50mL and at Different Dye Concentration 20-50 (mg/L)

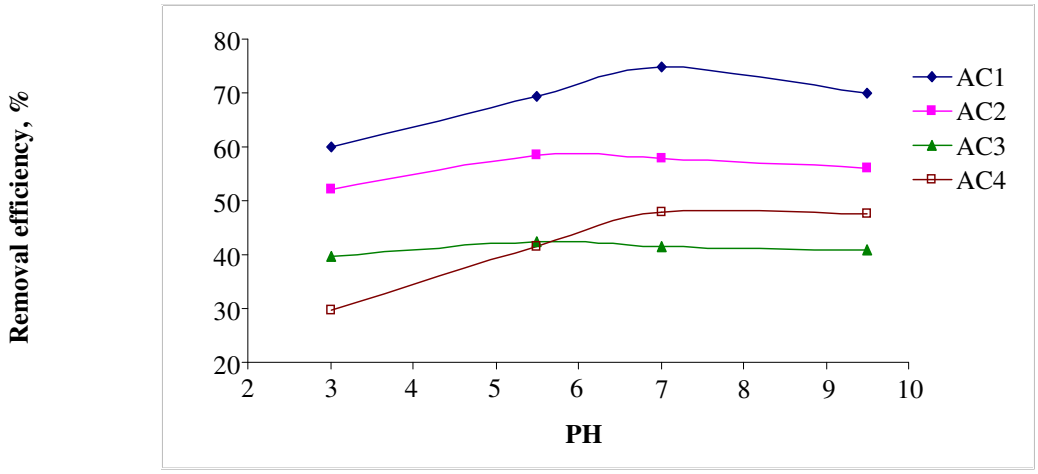

Figure-4
Effect of the Different pH on the Removal of MB Dye from Different Adsorbents Using 50 (mg/L) MB Dye Concentration, 2 Contact Hours and 0.03 g/50mL of Adsorbent

(a) **(b)** **(c)**

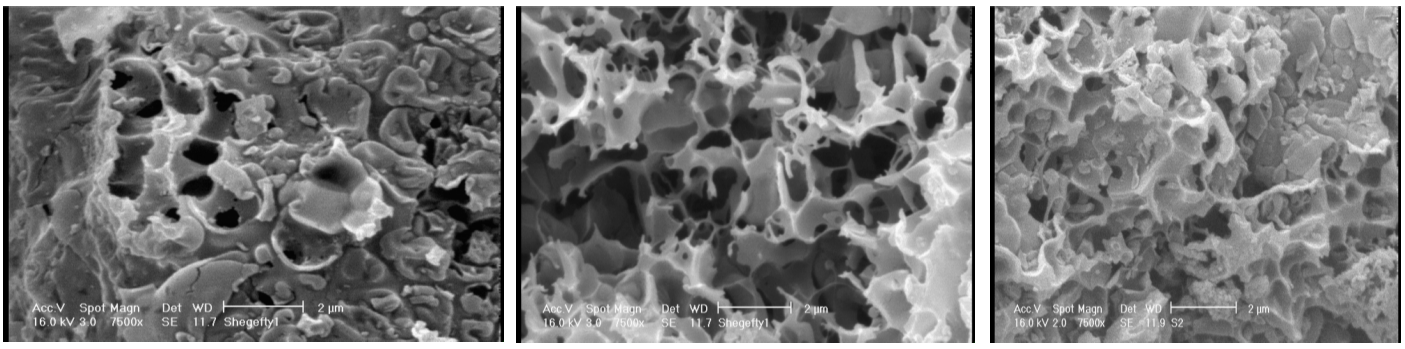

Figure-5
Scanning Electron Micrographs of (a) Raw Phragmites, (b) AC1 before Dye sorption and (c) with Dye Adsorbed

Conclusion

The results of the present work have shown that $ZnCl_2$ and H_3PO_4, which are acidic, are less effective in creating porosity than K_2CO_3 and NaOH, indicating that an acidic reagent is not suitable for preparing high porosity carbons from phragmites. The pore size is crucial for the ions to penetrate into pores for methylene blue. Langmuir isotherm models given were fitting better than Freundlich isotherm interpreting the adsorption phenomenon of MB. Therefore, AC1 can be used as a highly effective low-cost adsorbent for the removal of cationic dyes. The impedance spectra and cyclic voltametery of the AC1 exhibited the behavior for typical porous carbon electrodes of electrochemical capacitor. The presence of porosity can enhance utilization of the exposed surface for charge separation and provides low resistant pathways for the ions through the porous particles.

Generally, this research showed that the higher the methylene blue with a corresponding high surface area, high degree of activation, and expected sorption effectiveness in removal of small sized sorbates.

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