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Dried ridge gourd: An excellent source for ecofriendly activated carbon

Kashinath Barik*[,1], PallishreePrusti[2] & Soumya S Mohapatra[3]
[1]Department of Chemical Engineering, Indira Gandhi Institute of Technology Sarang, Odisha 759 146, India
[2]Mineral Processing Department, CSIR-Institute of Minerals and Materials Technology Bhubaneswar, Odisha 751 013, India
[3]Department of Chemical Engineering, National Institute of Technology Rourkela, Odisha 769 008, India
E-mail: kashinath.009@gmail.com

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In the current work, the activated carbon has been prepared from a resource which is considered as the waste and ecofriendly. In addition to above, the used raw material also does not contain the polluting element such as Sulphur or any others. The activated carbon prepared from dried ridge gourd (scrubbing sponge-luffa) by chemical activation methods mitigates the above stated requirements. For the characterization of prepared activated carbon and also determination of the efficiency of the activated carbon as an adsorbents, various types of characterization methods such as BET surface area analysis, morphology verification by SEM, EDX and FT-IR, and Methylene Blue separation experimentation are performed, respectively. The BET SSA is found to be 1221.57 m^2g^{-1}, which is comparable with the values reported in literature. The characterization clearly reveals the structure is very similar to honey comb pattern and identified micro pore volume is 0.407 cm^3g^{-1}. The removal efficiency of Methylene Blue (MB) by activated carbon (adsorbent) ensures its suitability for the separations and it seems that the experimental data are concurred with Langmuir isotherm of monolayer adsorption. The whole adsorption process is divided into three different regimes on the basis of their controlling parameters, which makes easy to select the appropriate operating zone for a process.

Keywords: Activated carbon, Chemical activation, Honey comb pattern, Monolayer adsorption

Activated carbon (AC) preparation has been an interesting area of research due to its wide applications. It has high porosity and very large surface area per unit volume and these characteristics favours for adsorption and chemical reactions to take place. AC is used for both industrial purpose and along with residential use and these applications include treatment of water purification, power plant and landfill gas emissions, and heavy metal adsorption. It can also be applied for air purification to remove volatile organic compounds, and colour and odour control. Activated carbon shows novel characteristics in the area of adsorption for fluoride/MB removal by impregnated with foreign metal ions ($Al^{3+}/Fe^{3+}/Fe^{2+}$) by allowing these ions deposition into its surface and inside the pores[1]. In addition to that the demands of activated carbon derived from biomass waste have been attracting the field of catalysis/electro catalysis, energy storage in capacitors, Li-ion batteries, CO_2 capture and H_2 storage[2,3].

Activated carbon is produced from carbonaceous resources like coal, petroleum coke, wood production, nutshells, and some agricultural products such as rice husk, apple pulp, and sugar cane bagasse by physical activation, chemical activation or physicochemical activation process. Preparation of the activated carbon from waste biodegradable material is more attractive to the current generation researchers due to the following reason: (1) It produces reliance as raw material, (2) decrease the production cost, and (3) environmental issue need not to be addressed as it is free from the above[4]. Therefore, in the current work, an attempt has been made to produce activated carbon from a waste biological resource. The activated carbon can also be prepared from organic materials waste plastics and tires[5,6]. However, although the waste management is done by considering these as the raw material, during and after preparation, environmental problems are monitored when it produces in a bulk quantity. Activated carbon preparation includes two stage of operation: carbonization and activation, and which can be achieved physically or chemically[7]. Raw sample will be first carbonized followed by activation step by steam or CO_2 or a combination of both in physical treatment process, whereas, in chemical treatment process, raw sample is impregnated by a chemical activating reagent and followed by heating process under an inert atmosphere[8].

Chemical activation methods have numerous benefits, as it is working in a single step by combining carbonization and activation, along with it can be executed at lower temperatures and therefore produces a better structure[9]. The chemical used in this method is usually a salt, an acid or a strong base[10]. This method involves impregnation of the raw sample with a chemical agent such as H_3PO_4, $ZnCl_2$, NaOH, KOH, etc. and then activated at a high temperature. The chemical activation method is always beneficial for making very high surface area AC[11-13]. It has been observed for the preparation of AC that among the several dehydrating agents, $ZnCl_2$ is the most extensively used chemical agent studied by many authors[14-17].

