Research Article

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Comparison of Various Characteristic Activated Carbon Prepared from Turmeric Industrial Waste through Different Activation Processes

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ABSTRACT

Different characteristic activated carbons were prepared from turmeric industrial waste by using various carbonization and activation methodology and the surface characteristics were determined using standard analytical methods. The difference in the pore volume of activated carbons was obtained by various activating agents used during the activation processes. The surface area and pore size volumes of these samples were estimated by nitrogen adsorption measurements at 77 K. The morphology of the newly prepared carbon sample was studied by scanning electron microscopy, the surface functional groups were investigated by Fourier transformation infrared spectroscopy techniques and the presence of graphitic structure were studied by X-Ray diffraction analysis. Physico-chemical characteristics such as bulk density, moisture content, ash content, matter soluble in water, matter soluble in acid, pH, iodine number, conductivity, porosity, pH_{zpc}, yield percentage and surface area were investigated to choose the suitability of the carbon as adsorbent for the dye removal processes. In this study, the results clearly prove that the activated carbon prepared from turmeric industrial waste by using H_2SO_4 carbonization process followed by activation at 800 °C under nitrogen atmosphere is chosen as the suitable adsorbent possessing highest surface area with better pore volume and iodine number for the removal of textile dyes from aqueous solution.

Keywords: Activated carbon; Carbonization; Surface area; Turmeric industrial waste.

1. INTRODUCTION

The presence of dyes and their traces in textile effluents engenders rigorous environmental issues to the living things. In order to eschew this it is very much essential to abstract even the traces of dye from the industrial effluents. For last few decades, scientists have focused on good economic adsorption technique by utilizing activated carbon. Activated carbon is one of the efficacious adsorbent for the adsorption of dyes from industrial effluents due to their sizably voluminous surface area, nano-porous character and chemical nature of their surface.

In general, activated carbons can be prepared from carbonaceous matter rich materials such as wood, agricultural wastes, coal and synthetic resins. Activated carbon adsorption has been cited by the US Environmental Protection Agency (USEPA) as one of the best available environmental pollution control technologies (Martin, 2012). One of the major challenges associated with adsorption using activated carbon is its cost-effectiveness. In the recent years, researchers have mainly concentrated on the preparation of activated carbon from various agricultural waste materials as an alternative for the available commercial activated carbon.

Many reports were explored on the development of low cost activated carbon adsorbents prepared from more frugal and available waste materials (Babel and Kurniawan, 2003).

The adsorptive properties of active carbon for removal of pollutants are well documented (Macias *et al.* 1993). To minimize the treatment expenses incurred by using activated carbon, the research work was carried out by using waste materials as alternative to commercial activated carbon. Rice husks (Youseff *et al.* 1990), fruit stones (Namasivayam and Periyasamy, 1993), Palm shell (Adinata *et al*. 2007), coconut shells (Alaerts *et al.* 1989), (Manju *et al.* 1998), peat moss (Allen *et al*. 2001), ferronia shell (Karthikeyan *et al.* 2012) and *Ipomoea carnia* stem waste (Karthikeyan *et al.* 2007) are some of the waste materials which have been endeavored for this type of treatment.

The surface area and porosity of the adsorbents play a major role in all kind of adsorption processes. Thus in recent years, some authors have started to interpret the

surface chemistry of activated carbon with the adsorption performance (Pereira*et al*. 2003) Therefore, carbons with excellent surface properties and specific functionalities to be developed are considered as very significant to create a high affinity for the adsorption of problematic pollutants in its solution. It will be beneficial to have an activated carbon with sufficient amount of super micro-porosity and meso-porosity for the enhanced solute adsorption.

In this present work, activated carbons were prepared from turmeric industrial waste by using various carbonizations and activation methodology and the surface characteristics were determined and analysed with various methods like Scanning Electron Microscopy (SEM), Fourier Transformation Infrared spectroscopy (FT-IR) and XRD analyses in order to understand the properties. The physico-chemical characteristics of various activated carbons were compared and finally chosen as the best suitable activated carbon for the removal of textile dyes from aqueous solution.

2. MATERIALS & METHODS

2.1 Carbonization and Activation Processes

Different characteristic activated carbon were prepared by using the following various carbonization and activation processes as given in the table 1.

