

## Adsorption of Methylene blue dye from Aqueous solution Using Sodium Carbonate Activated *Citrullus lanatus* (Water melon) Rind

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**Abstract:** The possibility of including *Citrullus lanatus* (water melon) rinds as one of agro-waste products that can be used as adsorbent for the adsorption of methylene blue dye from aqueous solution has been studied. Dry water melon rinds were carbonized at 500°C and activated at 700°C using anhydrous Na<sub>2</sub>CO<sub>3</sub> as the activating agent. Elemental analysis using EDXRF, proximate analysis under standard conditions and adsorption studies using UV-Visible spectroscopy for MB uptake determination supported with adsorbent morphological evidences from scanning electron microscopy were carried out. The results show that at 0.5M of the activant using the 250µm of the activated carbon 99.27% MB removal is obtained. Moreover, % removal of the adsorbate increases with increasing activation resident time, adsorbent-adsorbate contact time, initial adsorbate concentration and decreasing particle size. In addition low moisture, ash and carbon contents at 4.8,4.08 and 23.38 respectively as well as relatively high bulk density of 0.54gcm<sup>3</sup> and high alkaline pH of 10.7 of the activated adsorbent are essential for the high MB removal. The scanning electron microscopy demonstrates the presence of greater porosity of the activated carbon compared to the carbonized carbons which are responsible for the greater retention of the adsorbate by the activated form of the adsorbent. The adsorption data clearly fit into the Freundlich isotherm with high adsorption intensity (n=3.935), capacity (K<sub>f</sub> =7.05) and value of R<sup>2</sup>=0.9978 indicative of favorable adsorption of MB process onto the activated carbon from water melon rind.

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**Key words:** water melon rind, adsorbent, adsorbate, carbonized, activated carbons, sodium carbonate.

### Introduction

Industrial effluents particularly discharged from dyeing industries are the foremost causes of environmental pollution because they are highly colored with a large amount of suspended organic solid. There are more than 10,000 different commercial dyes and pigments in existence exist and about 7x10<sup>5</sup> tones are produced annually world wide (Imamura et al.,2002). Raw disposal of this dyed water into the receiving water body causes damage to aquatic lives. Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. As a matter of fact, the discharge of such effluents is worrisome for both toxicological and environmental reasons. The conventional wastewater treatments which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes, a conventional biological treatment process is not very effective in treatment of dyes wastewater. It is usually treated either by physical or chemical processes. However, these processes are very expensive and cannot effectively be used to treat the growing wide range of pollutants. It has long been recognized that the adsorptive process is one of the most effective methods for removal of dyes from the waste sewage (Deans et al., 1992; Nigam et al., 2000). The process

of adsorption has an advantage over the other methods due to its sludge free clean operation and possibility of complete removal of dyes, even from the diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption effectiveness for the organic compounds. The waste water discharged from industries exhibit high Biological oxygen Demand (BOD), high Chemical Oxygen Demand (COD), are highly colored, hot and alkaline, containing high amounts of dissolved solids (Rajeshwarisivaraj et al., 2001). Adsorption on activated charcoal has been found to be superior compared to other chemical and physical methods of wastewater treatment in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity of design. Gerard and Bathelemy (2003) opined that activated charcoal removed all the impurities in water than other methods of water purification such as distillation, filtration, reverse osmosis, deionization, etc.

The need to monitor, control and clean up waste water is becoming more important as a result of health risk posed to man and his environment. Although, the toxicity of the effluent has been known for many years, public awareness and sensitivity, combined with increasing and stiffer pollution control regulations

havia made the search for the solution to the problem most urgent. However, commercially available activated carbons are still relatively expensive due to the use of non-renewable and relatively high-cost resources, such as coal petroleum, which is unjustified in terms of pollution control applications (Sourja et al., 2005; Martin et al., 2003). In a country where economy plays a very big role, it is better to find out relatively low-cost adsorbents to be used in this field. Synthetic dyes are one of the main pollutant groups of water and wastewater. Dye contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; dye color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Garg et al., 2004; Robinson et al., 2002; Wang et al., 2005a; Hamdaoui, 2006; O'zer and Dursun, 2007). These materials are the complicated organic compounds and they resist against light, washing and microbial invasions. Thus, they cannot be decomposed easily (Wang et al., 2008b; Baldez et al., 2008). Direct discharge of dyes containing effluents into municipal environment may cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity were found amongst basic and diazo direct dyes (Lata et al., 2007; Wang et al., 2008). Therefore, it is highly necessary to reduce dye concentration in the wastewater. The conventional methods for treating dye containing wastewaters are electrochemical treatment (Fan et al., 2008; Gurses et al., 2002), coagulation and flocculation (Tak-Hyun et al., 2004), chemical oxidation (Oguz and Keskinler, 2007), liquid-liquid extraction (Muthuraman et al., 2008) and adsorption (Wang et al. 2005a; Wang et al., 2005b; Mohan et al., 2002). Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Lata et al., 2007; Wang et al., 2005b).