From the literature survey, it is found that although a lot of agro-wastes have been used as a source material for activated carbon preparation; a dried ridge gourd, which does not contain any polluting material have not been used. Therefore, in the current work, activated carbon is prepared from dried ridge gourd by using chemical activation method. Ridge gourd (scientific name-Luffa) is a genus of tropical and sub-tropical vines in the cucumber family. When the fruit of these species is fully ripened, it is very fibrous. This fibrous fruit can be considered as the basis of raw material as it is available in plenty of amount and at very low cost also.

The objective of this study is to prepare comparatively highly porous activated carbon from ridge gourd by chemical activation method. The products were examined by different characterization technique such as Scanning Electronic Microscope (SEM), Fourier Transfer Infrared Spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy (EDX) and physical properties from Ultimate and Proximate analysis and BET surface area. In addition to the above, the efficiency of the prepared adsorbent has also been experimented.

Experimental Section

Dried ridge gourd was collected from eastern part of Odisha, India. Thereafter, the washing was performed. Then cleaned ridge gourds were dried in sunlight for 15-20 days. Dried materials were kept inside a furnace for 24 h at 150°C for removal of moisture and other volatile impurities. Dried ridge gourd were crushed and sieved to 300-700 µm size range. The powdered precursor was impregnated with chemical activating agent $ZnCl_2$. In this regard, 500 gm dried ridge gourd powder was well mixed with 1.23 molar $ZnCl_2$ solution[16]. For this work, $ZnCl_2$ was used as it has characteristics of good chemical activating capacity and reduces the carbonization temperature. In addition to the above, it can also restrict the tar formation and supports carbon charring[18].

Figure 1 illustrates the schematic for the preparation of activated carbon. The slurry mixture was properly mixed and kept for 24 h for proper soaking in $ZnCl_2$. Then the mixture was heated in an electric oven at 100°C for 24 h. The resulted chemical impregnated samples were kept inside the muffle furnace and heated at a heating rate of 10°C min^{-1} till the temperature rises from room temperature to 650°C and at this temperature**,** the sample was hold for 2 hours in an inert atmosphere. To attain this, a constant flow rate (3 cm^3s^{-1}) of Argon was maintained

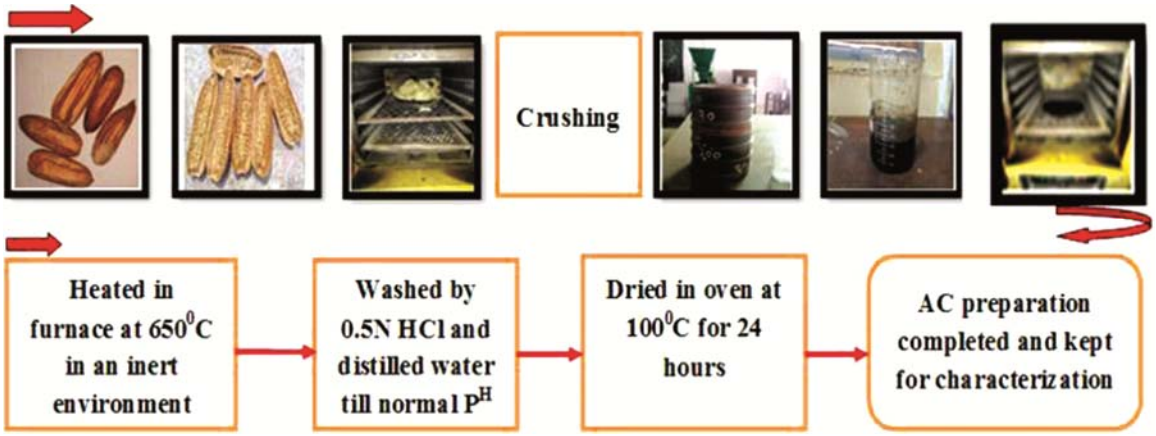

Fig. 1 — Schematic illustration of activated carbon preparation from ridge gourd.

from the beginning of heating process and it was continued till the sample reaches its initial temperature. The dried materials were initially washed with 0.5 N HCl for 2-3 times and then by distilled water washed to remove different residual organic and mineral matter. Finally the sample was washed with normal water until the washed solution does not depict neutral condition. Thereafter, the washed sample was dried for 24 h at 100°C inside in an oven and packed in a desiccator for further characterization process.