Table 1. Activated carbon prepared from Turmeric industrial waste by different activation Processes

S. No.	Name of the Activated Carbon	Carbonization and Activation Process
1	TWAC1	Acid Process – by H_2SO_4
2	TWAC2	Acid Process – by H_3PO_4
3	TWAC3	Impregnation with Na_2CO_3
4	TWAC4	Dolomite Process
5	TWAC5	Impregnation with Na_2SO_4

2.2 Acid Process

The turmeric industrial waste material was first ground and washed with doubly distilled water and then dried. The dried material thus obtained was treated with hydrogen peroxide (30% W/V) at room temperature for about 24 hrs to oxidize the adhering organic matter. The resulting material was exhaustively washed with doubly distilled water and then subjected to the temperature of 120 °C for the moisture removal and stored in a tight lid container.

2.2.1 Impregnation with H_2SO_4

The one portion of the above material was soaked well with 10% of H_2SO_4 solution for a period of 24 hrs. At the end of 24 hrs the excess of H_2SO_4 solution were decanted off and air-dried. Then the materials were placed in the muffle furnace to carbonize at 400 °C. After carbonization, the obtained carbons were washed sufficiently with Na_2CO_3 to remove cations. The obtained material was washed with plenty of water to remove excess of acid and dried. In order to eliminate the surface groups the thermal activation was carried out as the carbonized material was treated at 800 °C for 60 min in a furnace under N_2 flow (100 cm^3 min^{-1}). The resulting carbons were ground in a mill, washed with pure distilled water, and finally dried at 120 °C. The dried powders were sieved to get desired particle size and kept in tight lid container until used. The resulting carbons named as Turmeric Industrial Waste Activated Carbon-1 (TWAC1).

2.2.2 Impregnation with H_3PO_4

Another portion of the turmeric industrial waste material was activated with activating agents H_3PO_4 as same like the H_2SO_4 activation process described above, and they sieved to get desired particle size. The final product obtained was stored separately in vacuum desiccators until used. The resulting carbons named as Turmeric Industrial Waste Activated Carbon-2 (TWAC2).

2.3 Impregnation with Na_2CO_3

The turmeric industrial waste material to be carbonized was soaked with 10% Sodium carbonate solution for a period of 24 hrs. After impregnation, the liquid portion was decanted off and the material was dried. The dried mass was subjected to carbonization process at 400 °C, then powdered well and finally the material was activated at a temperature of 800 °C for a period of 20 min. The resulting carbon was named as Turmeric Industrial Waste Activated Carbon-3 (TWAC3).

2.4 Dolomite Process

A sufficient quantity of dried Turmeric industrial waste material was taken over a calcium carbonate bed and the upper layer of the waste was also covered with a layer of Calcium Carbonate. The whole material was carbonized at 400 °C, powdered well and followed by the thermal activation at 800 °C. After the activation, the material was repeatedly washed with plenty of water to remove calcium carbonate and dried at 110 °C. The resulting carbon was named as Turmeric Industrial Waste Activated Carbon-4 (TWAC4).

2.5 Impregnation with Na_2SO_4

The Turmeric industrial waste materials to be carbonized were soaked in 10% solutions of Sodium Sulphate for a period of 24 hrs. After impregnation, the liquid portion was decanted off and then dried. The dried

mass was subjected to carbonization process at 400 °C, powdered well and finally thermally activated at 800 °C for a period of 10 minutes. The resulting carbon was named as Turmeric Industrial Waste Activated Carbon-5 (TWAC5).

2.6 Characterization of the Activated Carbon

Moisture content (%) by mass, ash (on dry basis) % by mass, matter soluble in water, matter soluble in acid, pH, iodine number, conductivity, porosity, pH_{zpc} ,Yield percentage and surface area were analyzed as per standard procedures (ISI, 1989 and ASTM, 1980). pH and conductivity were analyzed using Elico make pH meter (model L1 -120) and conductivity meter (model M-180), respectively.

2.7 Surface Area and Pore Size Distribution Analysis

The N_2 adsorption-desorption isotherms of activated carbon were measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quanta Chrome Corporation) in order to determine the surface area and total pore volume. The surface area was calculated using the BET equation (Brunauer *et al*. 1938). In addition, the t-plot method applied to calculate the micropore volume and external surface area (Mesoporous Surface area). The total pore volume was estimated using liquid volume of adsorbate (N_2) at a relative pressure of 0.99. All the surface area was calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule was 0.162nm^2.