A considerable amount of work has also been reported in the literature regarding the adsorption of methylene blue (MB) on various adsorbent surfaces such as, activated carbon (Shaobin et al., 2005; El Qada et al., 2008), rice husk (Vadivelan and Kumar, 2005), peanut hull (Renmin et al., 2005), glass fibers (Sampa and Binay, 2005), Indian rosewood sawdust (Garg et al., 2004), neem leaf powder (Bhattacharyya and Sharma 2005), perlite (Doan et al., 2004), fly ash (Wang et al., 2005b), yellow passion fruit peel (Pavan et al., 2008), chitosan-g-poly (acrylic acid)/montmorillonite super adsorbent nanocomposite (Wang et al., 2008b), sand (Bukallah et al., 2007), silica nano-sheets derived from vermiculite (Zhao et al., 2008), natural phosphate (Barka et al., 2009),

cyclodextrin polymer (Crini, 2008) among other adsorbents.

The present research focuses on preparation of activated carbon from water melon peel which is hitherto termed a "waste". Conversion of this cheap and abundant agricultural waste into activated carbon will serve many purposes. First, unwanted agricultural waste is converted to useful, value-added adsorbents and second, the use of agricultural by-products represents a potential source of adsorbents which will contribute to solving part of the wastewater treatment problem (Tan et al., 2008). This agricultural waste is a source of low cost adsorbents than other adsorbents such as activated charcoals because they are readily available and finally, it will help in the decrease of the heap-log of waste from causing environmental hazards.

There has not been reportedly studied use of water melon peel as adsorbents for MB despite its relative abundance, cheapness and non-toxicity due to human feeding of the agricultural product.

#### **Experimental**

##### **Materials and reagent**

Watermelon peels were purchased from a market in Ile-Ife, Nigeria. The anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) was obtained from Aldrich and methylene blue is a laboratory reagent.

##### **Sample preparation**

The watermelon peels were washed with distilled water, reduced into small pieces by dicing them and dried under a shade for 48hours. They were dried in an air oven for 24hours at  $70^\circ\text{C}$  to constant weight. The temperature was maintained to prevent degradation of the watermelon peels. They were pulverized using a laboratory milling machine at the Department of Geology, Obafemi Awolowo University, Ile-Ife.

##### **Carbonization and activation**

The two- step activation which involves carbonization of the watermelon peel before the activation as described earlier with slight modification (Gimba et al, 2009).

The milled watermelon peel was first introduced into a muffle furnace at  $500^\circ\text{C}$  for 5mins after which they were removed, quenched with cold distilled water and sun dried to constant weight. These are the carbonized carbon watermelon rind samples, hereafter, referred to CCWR. The activating agent was sodium carbonate anhydrous at varying concentrations of, 0.01M, 0.025M, 0.05M, 0.075M, 0.10M, 0.50M and 1.00M separately. For instance, flaky pastes were made by mixing 10g of the carbonized samples with  $10\text{cm}^3$  of 0.01M  $\text{Na}_2\text{CO}_3$ . The mixture was introduced into a muffle furnace at  $700^\circ\text{C}$  for activation times of 5mins and 10mins separately. They were then quenched and washed in cold distilled water in order

to wash off all the uncombined sodium carbonate present in it by carrying out litmus test on the distilled water until negative. They were dried at room temperature after washing. The above processes were repeated in turn for each of the remaining concentrations. The activated carbon samples, referred hereafter as ACWR, were sieved into two different particle sizes of 250 $\mu\text{m}$  and 500 $\mu\text{m}$  using standard sieves.

### Characterization of the carbon samples

#### Elemental analysis

The elemental analysis of the raw, carbonized and activated watermelon rind were carried out using the Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria. The detection system for all the measurements is a Model XR-100CR a high performance X-ray Detector with preamplifier and a cooler system which uses a thermoelectrically cooled Si-PIN photodiode as an X-ray detector. The power to the XR-100CR is provided by a PX2CR power supply. The detector is coupled to the pocket MCA 8000A Multichannel Analyzer. The resolution of the detector for the 5.9 keV peak of  $^{55}\text{Fe}$  is 220 eV FWHM with 12 $\mu\text{s}$  shaping time constant for the standard setting and 186 eV FWHM with 20 $\mu\text{s}$  time constant for the optional setting. The optional setting used recast measurements with the resolution of 186 eV for the 5.9 peak of  $^{55}\text{Fe}$ . The quantitative analysis of samples was carried out using the XRF-FP Quantitative Analysis Software package. (CERD, 2015).

