Characterization and isotherm study of activated carbon production from mustard stalk by ZnCl$_2$ activation

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In the present study mustard stalk is used for production of activated carbon with potential application in removal of methylene blue dye in its aqueous phase prepared by chemical activation route using ZnCl$_2$. Mustard stalk activated carbon (MSAC) was prepared at an activation temperature of 650°C and using an impregnation ratio of 2.0 for 1.5 h of activation time. Different parameter such as initial methylene blue concentration, agitation time, pH and dosage of activated carbon were used for conducting adsorption studies in batch mode. MSAC was characterized using FESEM (field emission scanning electronic microscope) with EDX (energy dispersive X-ray spectrometer), and Brunauer-Emmelt-Teller (BET). The best fitted adsorption data was obtained by Langmuir isotherm model with an equilibrium adsorption capacity of 190.90 mg/g. BET surface area and total pore volume of MSAC were found to be 406 m^2/g and 0.328 cm^3/g, respectively.

Keywords: Adsorption, activated carbon, isotherm, ZnCl$_2$, mustard stalk.

Introduction

Activated carbon is a carbonaceous material which is black solid in appearance and bears a close resemblance with powdered or granular charcoal. Some of its important physical properties include high porosity which manifests itself in form of large internal surface area and sufficiently high mechanical strength. It finds widespread applications as adsorbents in treatment of domestic and industrial wastewater, purification of gases and as catalyst or catalyst supports[1]. Although activated carbon is widely used in industries, its high cost is a matter of concern with users, as result in recent times a lot of focus is shifted on development of low-cost alternatives to activated carbon.

The two main sources used practically for obtaining activated carbon of commercial grade are coal and lignocellulose rich agricultural residues. Among these two sources, agricultural wastes hold promise as it serves twin benefit of saving coal/coke which is still widely used as solid fuel in many parts of world and also in mitigating environmental pollution by successfully utilizing the agricultural waste generated in billions of kilograms annually. Some of the surplus agriculture residues which can be used in adsorbent produc-

tion include coconut shells[2], bagasse[3], oil palm waste[4], and rice husk[5]. Although many researchers have studied application of untreated or raw agricultural residues as adsorbents however its established scientific fact that activation could significantly augment adsorption capacity of them. Activated carbon manufacture is a two-step process in which carbonization precedes activation. The aim of carbonization is to increase the carbon content along with creation of initial porosity, while activation process improves the pore structure with further enhancement of porosity. High quality and reasonably priced activated carbon is still non available in Indian market and to meet demand from specialty chemical and other uses it is being imported. It is possible to obtain high-grade activated carbon from mustard crop residue mainly available in form of Mustard stalk (MS) which is available in abundance in India, since India is a prominent mustard cultivation country and annual production of mustard in India is 6.8 million tonnes[6]. After processing of one ton of the mustard seed, 1.8 tons of MS are generated[7]. A large amount of MS is either burnt loosely in rural areas for meeting energy needs or in manufacture of briquettes. Utilizing MS in preparing activated carbon will convert this waste which is

not even consumed as fodder, into a value-added product. MS due to its high carbon (40%) and low ash content can thus act as a good adsorbent.

The present study is focused on dye loaded wastewater which is generated in significant amount from textile and other units. Disposal of dye even in low concentrations into natural streams, rivers and other water bodies increases the toxicity as it is found to be carcinogenic and mutagenic to aquatic organisms[8]. Methylene blue (MB) is one of the most commonly used dye in industries. Most of the dye removal methods such as reduction, chemical precipitation, evaporation, solvent extraction, adsorption, ion exchange, filtration, and oxidation, are expensive for low dye concentrations and require the use of large reagent quantity and energy[9]. Among above mentioned methods, adsorption is an efficient method for dye removal. For carrying out large scale adsorption commercially available AC is costly rendering it economic unviable in waste water treatment. Thus, development of new and inexpensive adsorbents for MB removal from industrial effluent is need of hour. Recently, several low-cost adsorbents such as agro-waste and industrial by-products are used as AC precursor for the dye solution treatment. In general bio adsorbent is an amorphous form of carbon characterized by pores with small volume which leads to a significant increase in available surface area to support adsorption, or chemical reactions[10]. Among various biomass residues available, MS is an attractive alternative material that is widely available in many countries.