2.8 FTIR Spectra and SEM Analysis

The electronic structure of carbon samples was examined using BRUKER, OPUS-7.5.18 and spectrophotometer at National College, Trichy. Scanning electron microscopy (SEM) was used as focused electron beam to scan small areas of solid samples with TESCAN VEGA-3, Scanning Electron Microscope at National College, Trichy. Secondary electrons emitted from the sample and were collected to create an area map of the secondary emissions. Since the intensity of secondary emission is very dependent on local morphology, the area map is a magnified image of the sample.

2.9 X-Ray Diffraction Analysis (XRD)

XRD analysis of the carbon samples was carried out using Bruker AXS D8 Advance microprocessor at STIC, Cochin. The nature of the Carbon samples and the graphite planes present in it were studied by X-Ray diffraction analysis.

3. RESULTS & DISCUSSION

3.1 Physico-chemical Properties of Various Activated Carbons

The physic-chemical characteristics of different activated carbons prepared from turmeric industrial waste material are tabulated below in table 2.

Table 2. Physico chemical properties of turmeric industrial waste activated carbons

S. No.	Properties	Turmeric industrial waste activated carbons				
		TWAC1	TWAC2	TWAC3	TWAC4	TWAC5
1	pH	6.90	6.62	8.23	7.68	8.74
2	Moisture Content (%)	3.17	2.76	2.14	2.84	2.67
3	Ash Content (%)	2.05	2.12	2.84	2.56	3.17
4	Conductivity (ms /cm)	0.81	0.61	0.65	0.59	0.63
5	Specific Gravity	1.44	1.27	0.92	0.79	0.85
6	Bulk Density (g/mL)	0.45	0.47	0.51	0.46	0.52
7	Porosity (%)	53.64	51.06	48.34	47.02	46.27
8	Matter Soluble in water (%)	0.80	0.92	1.21	0.97	1.37
9	Matter Soluble in 0.25M HC1 (%)	1.15	1.19	1.25	1.22	1.32
10	Surface Area (m^2/g)	603.00	567.34	271.82	261.45	322.14
11	Iodine Number (mg/g)	721	651	446	405	471
12	pHzpc	5.9	5.3	4.8	4.4	5.0
13	Yield (%)	59.4	52.6	47.4	49.6	45.1

From table 2, the moisture content percentage of TWAC1 was found to be high. It shows extensive porosity introduced by H_2SO_4 process in the carbon structure. When compared to all processes, the moisture content of activated carbon prepared by sodium carbonate (TWAC3) process was less.

The ash content values from table 2 indicate that the overall ash content for all carbonization processes have lesser values. This is attributed to lower inorganic content and higher fixed carbon (Bansal *et al*. 2002).

The orders of surface area of carbons prepared by various processes are in order of TWAC1>TWAC2>TWAC5>TWAC3>TWAC4. The TWAC1 higher surface area of 603.00 $m^2 g^{-1}$ prepared by H_2SO_4 processes (acid process) may be due to the restricted pore shrinkage during activation.

Porosity is the main factor for increasing the adsorptive power of an activated carbon. TWAC1 has higher porosity than other carbons.

The H_2SO_4 process shows high iodine number value. This indicates that the carbon TWAC1 have the maximum adsorption capacity. Carbons with high surface area can be considered the most superior for adsorption of organic substances (Hu and Srinivasan, 1997).

Water soluble matter and acid soluble matter give the information about the amount of impurities present in carbon which affect the quality of water. But in our analysis, the data shows that all the samples contain very low amount of impurities.

Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in mg/g (typical range 500–1200 mg/g). It is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution. It is equivalent to surface area of carbon between 900 m^2/g and 1100 m^2/g. From table 2, it was clear that TWAC1 has higher Iodine number, indicating that it is best suitable for dye removal.

All carbon samples show significant nitrogen uptake at low relative pressure. That can be ascribed to the strong interaction between nitrogen molecules and the wall with closely spaced pores. Nitrogen adsorption for the TWAC3, TWAC4 and TWAC5 samples were low since the samples have such a low degree of activation and a low pore volume (Gregg and Sing, 1982).

3.2 Determination of Zero Point Charge (pH_{zpc})

The pH of the zero point charge (pH_{zpc}) has been determined by adding 0.2 g of activated carbon in glass stopper bottle containing 20 ml of 0.01 M NaCl solutions. The initial pH of these solutions has been adjusted by either adding 0.1 M NaOH or 0.1 M HCl. The bottles have been placed in an incubator shaker at 298 K for 24 hr, and the final pH of supernatant has been measured. The ΔpH = pH (final) - pH (initial) have been plotted against the initial pH, the pH at which ΔpH was zero was taken as the pH_{zpc} for the corresponding activated carbon. Fig. 1 clearly shows that the pH_{zpc} values were 5.9, 5.3, 4.8, 4.4 and 5.0 for TWAC1, TWAC2, TWAC3, TWAC4 and TWAC5 respectively.