Results and Discussion

After washing, pyrolysis and drying, the samples were characterized to identify the various nature of AC. The analysis include, proximate analysis, ultimate analysis, BET surface area measurement, surface morphology verification and mechanism of adsorption process.

The proximate analysis result is presented in Table 1. It is observed that the fixed carbon percentage in activated carbon is almost thrice that of raw precursor, which indicates its affinity for adsorption. Furthermore it also shows that the moisture percentage, volatile matter content, and ash content percentage decline in activated carbon. From this analysis it can be concluded that the prepared material can be used as a source material for activated carbon.

For further verification, ultimate analysis was performed. The result of ultimate analysis is presented in Table 2. It shows that the carbon content of AC increases from 43.06% to 73.18% due to the reduction in oxygen and other volatile content from the total calculation. In addition to the above, the occurrence of high degree of affinity is also considered one factor at high temperature[19]. The decrement in hydrogen and nitrogen values are observed because of the activating agent $ZnCl_2$ helps in the removal of H and O from ridge gourd sample as H_2O and H_2.

Table 1 — Proximate analysis of raw precursor and activated carbon

Sample	Moisture (wt.%)	Volatile matter (wt.%)	Fixed carbon* (wt.%)	Ash (wt.%)
Raw precursor	5.53	43.41	44.34	6.72
Activated carbon	2.23	14.67	79.89	3.01

*From difference

Table 2 — Ultimate analysis of raw precursor and activated carbon

Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O* (wt.%)
Raw precursor	43.06	6.08	1.21	0.11	49.5
Activated carbon	73.18	2.89	0.56	0	23.37

*From difference

As the aforestated evidence does not ensure that the precursor material is activated carbon, the surface area of the samples needs to be monitored. The BET analyses of the samples were performed and the result is presented in Table 3. The obtained BET specific surface area clearly indicates that the prepared material is activated carbon. The obtained value is comparable with many values reported with the literature. In addition to the above the achieved specific micro-volume also supports the attainment of the above mentioned. For the identification of the reason behind the achieved of the above state values, the surface morphology of prepared activated carbon is analyzed. The surface texture is determined by using a Scanning Electron Microscope (Zeiss make). Surface topography of both the raw precursor and activated carbon at different magnification are illustrated in Fig. 2 and Fig. 3, respectively.

In case of AC, various pores are observed at different areas of activated carbon prepared from ridge gourd sample. It is also identified that the width of the pore in case of AC is more than the raw precursor due to the removal of volatile matter present

Table 3 — BET analysis of raw precursor and activated carbon

Sample	BET SSA(m^2g^{-1})	V_{tot}(cm^3g^{-1})	V_{micro}(cm^3g^{-1})
Raw precursor	61.36	0.0597	0
Activated carbon	1221.57	0.8792	0.407

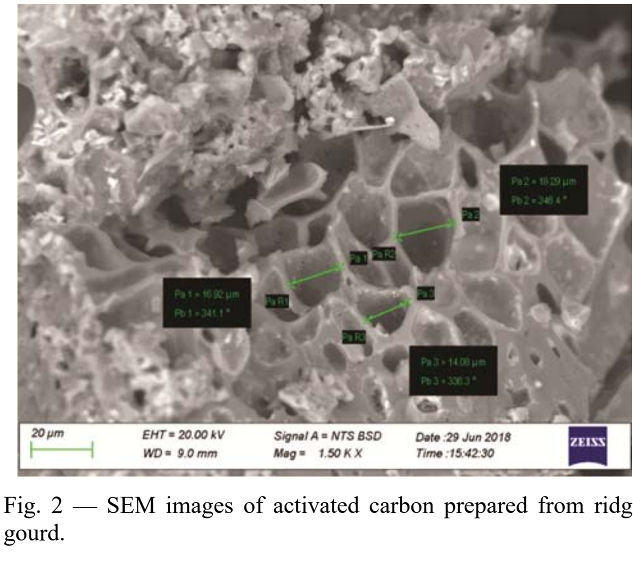

Fig. 2 — SEM images of activated carbon prepared from ridge gourd.

in the raw precursor. In addition to the above, the distribution of the pores in the raw precursor is non uniform. The micro-pores present in the activated carbon prepared from raw ridge gourd sample can contribute towards gas adsorption.