Activated carbon can be obtained either by chemical activation or physical activation routes. However chemical activation offers dual advantage of being carried out at lower temperature and offering higher yield. Literature abound with extensive work on the production and quality of activated carbon using different chemical reagents[11,12]. Among these $ZnCl_2$ have properties like being easily vaporized and undergo decomposition at about 400°C, leading the carbon matrix to lose its protection and burn out quickly[1] also the initial reaction temperature of $ZnCl_2$ is lower than that of other commonly used agent namely H_3PO_4, due to this activation response of $ZnCl_2$ is faster. Thus $ZnCl_2$ is faster chosen in present study. Published work is available in which chemical activation with $ZnCl_2$ is done for production of activated car-

bon from cherry stones[14], paper mill sludge[15], and pistachio-nut shell[16]. Another advantage of chemical activation by $ZnCl_2$ is that it leads to efficient pore development in the carbon structure along with improved yields of carbon. Also mesoporous material is needed for adsorption of larger molecules such as dyes[17]. These conditions help in meeting requirements of both producer and end users of product as higher yield at expense of lower energy and operating cost is always a desirable situation.

Currently, no study is available in literature on the production of MSAC for dye removal from wastewater. In the present study, MS was used a base carbonaceous material for preparing activated carbon using chemical activation with $ZnCl_2$. For prepared MSAC parameters like pore sizes, specific surface areas, and pore volumes were determined. Also isotherm and equilibrium were studied.

Material and methods:

Materials:

The MS was procured from a village near Jaipur in Rajasthan state of India. The collected stalk was cut into smaller pieces for fast drying. Zinc chloride ($ZnCl_2$) (analytical grade) used for the chemical activation was procured from Merck (India) Ltd. The ultimate and proximate analysis of MS is given in Table 1. The physio-chemical property of adsorbate viz. MB used in present study is given in Table 2.
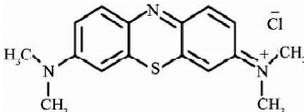
Table 1. Proximate and ultimate analyses of MS

Proximate analysis (as received wt %)		Ultimate analysis	
Moisture	9.58	C	39.71
Volatile	71.92	H	5.87
Fixed carbon	12.65	O	0.68
Ash content	4.41	N	42.48
		Calorific value (MJ/kg)	16.949

Preparation of the activated carbons:

Activation process for obtaining MSAC was carried out in following steps: (i) MS and $ZnCl_2$ solution were mixed well and kept for 24 h. (ii) Mixture of MS and $ZnCl_2$ solution was overnight dried at 105°C in oven to obtain impregnated sample. (iii) Impregnated sample were taken into crucible and put into furnace for carbonization at 650°C for 1.5 h.

Table 2. The physio-chemical property of adsorbate

Adsorbate	Chemical structure	Mol. wt. (g mol^{-1})	λ_{max} (nm)	Ref.
MB ($C_{16}H_{18}ClN_3S$)		319.85	664	18

(iv) The crucibles were left in the furnace for 24 h to cool down at room temperature. The carbonized MS sample activated by $ZnCl_2$ was subjected to washing using hot and cold distilled water until the pH value reached 7.0. After that, it was dried in a oven at 105°C for overnight followed by weighing and packing in sealable plastic bags for further use.

Characterization of the MSAC:

MS and MSAC were characterized by FESEM with EDX (Nova Nano FE-SEM 450 (FEI) available at MRC lab, MNIT Jaipur). SEM and EDS were used for the morphological and elemental analysis of adsorbents. The specific surface area of the MSAC was determined by N_2 adsorption (at 77 K), using a BET surface area analyzer (St 1 on NOVA touch 1LX).

Equilibrium and isotherms studies:

To ascertain the effects of pH, MSAC dose, initial dye concentration experiments were conducted and adsorption isotherms were constructed. Fixed amount of adsorbent (0.04 g) was mixed with 100 mL aqueous MB dye solutions with concentration ranging from 10–30 mg/L in 250 mL stoppered glass (Erlenmeyer flasks) to obtain adsorption equilibrium. Mixture was subjected to agitation at 160 rpm for 180 min. After that dye solution (paced in a centrifuge tube) was centrifuged for 15 min at 3000 rpm due to which the char particle settles at the bottom of the tube. UV spectro-photometer was used for obtaining concentration of MB solution. Removal percentage (R) of MB dye by the adsorbents and the amount of MB adsorbed at equilibrium, q_e (mg/g) was calculated by the following eqs. (1) and (2) respectively,

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_e} \times 100 \qquad (1)$$

$$q_e = \frac{(C_o - C_e)V}{C_W} \qquad (2)$$

where C_o and C_e (mg/L): concentrations of MB dye solution at initial and equilibrium state, V (L): volume of the MB dyes solution, and W (g): weight of adsorbent.