#### Determination of physico-chemical properties

These involve the determination of moisture content, dry matter, Ash content, Carbon yield and Bulk density. The methods employed in these determinations were adopted from an earlier work (Gimba et al., 2009).

Preparation of methylene blue (MB) stock solution

The stock solution of the methylene blue dye was prepared by taking 0.12g of the MB and dissolving in 10 $\text{cm}^3$  distilled water. It was transferred into a 100 $\text{cm}^3$  standard flask, shaken and made up to mark (Gimba et al., 2009). Different concentrations of the MB were prepared by taking each of 0.1 $\text{cm}^3$ , 0.2 $\text{cm}^3$ , 0.3 $\text{cm}^3$ ,

0.4 $\text{cm}^3$ , 0.5  $\text{cm}^3$ , 0.6  $\text{cm}^3$  and 0.7 $\text{cm}^3$  of the prepared stock solution and transferred into standard flask and made up to the mark with distilled water. This done in order to determine the effect of varying different concentrations of MB with a constant known mass.

#### Adsorption of methylene blue

Double beam UV-visible spectrophotometer (Shimadzu-1700, Japan) at wave length of 668 nm was used to determine MB concentrations before, during and after adsorption process. (Salman and Almutairi, 2013).

Clean columns were bedded with cotton wool loaded with 60mg of ACWR of particle size 250 $\mu\text{m}$  of 0.1M  $\text{Na}_2\text{CO}_3$  concentration activated for 5minutes. These were equilibrated with 2 $\text{cm}^3$  of distilled water. 4 $\text{cm}^3$  of the MB stock solution was passed through the equilibrated column and the effluent absorbance was taken using ultraviolet-visible spectrometer. The due process was repeated for other samples that were activated at 5mins and 10mins and other concentrations.

In order to study the effect of varying MB concentration on the adsorption uptake, a batch process was used where 25 $\text{cm}^3$  of MB solutions with known initial concentrations were prepared in series of 25  $\text{cm}^3$  volumetric flasks. 0.20 g of watermelon rind activated charcoal of 0.5M  $\text{Na}_2\text{CO}_3$  with particle size 250 $\mu\text{m}$  activated for 10minutes was added into each flask covered to reach equilibrium for 24h.

The effect of contact time on the % removal of MB was studied by repeating the above process

at 7 and 21 using the same sample of ACWR (0.5M  $\text{Na}_2\text{CO}_3$ ) above.

The concentration of MB was determined at the end of adsorption in each case..

### Scanning electron microscope (SEM) analysis

The SEM images of sample of the ACWR that gave the highest %RE of MB, that is, sample activated with 0.5M  $\text{Na}_2\text{CO}_3$  and its carbonized form were obtained using a scanning electron microscope (S-2150, Hitachi High-Technologies Corp., Japan) before and after adsorption.

## Results And Discussion

### Elemental Analysis Unit?

**Table 1: Elemental Analysis of Raw, Carbonized and Activated Watermelon Rinds**

Samples (ppm)	K	Ca	Mn	Fe	Ni	Cu	Zn	Rb	Se	Co	Mo
Raw WR	2.2037	6925	956	2788	2098	3086	2218	954	527	929	240
CWR	2.5866	9105	270	3885	796	1011	1074	371	191	285	114
ACWR	5.7976	65473	2469	73602	119	223	677	-	-	-	-

Table 1 shows the elements and their concentrations (ppm) that can be detected and determined by EDXRF in the samples of *citrulus*

*lunatus* rind. It can be seen that while the concentrations of K, Ca, Mn and Fe trend in the order: raw (RCWR) < carbonized (CCWR) < activated

(ACWR) those of Ni, Cu, Zn, Rb, Se, Co and Mo go in the reverse order with zero level of the last four elements in the ACWR. The observed trend may not be unconnected with the effect of increasing processing temperature from the raw (26<sup>0</sup>C) to carbonization (500<sup>0</sup>C) and then to activation (700<sup>0</sup>C), which could have resulted into concentration and volatilization effects of the compounds of these elements in the first (K-Fe) and second (Ni-Mo) categories respectively. Increased concentrations of the first set of elements may be attributed to reduction in the amount of interfering or masking agents such as protein/volatile rind components as one proceeds from carbonization to activation in line with Mozammed and Masahirom (2002), Gimba *et al* (2009), Turoti and Bello (2013).