For the determination of composition of activated carbon, the elemental analysis is performed. Fig. 4 exhibits the elemental analysis by EDS spectra. The Table 4 represents the weight percentage of various elements present in AC in the located portion of Fig. 4. The analysis reveals that the activated carbon composed of Carbon, Oxygen, Potassium, Zinc and Chlorine. The last elements are the outcomes of chemical activating agent $ZnCl_2$ because for improper washing and whereas first three elements belong to its initial composition. However, uniform washing a bulk quantity of AC is not always possible, which may left some amount of chemical agent inside it. As the AC is free from any element depicting environmental problem, it is better AC than the AC produced from source such as rice husk, coconut shell and ore coke.

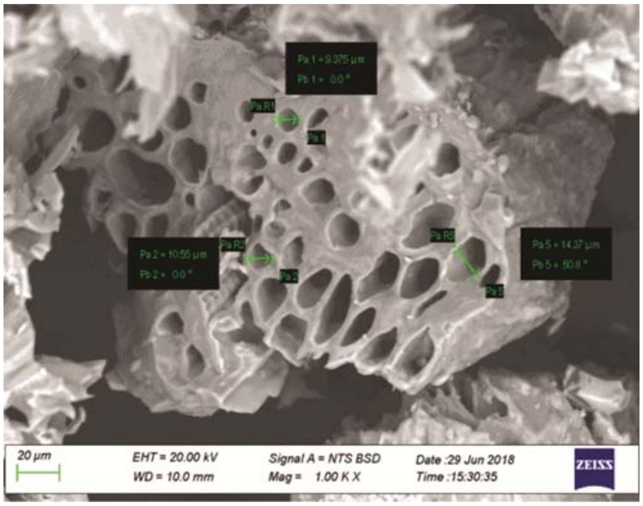

Fig. 3 — SEM image of raw precursor.

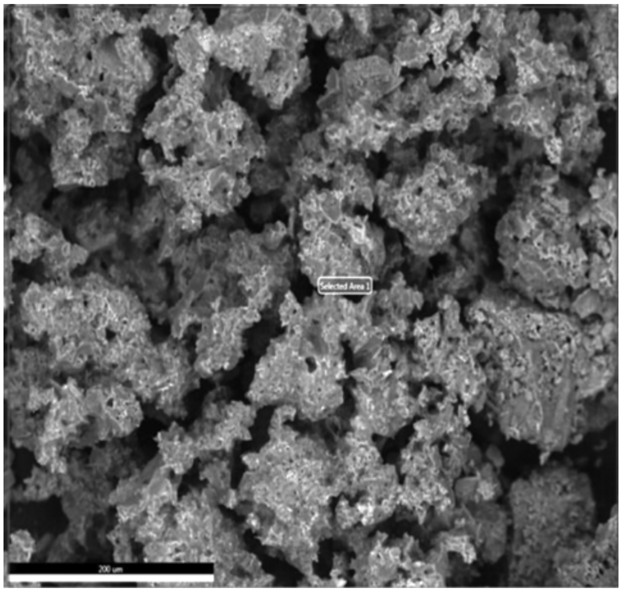

Fig. 4 — EDX of activated carbon.

In addition to the elemental analysis, the FT-IR (Perkin-Elmer; Spectrum GX) results have also been shown in Fig. 5. This analysis gives the functional groups present in the sample. Sample of 2% is mixed with 98% of KBr, placed in an oven at 100°C for 3 h to free of surface moisture or carbon dioxide molecules. Then, FT-IR analysis is performed. During the analysis the percentage of transmission of samples is recorded over spectral range of 400–4000 cm^{-1}. Incorporating Table 5 in Fig. 5, it reveals that the major shift are observed at wave number of 415,

Table 4 — Elemental analysis result of activated carbon (Fig. 4) by EDX

Element	Wt. (%)	Atomic (%)	Net Int.
C	77.42	73.98	83.22
O	18.17	20.69	66.52
K	2.65	2.25	31.37
Zn	1.12	1.97	18.78
Cl	0.64	1.11	10.01

Table 5 — FTIR spectrum band assignments

Wave number (cm^{-1})	Assignments
415-545	C-C Stretching
1077-1289	C-O in carboxylic acids, alcohols, phenol, esters, ethers
1420	C-O Asymmetric stretching
1609	C=C Stretching in vibration in aromatic
2330	C≡C Stretching vibration in alkyne absorption
2924	C-H stretching vibration in methyl group
3574	O-H stretching vibration in free O-H