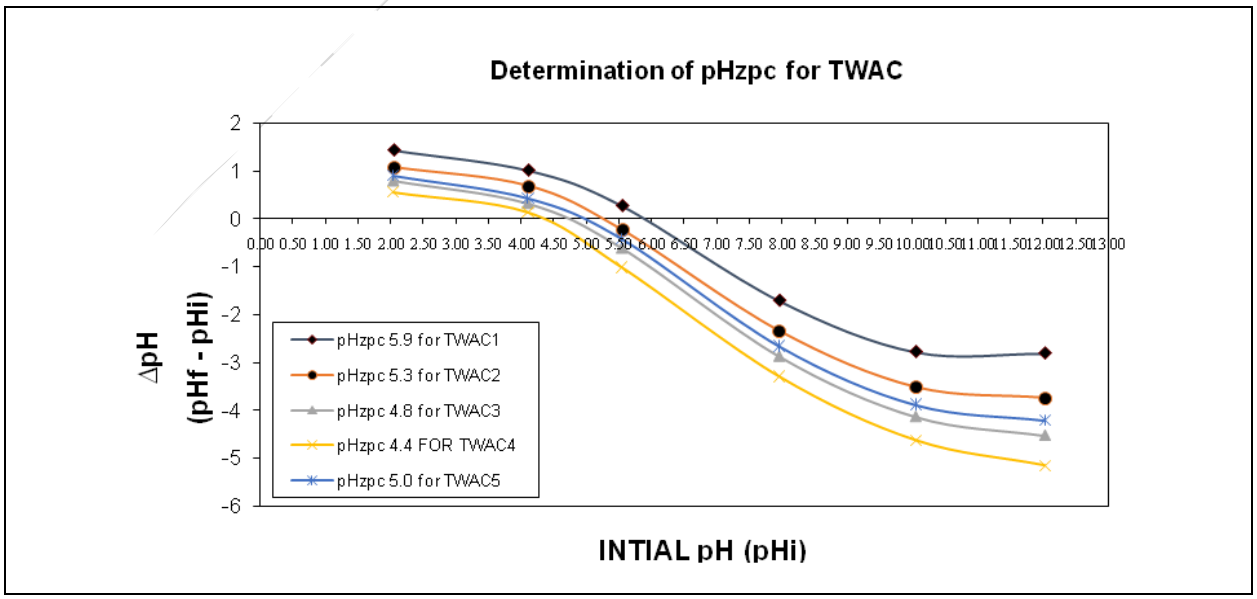

Fig. 1: Determination of pH_{zpc} for TWAC

3.3 Scanning Electron Microscope

SEM micrographs (Fig. 2) of activated carbon particles showed cavities, pores and more rough surfaces on the carbon samples. Granular pores and cavities will increase the surface area of the adsorbent. SEM photograph of TWAC1 shows that the surface is pitted and fragmented due to the carbonization with H_2SO_4 acid and activation process. The surface area of the TWAC1 will be enhanced by the presence of more porosity and cave type openings, which can hold more solute from solution during adsorption (Khattri and Singh, 1999).

3.4 FTIR Analysis of the Chosen Adsorbent

In Fig. 3, the FT-IR spectrum of the various activated carbon prepared from Turmeric Industrial waste by using different activation processes clearly indicates the presence of the different functional groups. In general evaluation, the carbon contains four classes of surface oxides: carboxyls, lactones, phenols and carbonyls. The concentration of the surface groups varied, depending on the various types of activation conditions. The assignment of the specific wave number to a given functional group was not possible because the adsorption bands of various functional groups overlap and shift depending on their molecular structure and environment. Shifts in absorption position may be caused by factors such as intramolecular and intermolecular hydrogen bonding, steric effect and degree of-conjugation. For instance, within its given range, the position of C=0 stretching band (common to carbonyls, carboxylic acids and lactones) is determined by many factors, such as:

i. The physical state
ii. Electronic and mass effects of neighboring substituent's
iii. Conjugation
iv. Hydrogen bonding and
v. Ring strain (Kendall, 1996).