Results and discussion

Characterization of sample:

FESEM-EDX analysis:

Chemical composition of MSAC determined using FESEM with EDX is shown in Fig. 1 form which it is evident that activation significantly enhances carbon content of MSAC as compared to raw MS. This can be attributed to the fact that during activation and pyrolysis processes, the MS decompose leading to increase in carbon content. In Fig. 1 depicting MSAC elemental composition, the C and O peaks are seen. The maximum value of carbon (80.84%) has been shown in results. From Fig. 1(b), it is clearly seen that in MSAC obtained by $ZnCl_2$ activation, no Zn is present due to the washing with 0.5 N HCl leading to complete removal and release of Zn from closed pore to open pores. Thus it can be inferred that for obtaining high carbon content $ZnCl_2$ is a suitable dehydrating agent. Fig. 1(a) present FESEM image of the MS in which some fibrous, flat and irregular long flakes are visible on the surface of MS. SEM images showed no pores on MS morphology.

Chemical activation of MS leading to formation of MSAC shows more distributed pores (Fig. 1(b)), which are a result of cellular structure modification due to $ZnCl_2$ activation.

BET analysis:

BET analysis of MSAC is presented in Table 3 from which it can be seen that the porous structure and surface area MSAC increases in comparison to raw MS when subjected to $ZnCl_2$ activation along with carbonization. Surface area of MSAC is found to be 406 m^2/g. Formation of mesopores and deformation of macropores with the $ZnCl_2$ effect is the reason behind increase in the average pore radius and pore volumes.
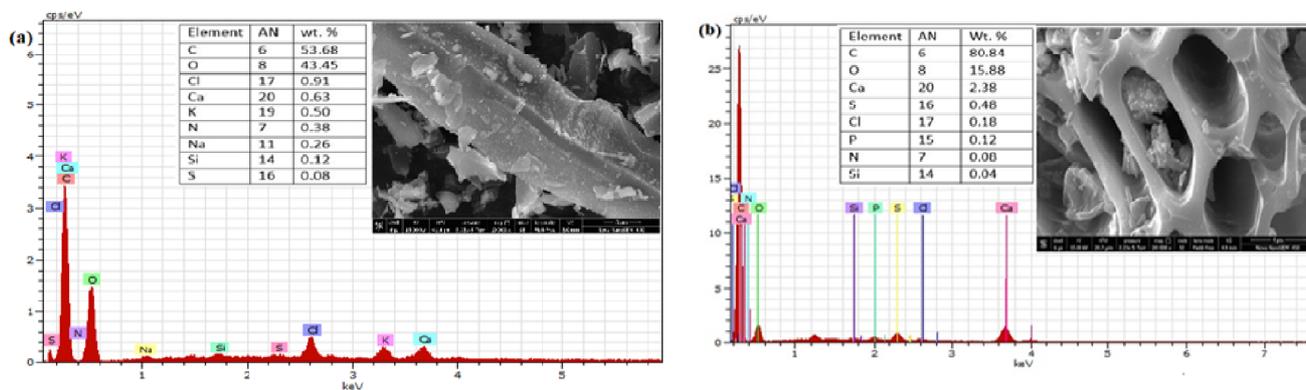
Fig. 1. FESEM image of: (a) MS and (b) MSAC prepared with ZnCl$_2$ activation.

Table 3. The BET surface areas, total pore volumes and average pore radius of the MSAC and raw MS

	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore radius (Å)
MS	95	0.081	13.2
MSAC	406	0.32	15.77

Effect of different parameter on MB adsorption:

Effect of adsorbent dose:

Adsorption of MB on MSAC dosage in batch mode was studied and the % removal of MB was found to vary linearly with the dosage of the MSAC (Fig. 2(a). MSAC dosage range was taken from 0.01 to 0.06 g/100 mL of aqueous MB and agitation time upto 180 min. Fig. 2(a), shows that % removal increases as the MSAC dosage increases up to 0.04 g and afterwards no significant effect on % removal is seen. There-

fore, a dose of 0.04 g of MSAC was taken as an optimum value for achieving better adsorption of MB.

Effect of initial concentration of MB:

In batch mode, for effect of C_o of MB in range of 10–25 mg/L was studied at optimal 0.04 g MSAC dosage, agitation time (180 min). Fig. 2(b) the effect of C_o of MB on the adsorption capacity of MSAC. Also graph shows that an increase in agitation time leads to an increased MB adsorption on MSAC. A increase in C_o of MB from 10 to 25 mg/L leads to a decrease in equilibrium percentage removal of MB from 99.65 to 87.3%. This variation is attributed to higher MB adsorption due to presence of larger mass transfer driving force. Adsorption of MB on tea waste[19] also shows same trends.