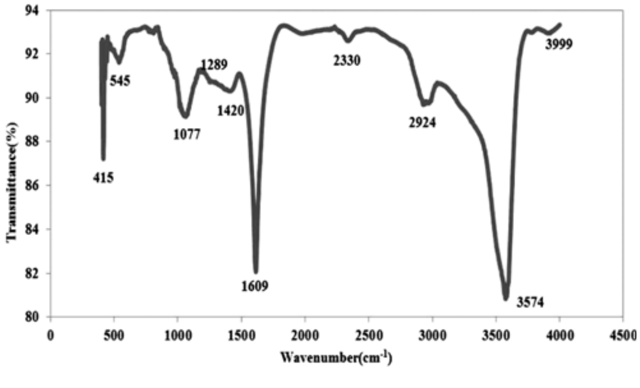

Fig. 5 — FTIR analysis of activated carbon prepared from ridge gourd.

1077, 1609, 2330, 2924, 3574 cm^{-1}, which confirms the presence of functional group such as C-C, C-O, C=C, C≡C, C-H and O-H, respectively[20]. These are the functional groups responsible for adsorption process by the interaction of activated carbon prepared from ridge gourd with adsorbate.

Methylene Blue (MB) is used as an adsorbate for the evaluation of removal efficiency of activated carbon due to its strong interactive nature with the solids[21,22]. MB solution is prepared by using 10 mL of MB in 100 mL of distilled water. Prepared activated carbon is added with the MB solution in conical flask. The solution is well mixed at 30°C by using a shaker for 5 min and left one hour. Then the solution is filtered and permeateis collected. The concentration of MB in the prepared sample is determined by a UV-spectrophotometer (SYSTRONICS; PC Based Double Beam Spectrophotometer 2202) at its wavelength of 660nm[23]. The removal efficiency of dye and the amount of dye adsorbed on activated carbon (q_e) are calculated by using the equation (1) and (2), respectively.

$$\text{Percentage of Removal Efficiency} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad \dots (1)$$

$$q_e = \left(\frac{C_i - C_e}{W}\right) V \quad \dots (2)$$

Where, C_i and C_e are initial and equilibrium concentration of adsorbate (MB) in mgL^{-1}, respectively. q_e is the amount of adsorbate (mgg^{-1}) adsorbed on adsorbent at equilibrium. V is the volume of solution in liter and W is the weight of dry adsorbent used in gram.

Figure 6 explains the effects of the interaction between contact times of adsorbate with adsorbent to find out the corresponding removal efficiency in percentage. It is observed that, as the contact time increasing the removal efficiency also increases. The variation in amount of dye adsorbed with contact time is also highlighted by Fig. 6. For the better understanding, the whole adsorption process is divided into three different zones by considering removal efficiency, contact time, and adsorbent does as the controlling parameters. If high removal efficiency is the target, then directly operation in Zone-3 is recommended for fast attainment of very high value of efficiency. Zone-1 is advised to consider only under significant removal in trial to attain within very short span of time. In the current analysis, Zone-2 is considered as transition zone due to the alteration of adsorption mechanism from monolayer to multilayer. The effect of adsorbent dosage (0.1-0.6 g/L) on removal efficiency of dye and amount of dye adsorbed are studied at temperature 30°C (120 min) as shown in Fig.7. From this, it is observed that, 86 % of removal efficiency is achieved only by 0.3 g/L of adsorbent and this can be considered one of the advantages when compared with literature. This may be due to the increment in adsorbent dosage which enhances the available adsorption sites for interaction between adsorbate and adsorbent. However, further increment in adsorbent dose, the removal efficiency does not alter significantly. Furthermore, it is also revealed that the adsorption amount declines as the

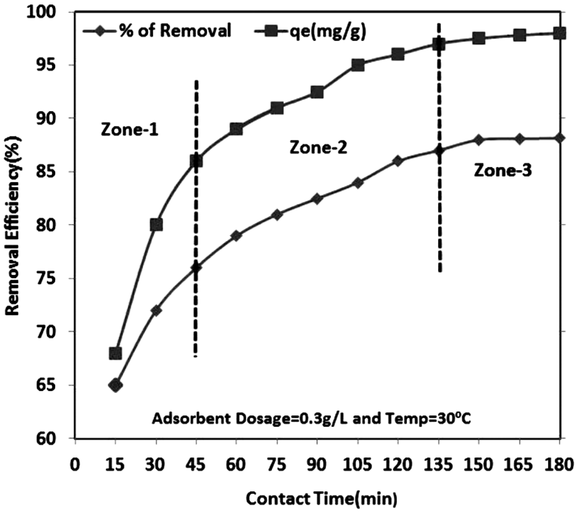

Fig. 6 — Effects of contact time on removal efficiency and amount of MB adsorbed on AC.