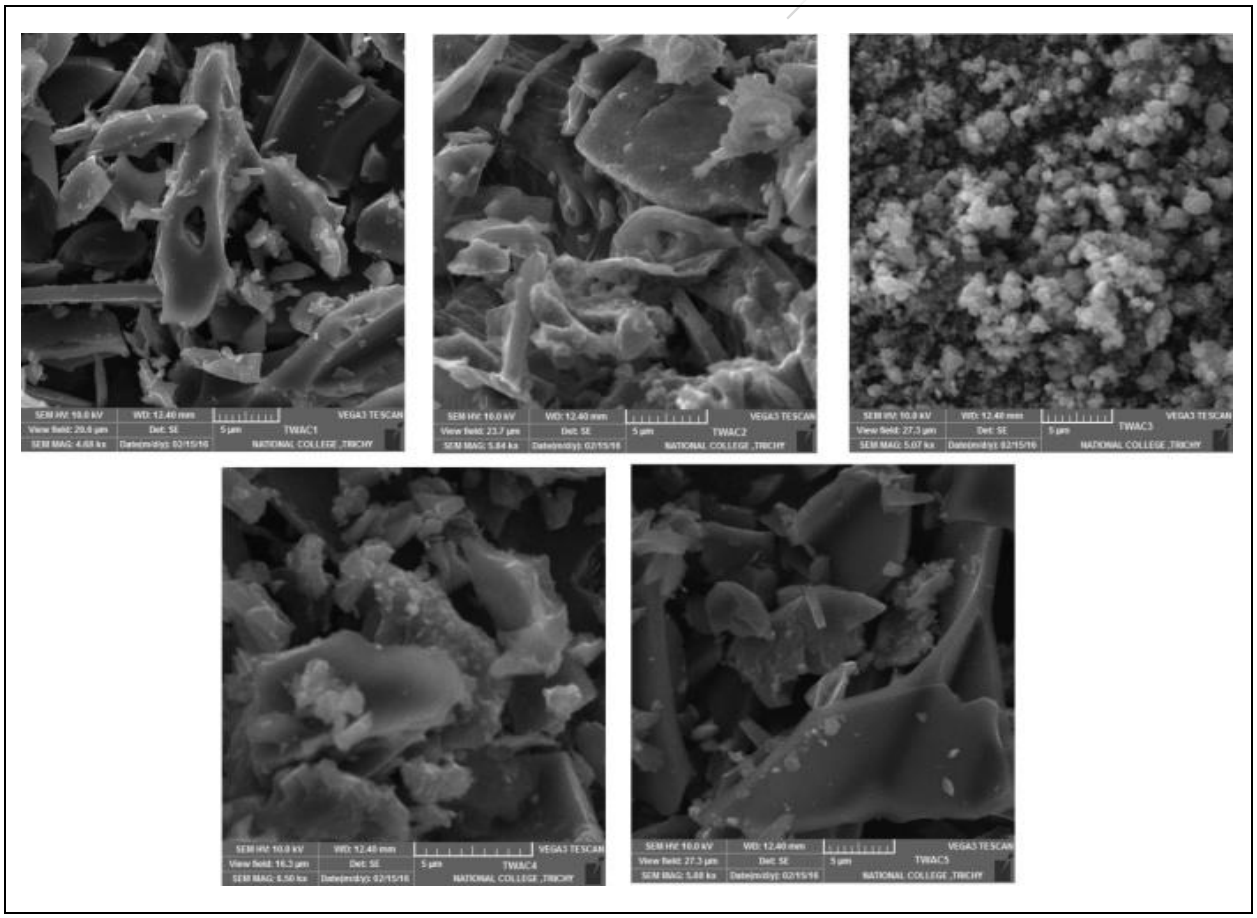

Fig. 2: SEM Photograph of TWAC1, TWAC2, TWAC3, TWAC4 and TWAC5

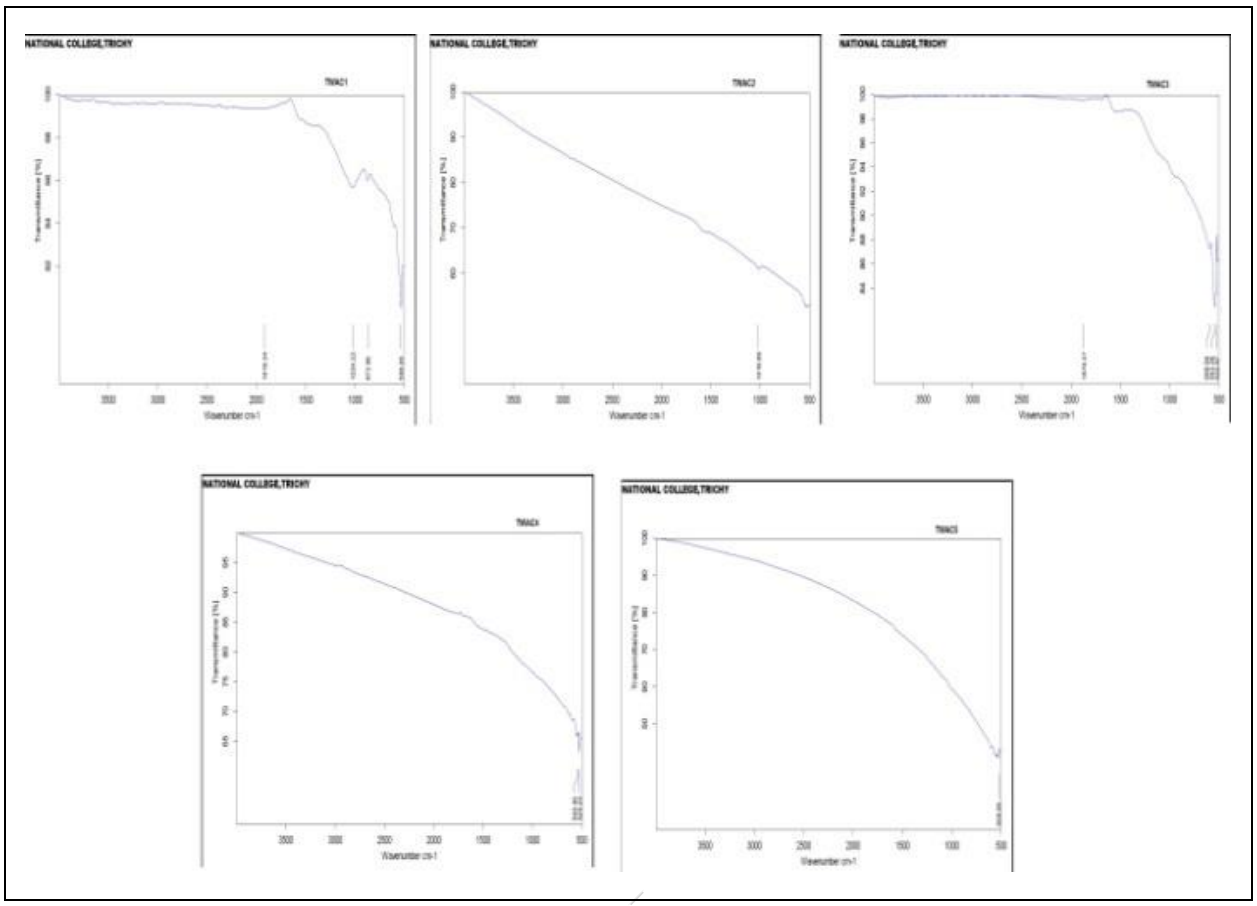

Fig. 3: FT-IR Spectrum of TWAC1, TWAC2, TWAC3, TWAC4 and TWAC5

The FT-IR absorption bands of oxygen groups on the surface of activated carbon prepared using Turmeric Industrial waste by various processes were likely to be affected by some or all of the factors listed above. Most of the carbons exhibit similar IR spectroscopic features; those are very intense/sharp-OH stretching of carboxyl, phenol and alcohol vibration around 1024 cm^{-1} and aliphatic CH stretching absorption around 1918 cm^{-1}. Saturated aliphatic ethers show a strong band in the region around 1100 cm^{-1} is attributed to carbonyl groups, and broad band in the region 1500 to 1900 cm-1 due to C=0 stretching. The group of bands appearing in the region 1870 cm^{-1} corresponding to $–CH_2$ deformation and appearing around 600–1500 cm^{-1} show the presence of C=C ie, C-C bond in alkenes.

The broad band observed in the region of 1000 to 1250 cm^{-1} can be assigned due to a characteristic absorption of -OH group. These results are in good agreement with the findings of many investigators (Zawndski, 1981).

3.5 XRD Analysis of the Chosen Activated Carbons

Fig. 4 shows the XRD patterns of activated carbons obtained by different impregnation processes. The peaks observed in XRD patterns near $2\theta = 25^{o}$, 45^{o} and 48^{o} for all carbons are due to graphitic crystallites of carbons, which correspond to the (002) and (100), (101) lines of the graphitic structure.