#### Physico-Chemical Parameters

Table 1 shows the ACWR samples generally have lower, %moisture content (MC), %C -yield (except for the sample of 0.075%) and %ash content but greater % dry matter, pH and bulk density compared to those of CCWR which can be attributed to the presence of the anhydrous AA. There is no particular trend between the concentration of the AA and any of these parameters which most probably indicate that they are unlikely the only or major factors that may influence the adsorptivity of the carbon matrixes obtained from the water melon samples. The % dry matter of all the ACWR samples falls within the range of 94.8-96.8% which are higher than that of the CCWR and again no particular trend with the variation in concentration of the AA similar to the results obtained earlier (Turoti and Bello,2013). The sample activated with 0.05M Na<sub>2</sub>CO<sub>3</sub> that has the highest % dry matter has the least % MC. The ash content of

adsorbents is a measure of inorganic impurities in its carbon and has been found to reduce the efficiency of re-activation of carbons the higher its content and is expected to be lower in the activated than in the carbonized samples of the same precursor (Bansode *et al*, 2003., Turoti and Bello, 2013). In this work, the smallest % ash content is obtained in the sample activated with 0.5M AA. The %C of the ACWR, are lower than that of the CCWR except that of 0.075M. It is most probable that the presence of the AA generally leads to the decomposition of the organic materials releasing volatiles at the relatively high temperature of activation and simultaneously developing microporous structure (Malik *et al*, 2006). The sample of 0.5M has the least %C-yield of 23.58%. The activation of the carbon yielding a higher degree of mesoporosity may probably have occurred in the activated carbon.

Both the CCWR and the ACWR have alkaline surfaces but all the latter are more so with the sample of 0.5M as one of the two most alkaline. A separate determination (not in Table 2) the pH of the raw precursor is 6.0. Thus this chemical parameter increases in the order: raw (acidic) < CCWR (alkaline) < ACWR (alkaline), similar to earlier work (Turoti and Bello, 2013, Gimba *et al*, 2009). For adsorption of a basic dye, such as MB, increasing pH of an adsorbent leads to greater affinity for the adsorbate. All the ACWR have greater bulk density than the CCWR and falls within the range of 0.50-0.60 gcm<sup>-3</sup> which are higher than the minimum requirement of 0.25gcm<sup>-3</sup> for applications required in removal of pollutants from wastewaters (AWWA, 1991). Generally, higher bulk density carbons hold more adsorbate per unit volume (Jibril *et al.*, 2007).

**Table 2: Physico-Chemical Parameters of Carbonized and Activated Water melon rind**

Samples by molarity of AA	%Moisture Content	%Dry Matter	%Ash	%Carbon Yield	pH	Bulk Density
0.01M	5.2	94.8	4.62	26.70	10.3	0.54
0.025M	4.0	96.0	4.63	26.76	10.6	0.56
0.05M	3.2	96.8	5.36	30.98	10.3	0.50
0.075M	4.0	96.0	6.02	34.79	10.7	0.60
0.10M	5.2	94.8	5.53	31.96	10.6	0.50
0.5M	4.8	95.2	4.08	23.58	10.7	0.54
1.0M	4.8	95.2	4.13	23.87	10.3	0.52
CCWR	6.0	94.0	5.73	33.10	10.2	0.48

#### Adsorption studies

In the present report the factors that are considered essential for the removal of the adsorbate (MB) in aqueous medium will be discussed, relate this to some of the relevant physico-chemical properties, their fittings to Freundlich isotherm and provide evidence from scanning electron microscope (SEM).

Effect of Resident (activation) time and initial concentration of MB

As can be seen in Table 3 both the %RE and the equilibrium amount of MB adsorbed per unit mass of the adsorbent ( $q_e$ ) are favored at 10 than 5 minutes activation time for each initial concentration ( $C_0$ ) of MB. However, there is no uniform trend of both

indices with the varying  $C_0$  which is reminiscent of such trend.

**Table 3: Effect of Activation Time and Varying Concentration of Activating agents on Removal of Methylene Blue**

Samples (250 $\mu$ m)	5mins					10mins			
	Conc of AA (M)	$C_0$ (g/L)	$C_e$ (g/L)	$C_a$ (g/L)	%RE	$q_e$ (mg/g)	$C_e$ (g/L)	$C_a$ (g/L)	%RE
0.01	1.199	0.119	1.080	90.05	72.01	0.073	1.126	93.88	75.07
0.025	1.199	0.171	1.028	85.74	68.53	0.017	1.183	98.60	78.84
0.050	1.199	0.284	0.915	76.31	61.02	0.262	0.937	78.14	62.48
0.075	1.199	0.237	0.963	80.26	64.17	0.084	1.154	92.99	74.36
0.10	1.199	0.376	0.814	67.90	54.29	0.365	0.835	69.58	55.64
0.50	1.199	0.023	1.167	98.08	77.81	0.009	1.191	99.27	79.37
1.0	1.199	0.046	1.144	96.09	76.23	0.028	1.171	97.66	78.09

In most of the physico-chemical properties reported in the earlier section. The same sample containing 0.5M AA has the highest %RE and  $q_e$  in both activation times even though the adsorption parameters were not concentration dependent. As stated earlier, this sample has the least %ash content, %C-yield but highest pH which might have contributed to its highest adsorption characteristics.