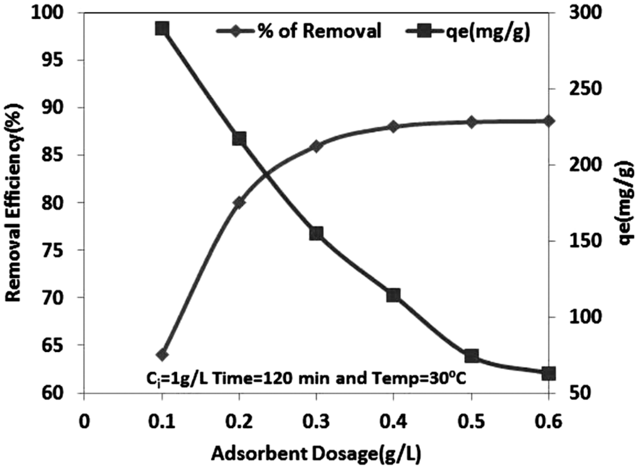

Fig. 7 — Effects of adsorbent dosage on removal efficiency and amount of MB adsorbed on AC.

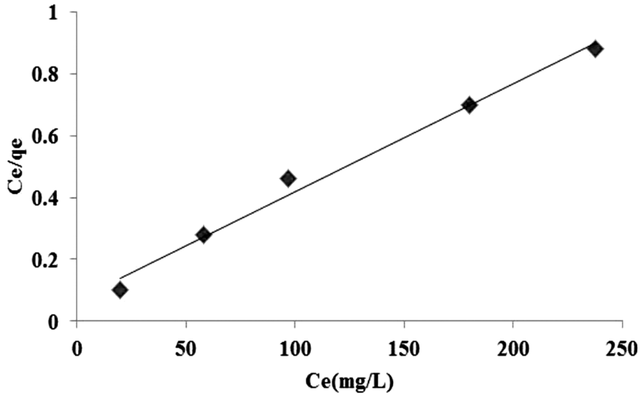

Fig. 8 — The Langmuir isotherm for adsorption of MB onto AC.

amount of activated carbon increased in the above condition. This may be happen due to two reasons; first one similar the solution may be lead to unsaturation of adsorption sites through the adsorption process for increase in adsorbent dosage at invariable MB and second one due to the particulate contact such as aggregation causing from high adsorbent dosage[22].

The empirical equation obtained from experimental data follows the mathematical nature of Langmuir isotherm (Fig. 8). Therefore, for the current separation process, monolayer adsorption on a homogenous surface without interaction between adsorbates is expected[24,25]. Adsorbent isotherm elucidates the type of interaction between adsorbate (MB) and adsorbent (AC) molecule at equilibrium conditions.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{1}{q_{\max}} C_e \qquad \ldots (3)$$

Where, ‘b’ is the Langmuir isotherm constant (Lmg^{-1}) and ‘q_{max}’ is the maximum adsorption capacity (mgg^{-1}).

Another important factor related to adsorption phenomenon described by Langmuir Isotherm is the analysis of separation factor termed as R_L, which signifies the type of adsorption process. The equation (4) describes the formula to find the magnitude of R_L and, the value illustrates the shape of isotherm as expressed below[26].

$$R_L = 1/(1+bC_0) = \begin{cases} >1, \text{ unfavorable} \\ =1, \text{ linear} \\ <1, \text{ favorable} \\ =0, \text{ irreversible} \end{cases} \qquad \ldots (4)$$

Table 6 — Langmuir isotherm model constants for adsorption of MB onto AC

Parameters	Values
q_{max}	285.71 (mgg^{-1})
b	0.499
R^2	0.98
R_L	0.200-0.589(favorable)

where, C_o is the highest initial concentration of adsorbate (MB) in mgL^{-1}. The magnitudes of various parameters related to Langmuir isotherm are presented in Table 6.