Effect of pH:

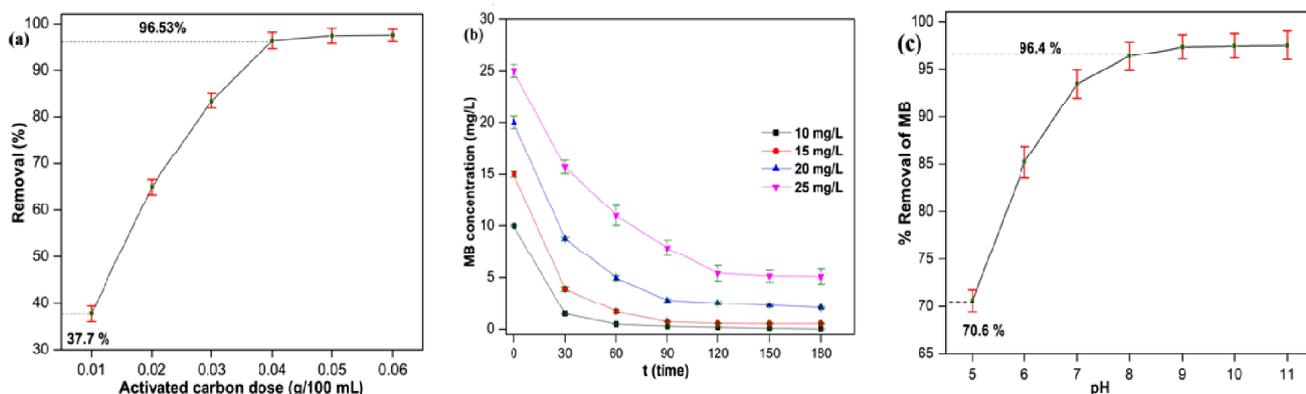Another important factor for study of adsorption of MB on

Fig. 2. (a) Effect of MSAC dosage on removal of MB (contact time (t) = 180 min, C_o = 10 mg/L, temperature = 30°C, pH = 8.0). (b) Effect of contact time and initial concentration on MB adsorption (contact time (t) = 180 min, adsorbent dose = 0.04 g, temperature = 30°C, pH = 8.0). (c) Effect of pH on MB removal (C_o = 10 mg/L, adsorbent dose = 0.04 g, contact time (t) = 180 min, temperature = 30°C).
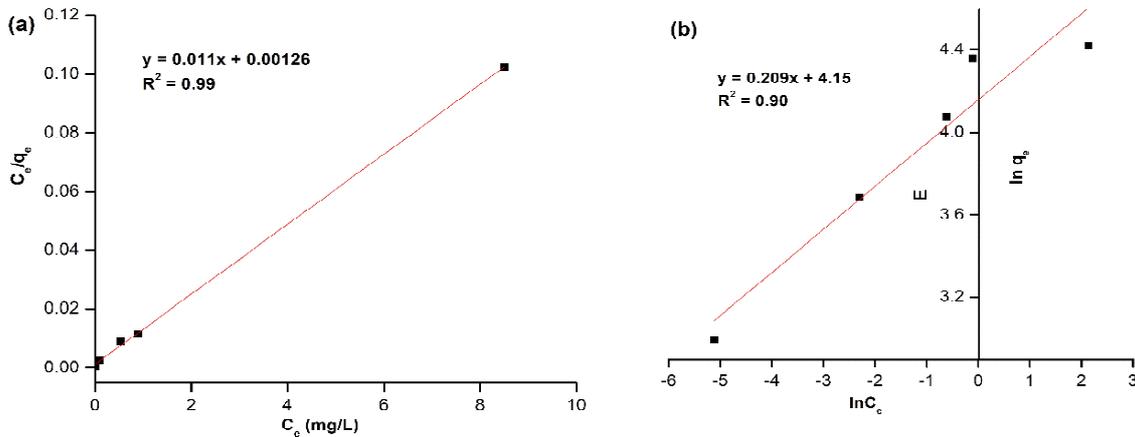
Fig. 3. (a) Linearized Langmuir isotherm for MB adsorption by MSAC, (b) linearized Freundlich isotherm for methylene MB adsorption by MSAC.

the adsorbent is pH. Effect of pH on % MB using MSAC is presented in Fig. 2(c). The removal percentage of MB increased from 70.6% at pH 5 to 96.4% at pH 8. The percentage removal of MB increases slowly upto pH 8 and then equilibrium is reached. Maximum percentage removal (97.55%) of MB appeared in the pH range of 9–11. This is due to the fact that adsorption depends on adsorbent surface and structure of MB[20]. When the pH rise the dye becomes more and more de-protonated because the MB dye is in acidic medium. Low pH range, inhibits percentage removal of MB due to the possibility of occurring positive charge at the surface of MSAC[21]. However, beyond pH 8 when the medium becomes basic in nature there seems to be a significant change in polarity as color removal increases (solution becomes light blue) monotonically with pH. Thus a low pH (<6) is unfavourable for MB color removal by MSAC.