#### Effect of Adsorbent dosage on %RE and $q_e$

Using the sample that has the highest % RE as found in the previous section but varying adsorbent dosages of particle size of 500  $\mu$ m using the same MB initial concentration of 1.199g/L, Table 4 shows that increasing adsorbent dosage from 60-120mg, the %RE increases from 41.56-70.97% in line with some previous studies (Shahryari et al.,2010., Obuge and Evbuomuran, 2014) s.

**Table 4: Effect of Adsorbent Dose on % Removal of Methylene Blue**

Samples	$C_0$ (g/L)	$C_e$ (g/L)	$C_a$ (g/L)	%RE	$q_e$ (mg/g)
0.5M Na <sub>2</sub> CO <sub>3</sub> (500 $\mu$ m)					
60mg	1.199	0.7009	0.4985	41.56	207.71
80mg	1.199	0.6214	0.5780	48.19	180.63
100mg	1.199	0.4829	0.7164	59.73	179.10
120mg	1.199	0.3482	0.8512	70.97	177.33

On the other hand, adsorption capacity ( $q_e$ ) i.e. the amount of adsorbate adsorbed per unit mass of the adsorbent decreases with increase in the adsorbent dose in agreement with some previous studies (Turoti and Bello, 2013). The addition of adsorbent may increase the number of adsorption sites but the dye could have more difficulties in approaching these sites

because of its dimensions factor.. A large amount of adsorbent creating complexes of particles leads to a reduction of the total adsorption area and therefore a decrease in the amount of adsorbate per the adsorbent unit.

#### Effect of contact time and varying initial concentration of MB

**Table 5: Effect of Contact Time and different concentrations of MB solutions on Adsorption Equilibrium**

Volume (cm <sup>3</sup> )	7hr					21hr			
	$C_0$ (g/L)	$C_e$ (g/L)	$C_a$ (g/L)	%RE	$q_e$ (mg/g)	$C_e$ (g/L)	$C_a$ (g/L)	%RE	$q_e$ (mg/g)
0.1	0.125	0.080	0.045	34.99	5.450	0.023	0.102	81.56	12.70
0.2	0.236	0.093	0.143	60.66	17.88	0.055	0.181	76.77	22.64
0.3	0.346	0.186	0.160	46.29	20.00	0.021	0.324	93.86	40.55
0.4	0.359	0.185	0.174	48.52	21.76	0.021	0.338	94.08	42.19
0.5	0.361	0.163	0.198	54.90	24.75	0.076	0.284	78.68	35.46
0.6	0.623	0.164	0.459	73.63	57.35	0.077	0.546	87.66	68.28
0.7	1.552	0.084	1.071	92.73	133.9	0.065	1.091	94.41	136.4

For varying MB concentration, data were taken at equilibrium times of 7 and 21hours as can be seen in Table 5. An increase in the initial MB concentration

(from addition of the 0.1cm<sup>3</sup> to 0.7cm<sup>3</sup> of MB) generally leads to an increase in the adsorption capacity of ACWR and this may be attributed to an

increase in the driving force for the mass transfer between the aqueous phases and the solid phase (Akram et al., 2015., Kumar, 2010). Furthermore, the increase of adsorption capacity of ACWR with increasing initial MB concentration may be due to higher thermodynamic interaction between MB and the adsorbent. For constant dosage of adsorbent, at higher initial concentrations of MB, the available adsorption sites of adsorbent become fewer. The removal of dye by adsorption onto the ACWR is time dependent for each tested initial concentration. However, whereas the %RE and  $q_e$  are generally concentration dependent at the shorter time (7hr) period only the latter parameter ( $q_e$ ) is so at the longer contact time (21hr). Slow diffusion onto the external surface was followed by fast pore diffusion into the intra-particle matrix to attain rapid equilibrium as contact time increases.