3.6 Comparison of Percentage of Dye Removal

The Acid yellow 17, Basic Green 4, Reactive Blue 2 and Direct Red 28 were chosen for the analysis of adsorption kinetics for TWAC1 at room temperature. The acid, reactive and direct type dyes are having anionic character and basic dyes are cationic character. Fig. 5 clearly indicates that the percentage of anionic and cationic dye removal for five different activated carbons prepared from Turmeric industrial waste. A strong connection between surface area and surface groups of the customized activated carbons and percentage of dye removal through adsorption can be observed (Sivakumar *et al*. 2012). The extent of adsorption of Basic Green 4 dye was very high, but for all other anionic type dyes shows very low adsorption. The following order was shown during the time of adsorption process.

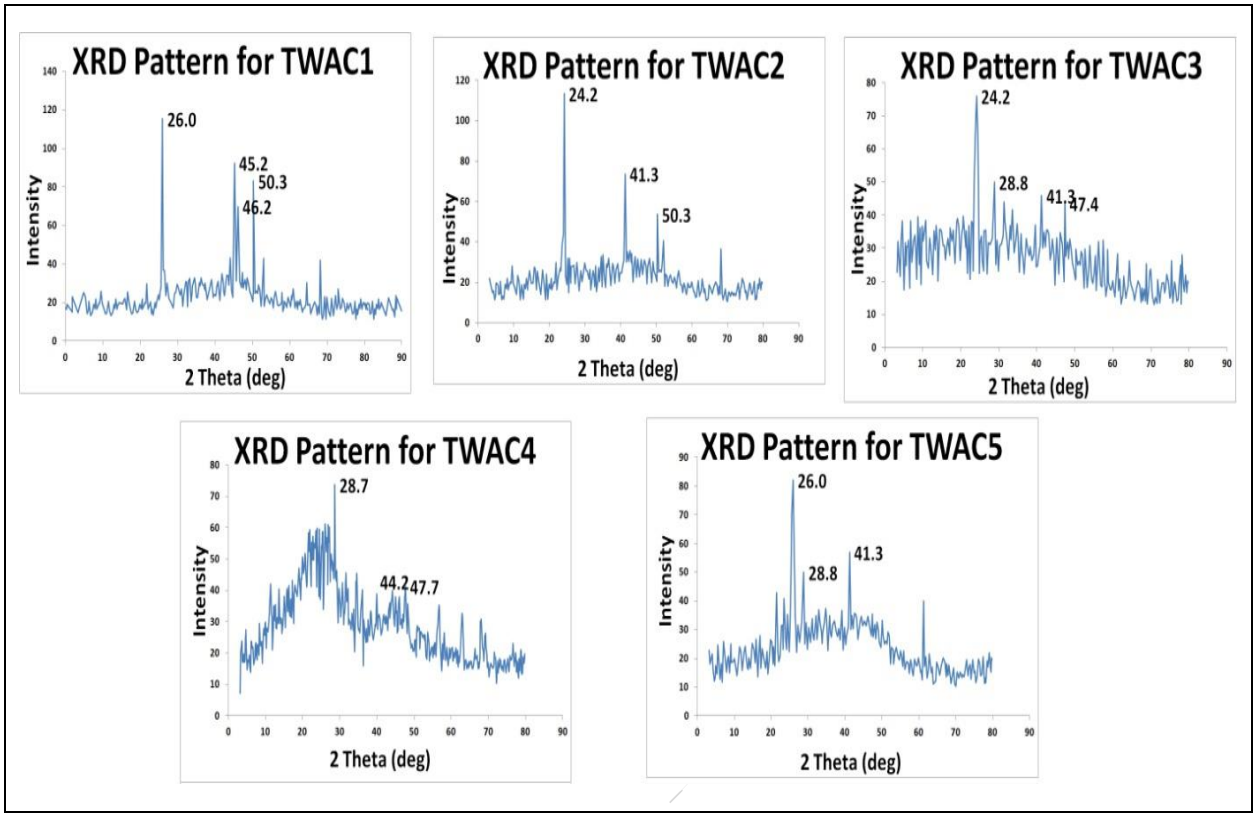

Fig. 4: XRD pattern for TWAC1, TWAC2, TWAC3, TWAC4 and TWAC5

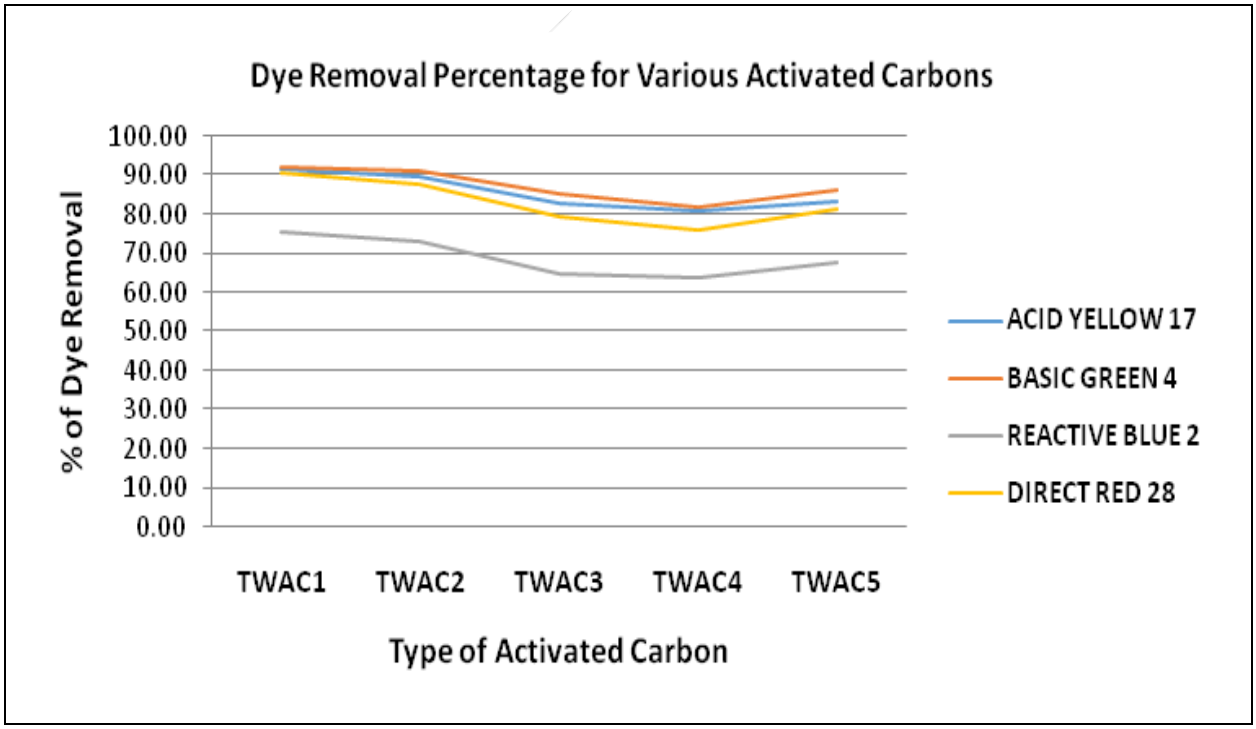

Fig. 5: Percentage of dye removal by turmeric industrial waste activated carbons

Basic Green 4>Acid Yellow17>Direct Red> Reactive Blue 2

This is mainly because of the higher molecular size of the corresponding dye species. Direct Red 28 and Reactive Blue 2 posses' high molecular weight and hence they occupy larger area in the chosen adsorbents (Raffiea Baseri *et al*. 2012). The maximum removal percentage of dye contents varies from 75.48 to 92.31 by using TWAC1. Based on the comparison data, the TWAC1 type activated carbon is the best suitable Carbon for the removal of textiles dyes from aqueous solutions.

4. CONCLUSION

Low cost activated carbons can be produced with moderate surface area from Turmeric industrial waste by using various carbonization and activation processes. Based on the comparison of the characteristics of activated carbons produced by various carbonisation and activation methods the Sulphuric acid impregnated process is considered as a better suitable activation process. The highest surface area obtained for activated carbon prepared using Turmeric industrial waste by H_2SO_4 process followed by activation at 800 °C under a nitrogen atmosphere is 603 m^2g^{-1}. The activated carbon prepared from above process is conveniently used for the organic, inorganic effluent removal and also for the removal of textile dyes by adsorbing the organics from the solution. Based on the comparison of percentage of adsorption of various dyes, the TWAC1 type activated carbon can be considered as a very efficient for the removal of textiles dyes from aqueous solutions.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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