Conclusion

In this work, the activated carbon has been synthesized from the ridge gourd and investigated the efficiency of the product. The prepared material characteristics have been revealed by using characterization techniques such as proximate and ultimate analysis, BET surface area measurement, surface morphology by SEM, functional group identification by FT-IR, and elemental analysis by EDX. Based on the characterization of the activated carbon, the followings are the conclusion.

1. The fixed carbon percentage increases nearly 36% as established by proximate analysis.
2. The ultimate analysis revealed that carbon is found to be 73.18% of activated carbon without any sulfur contain.
3. The specific surface area is found to be 1221.57 m^2/g from BET surface analysis with the standard specific micro pore volume of 0.407 cm^3/g, which is responsible for absorption.
4. The comparative analysis performed by using SEM of activated sample and raw precursor indicates the enhancement of micro-pore.
5. The elemental analysis by EDX shows a significant percentage of carbon is present in the activated sample.
6. Presence of different bands like C=C, C≡C, C-H, C-O, O-H clearly indicate the constraint in the applicability and the preliminary information for the designer using activated carbon.
7. The adsorptions of MB and removal efficiency value prove that it is an excellent adsorbent. The recommended distinguished regime make easy for a decision maker to select the appropriate operating zone for a process.
8. The absorption of MB follows the trend of Langmuir adsorption isotherm.

References

1 Wong S L, Ngadi N, Inuwa I M & Hassan O, *J Clean Prod*, 175 (2018) 361
2 Ariharan A & Viswanathan B, *Indian J Chem Technol*, 25 (2018) 140
3 Tang W, Zhang Y, Zhong Y, Shen T, Wang X, Xia X & Tu J, *Mater Res Bull*, 88 (2017) 234
4 Chong Q, Yao C & Jian-min G, *Mater Lett*, 135 (2014) 123
5 Cunliffe M & Williams P T, *Energ Fuel*, 13(1999) 166
6 Teng H, Serio M A, Wojtowicz M A, Bassilakis R & Solomon P R, *Ind Eng Chem Res*, 34 (1995) 3102
7 Rodriguez R F & Molina S M, *Carbon*, 30 (1992) 1111
8 Mohd A Y, Al-Qodah Z & Zanariah N C W, *Renew Sustain Energy Rev*, 46 (2015) 218.
9 Ioannidou O & Zabaniotou A, *Renew Sustain Energy Rev*, 11 (2007) 1966.
10 Jeyaseelan S & Lu G, *Environ Technol*, 17 (1999) 667.
11 Xu J, Chen L, Qu H, Jiao Y, Xie J & Xing G, *Appl Surf Sci*, 320 (2014) 674.
12 Diasa J M, Alvim-Ferraza C M C, Almeidaa M F, Utrilla J R & Sanchez-Polo M, *J Environ Manage*, 85 (2007) 833.
13 Ioannidou O & Zabaniotou A, *Renew Sustain Energy Rev*, 11 (2007) 1966.
14 Mohanty K, Naidu J T, Meikap B C & Biswas M N, *Ind Eng Chem Res*, 45 (2006) 5165.
15 Olivares M M, Fernandez G C, Macias G A & Gomez S V, *Appl Surf Sci*, 252 (2006) 5967.
16 Das D, Samal D P & Meikap B C, *J ChemEng Process Tech*, 6 (2015) 5.
17 Srinivasakannan C & Abu B M Z, *Biomass Bio Energy*, 27 (2004) 89.
18 Hayashi J I, Kazehaya A, Muroyama K & Watkinson A P, *Carbon*, 38 (2000) 1873.
19 Kumar A & Jena H M, *Appl Surf Sci*, 356 (2015) 753.
20 Socrates G, Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3rd ed., John Wiley & Sons Ltd., West Sussex, (2001).
21 Hameed B H, Din A T M & Ahmad A L, *J Hazard Mater*, 141 (2007) 819.
22 Maryam K, Nahid G, Babak M & Mohsen R, *J Chem*, 383 (2013) 985.
23 Baayar C A, *J Hazard Mater*, 135 (2006) 232.
24 Wang Y X, Ngo H H & Guo W S, *Sci Total Environ*, 533 (2015) 32.
25 Vadivelan V & Kumar K V, *J Colloid Interface Sci*, 286 (2005) 90.
26 Ozsinl G, Kilic M, Varol E A & Putun A E, *Appl Water Sci*, 9 (2019) 2.