Adsorption isotherm:

Adsorption isotherm at equilibrium state gives distribution of adsorbed molecules between liquid and solid phase. In present work Langmuir, and Freundlich adoption isotherm models were used. Results of MB adsorption study using these models are given in Table 4.

Table 4. Langmuir and Freundlich isotherm constant for MB dye on MSAC

Langmuir isotherm			Freundlich isotherm		
Q_m (mg/g)	K (L/mg)	R^2	$1/n$	K_f (mg/g)(L/mg)$^{1/n}$	R^2
190.90	8.73	0.999	0.209	63.43	0.90

The Langmuir isotherm model is valid for monolayer and homogeneous sites with a uniform distribution of energy level within the adsorbent surface. The Langmuir isotherm is given by linear equation represented by the following equation (eq. (3))[22],

$$\frac{C_e}{q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \tag{3}$$

where q_e: amount of dye adsorbed at the equilibrium time in mg/g. C_e: equilibrium concentration of MB in mg/L. Q_m: maximum adsorption capacity corresponding to complete monolayer coverage in mg/g. K: Langmuir constant related to energy of the adsorption in L/mg. Slope ($1/Q_m$) and intercept ($1/Q_m K$) of straight line is obtained (Fig. 3a), which shows that the adsorption of MB follows Langmuir isotherm model.

The Langmuir isotherm model indicates the best fitting of MB adsorption data on homogeneous nature of MSAC, which means that each dye molecule/MSAC adsorption has equal adsorption activation energy; the results also points towards existence of monolayer coverage of MB dye molecule over outer surface of prepared MSAC. Rice husk biochar activated carbon[23] also show similar trends during dye adsorption studies. Values of slope (Q_m) and intercept (K) calculated from linear plot are given in Table 4.

The Freundlich isotherm[24] as opposed to Langmuir is valid where heterogeneous and non-ideal adsorption sites are present on the adsorbent surface. Mathematically it expression for it is:

Table 5. Adsorption capacity of other biomass based activated carbon prepared using $ZnCl_2$

Material	Dye, isotherm model	Adsorption capacity(mg/g)	Ref.
MSAC	Methylene blue, Langmuir isotherm	190.90	In present study
Coffee husks	Methylene blue, Langmuir isotherm	263	25
Buriti shells	Methylene blue, Langmuir isotherm	274.62	26
Macadamia nut endocarp	Methylene blue, Langmuir isotherm	194.7	27
Sunflower seed husk	Methylene blue, Langmuir isotherm	240	28

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where K_f $((mg/g)(L/mg)^{1/n})$: Freundlich constant related to adsorption capacity. $1/n$: dimensionless heterogeneity factor.

Linear form of eq. (4) is obtained by taking the logarithmic of both sides which gives:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (5)$$

The above equation corresponds to a equation of straight line and gives a linear plot between $\ln q_e - \ln C_e$, this establishes validity of the Freundlich model and same is shown in Fig. 3(b). Obtained value of n (4.78) > 1 and this indicates a favorable condition for adsorption of MB onto the MSAC.

The R^2 values of Langmuir and Freundlich is 0.99 and 0.90 respectively shown in Table 4. So in present study Langmuir model better depicts monolayer adsorption of MB on the surface of MSAC. Also MSAC adsorption capacity is comparable to the activated carbon produced from other biomass feedstock using $ZnCl_2$ activation as shown in Table 5.

Conclusion

From the present work it can be concluded that, MSAC possessing a high surface area with a large pore structure can be easily produced by chemical activation with $ZnCl_2$ which can be used as a suitable adsorbent for efficient removal of MB from aqueous solution. For obtaining high % removal of MB using MSAC, optimum pH of 8 should be maintained around which 97.55% removal is achieved at a MB concentration of 10 mg/L for a 180 min study. The characterization results showed that the BET surface area and total pore volume of the activated carbon prepared under the optimum conditions were 406 m^2/g, 0.32 cm^3/g respectively, and also it has high carbon content (80.84%) along with highly porous surface with cracks, channels and large holes. The equilibrium data were analyzed using Langmuir and Freundlich isotherms of which Langmuir model gives better data fit as it has higher R^2 value of 0.99. The maximum adsorption capacity was found to be 190.90 mg/g.

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