### Effect of Particle size of Adsorbent

Table 6 shows that varying particle size of adsorbent has effect on the %RE and  $q_e$  when MB in aqueous solution comes in contact with the same ACWR activated with 0.5M  $\text{Na}_2\text{CO}_3$  for 10mins using particle sizes of 250 and 500 $\mu\text{m}$ . This result is attributed to the common view that surface area increases as particle size of a sorbent decreases presenting greater effective contact points or collision with the adsorbate (MB). Decrease of the particle size is accompanied by decrease in inter-particulate distance, hence decrease in inter space volume resulting into increase in bulk density and greater retention of, and affinity for, the adsorbate compared to particles of larger size (Itodo et al., 2010., Turoti and Bello, 2013).

**Table 6: Effect of Particle Size of Adsorbent on % Removal of Methylene Blue**

Samples 0.5M $\text{Na}_2\text{CO}_3$ (10mins activation)	$C_0$ (g/L)	$C_e$ (g/L)	$C_a$ (g/L)	%RE	$q_e$ (mg/g)
250 $\mu\text{m}$ 60mg	1.199	0.0883	1.1905	99.2	79.37
500 $\mu\text{m}$ 60mg	1.199	0.1414	1.0579	88.2	70.53

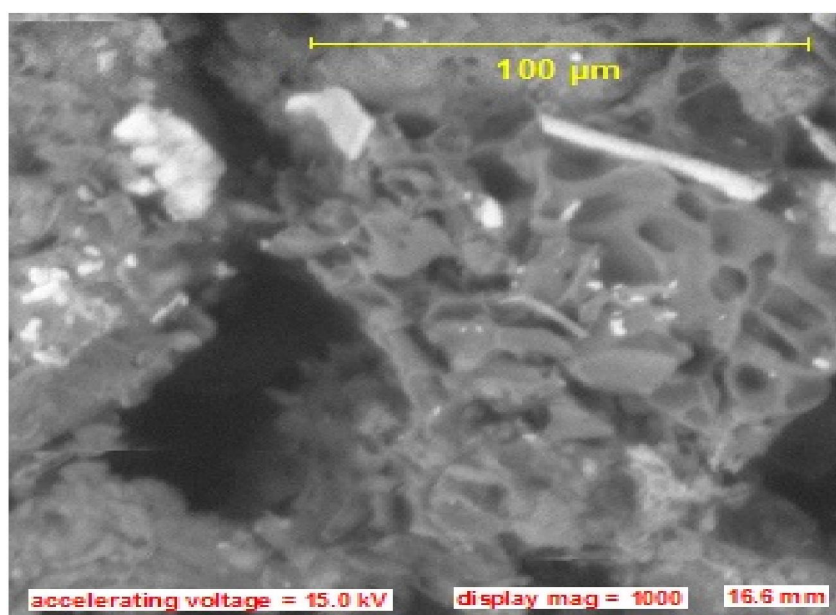


Fig.1: SEM images of the CCWR before adsorption (after carbonization).

### Scanning Electron Microscopy

The purpose of this section is to showcase the differentials in the morphology of the ACWR and CCWR using the most effective sample (0.5M AA) that gives the highest %RE in comparison to the CCWR employing scanning electron microscopy as described in the experimental section. Figure 1 shows that the SEM image has no deposit of the white AA ( $\text{Na}_2\text{CO}_3$ ) particles which is also absent after adsorption of the MB in Fig.2. Moreover there are

only few pores in the CCWR relative to the ACWR where there are more conspicuous white colored distribution of the powdery AA (see Fig.1 compared to Fig.3 (all images were taken under the same conditions)). SEM image shows wide variety of pores present in the ACWR (Fig.3) along with some fibrous structures. The  $\text{Na}_2\text{CO}_3$  impregnated carbon consists of more canals indicated by pitted and fragmented surfaces than the untreated carbon. Those imperfections are not seen in case of carbonized

sample. The structural features shown in the SEM images of both CCWR and ACWR indicate more than

one layer of adsorption of MB which fingers on the possibility of data fitting into the Freundlich isotherm.

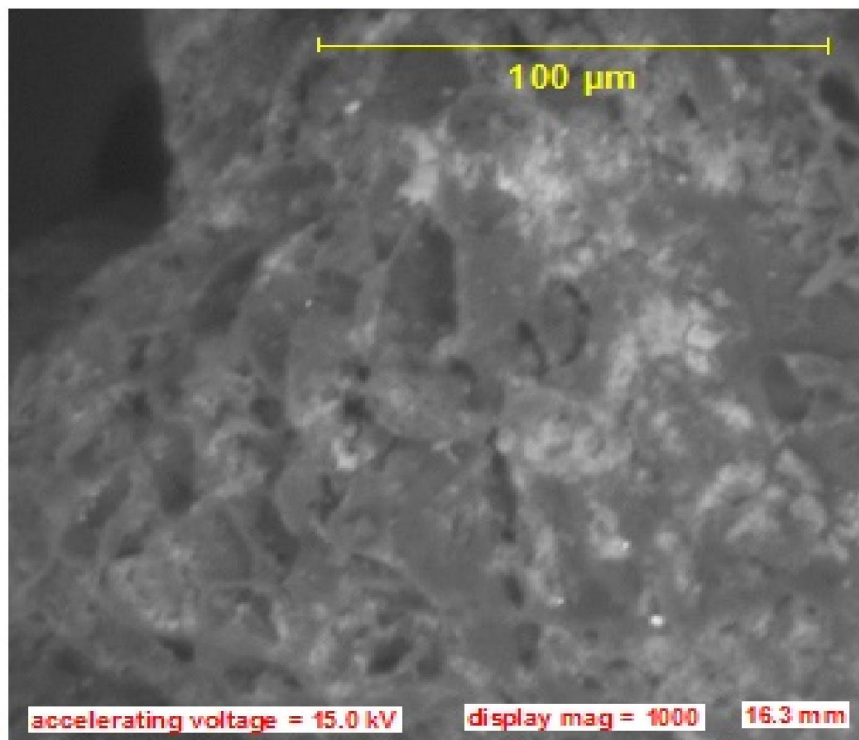


Fig.2. SEM image of the carbonized sample after adsorption.

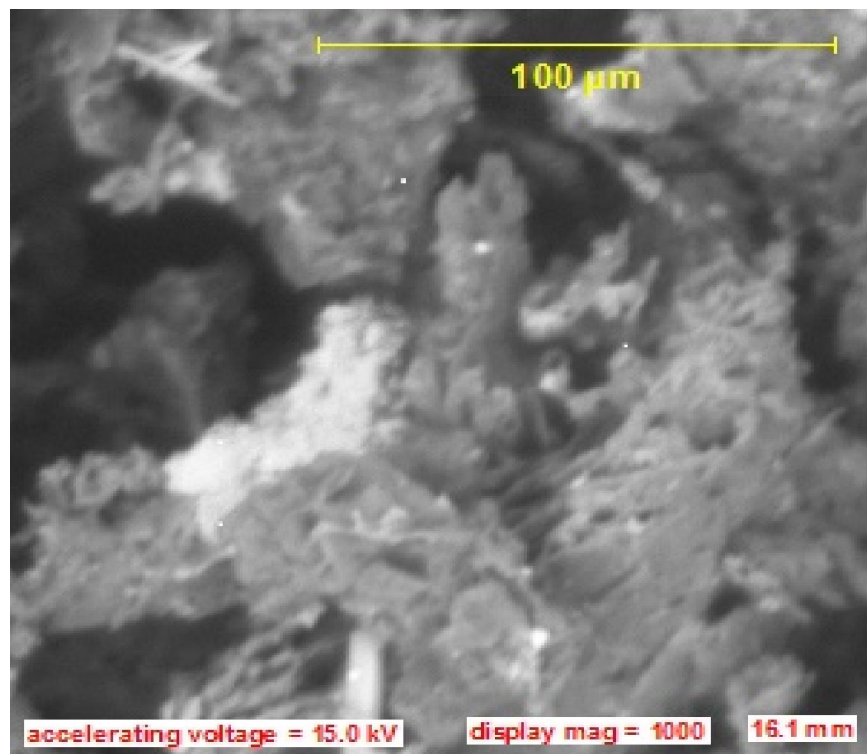


Fig.3: SEM image of ACWR sample with 0.5M Na<sub>2</sub>CO<sub>3</sub> before MB adsorption (after activation)

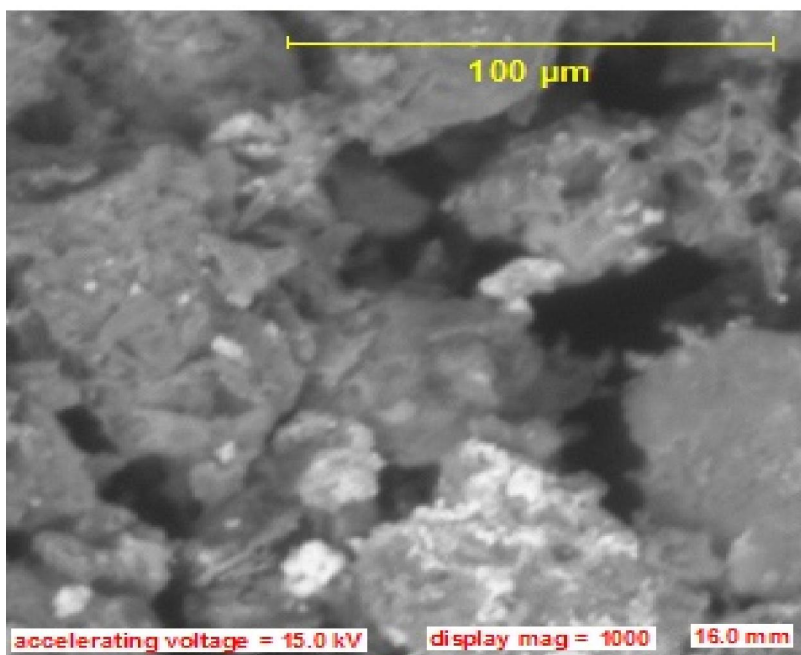


Fig.4: SEM image of ACWR sample with 0.5M Na<sub>2</sub>CO<sub>3</sub> after adsorption

#### Freundlich Isotherm

The plot of  $\log q_e$  against  $\log C_e$  to obtain the Freundlich's isotherm parameters.  $K_f$  and  $n$  characteristic of a sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models (Guadalupe et al, 2008). Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data, the smaller  $1/n$ , the greater the expected heterogeneity. The constant  $K_f$  is an approximate indicator of

adsorption capacity, while  $1/n$  is a function of the strength of adsorption in the adsorption process (Voudrias et al, 2002). If  $n = 1$  then the partition between the two phases are independent of the concentration. If value of  $1/n$  is below one it indicates a normal adsorption. On the other hand,  $1/n$  being above one indicates cooperative adsorption (Mohan and Karthikeyan, 1997). This expression reduces to a linear adsorption isotherm when  $1/n = 1$ . If  $n$  lies between one and ten, this indicates a favorable adsorption process (Goldberg, 2005).

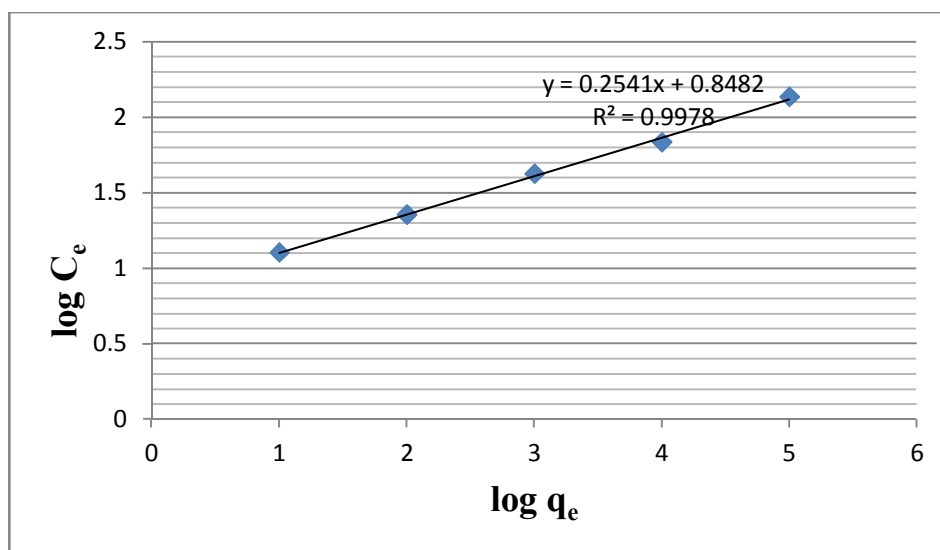


Fig.2: Freundlich isotherm plot of Adsorption of MB unto 0.5M Na<sub>2</sub>CO<sub>3</sub> ACWR



From the plot in Fig.2, the value of  $1/n = 0.2541$ ,  $K_f = 7.050$  while  $n=3.935$  indicating that the adsorption of MB unto ACWR is favorable and the  $R^2$  value is 0.9978 which shows that the adsorption data fit well into the Freundlich isotherm as earlier predicted from the multi-layer adsorption, as opposed to the monolayer, obtained from SEM images. This was confirmed by low  $R^2$  in the unreported Langmuir isotherm into which the adsorption data do not fit well.

### Conclusion

This study has shown that water melon rinds is a new, cheap and easily available agricultural waste from which activated carbon could be produced for effective waste water treatment containing basic dye pollutants such as methylene blue. In a two-step activation of water melon using  $\text{Na}_2\text{CO}_3$  as the activating agent at 0.5M can remove up to 99.27% methylene blue in an aqueous solution. The activated water melon rind achieves this feat of adsorption efficiency due to relatively high pH, density and dry matter as well as low moisture content, ash and carbon content as the physico-chemical characteristics.

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