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 citrus 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 Na₂CO₃ as the activating agent. Elemental analysis using EDXRFl, 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⁻³ 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 (K₉=7.05) and value of R²=0.9978 indicative of favorable adsorption of MB process onto the activated carbon from water melon rind.


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 7x10⁶ tons 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
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’zër 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; G’urses 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 (Bhattacharryya 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 (Na<sub>2</sub>CO<sub>3</sub>) 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 48 hours. They were dried in an air oven for 24 hours at 70°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°C for 5 minutes 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 cm<sup>3</sup> of 0.01M Na<sub>2</sub>CO<sub>3</sub>. The mixture was introduced into a muffle furnace at 700°C for activation times of 5 minutes and 10 minutes 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 250µm and 500µm 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 55Fe is 220 eV FWHM with 12µs shaping time constant for the standard setting and 186 eV FWHM with 20µs time constant for the optional setting. The optional setting used recast measurements with the resolution of 186 eV for the 5.9 peak of 55Fe. 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 10cm³ distilled water. It was transferred into a 100cm³ standard flask, shaken and made up to mark (Gimba et al., 2009). Different concentrations of the MB were prepared by taking each of 0.1cm³, 0.2cm³, 0.3cm³, 0.4cm³, 0.5 cm³, 0.6 cm³ and 0.7cm³ 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 250µm of 0.1M Na₂CO₃ concentration activated for 5minutes. These were equilibrated with 2cm³ of distilled water. 4cm³ 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 25cm³ of MB solutions with known initial concentrations were prepared in series of 25 cm³ volumetric flasks. 0.2 g of watermelon rind activated charcoal of 0.5M Na₂CO₃ with particle size 250µM 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 Na₂CO₃) 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 Na₂CO₃ 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>
<thead>
<tr>
<th>Samples (ppm)</th>
<th>K</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Rb</th>
<th>Se</th>
<th>Co</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw WR</td>
<td>2.2037</td>
<td>6925</td>
<td>956</td>
<td>2788</td>
<td>2098</td>
<td>3086</td>
<td>2218</td>
<td>954</td>
<td>527</td>
<td>929</td>
<td>240</td>
</tr>
<tr>
<td>CWR</td>
<td>2.5866</td>
<td>9105</td>
<td>270</td>
<td>3885</td>
<td>796</td>
<td>1011</td>
<td>1074</td>
<td>371</td>
<td>191</td>
<td>285</td>
<td>114</td>
</tr>
<tr>
<td>ACWR</td>
<td>5.7976</td>
<td>65473</td>
<td>2469</td>
<td>73602</td>
<td>119</td>
<td>223</td>
<td>677</td>
<td>159</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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°C) to carbonization (500°C) and then to activation (700°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 Masahirim (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 Na₂CO₃ 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⁻³ which are higher than the minimum requirement of 0.25gcm⁻³ 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**

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

**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 (qₑ) are favored at 10 than 5 minutes activation time for each initial concentration (C₀) 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**

<table>
<thead>
<tr>
<th>Samples (250µm)</th>
<th>5mins</th>
<th>10mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc of AA (M)</td>
<td>$C_0$ (g/L)</td>
<td>$C_e$ (g/L)</td>
</tr>
<tr>
<td>0.01</td>
<td>1.199</td>
<td>0.119</td>
</tr>
<tr>
<td>0.025</td>
<td>1.199</td>
<td>0.171</td>
</tr>
<tr>
<td>0.050</td>
<td>1.199</td>
<td>0.284</td>
</tr>
<tr>
<td>0.075</td>
<td>1.199</td>
<td>0.237</td>
</tr>
<tr>
<td>0.10</td>
<td>1.199</td>
<td>0.376</td>
</tr>
<tr>
<td>0.50</td>
<td>1.199</td>
<td>0.023</td>
</tr>
<tr>
<td>1.0</td>
<td>1.199</td>
<td>0.046</td>
</tr>
</tbody>
</table>

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.

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

<table>
<thead>
<tr>
<th>Samples 0.5M Na$_2$CO$_3$(500 µm)</th>
<th>$C_0$ (g/L)</th>
<th>$C_e$ (g/L)</th>
<th>$C_a$ (g/L)</th>
<th>%RE</th>
<th>$q_e$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60mg</td>
<td>1.199</td>
<td>0.7009</td>
<td>0.4985</td>
<td>41.56</td>
<td>207.71</td>
</tr>
<tr>
<td>80mg</td>
<td>1.199</td>
<td>0.6214</td>
<td>0.5780</td>
<td>48.19</td>
<td>180.63</td>
</tr>
<tr>
<td>100mg</td>
<td>1.199</td>
<td>0.4829</td>
<td>0.7164</td>
<td>59.73</td>
<td>179.10</td>
</tr>
<tr>
<td>120mg</td>
<td>1.199</td>
<td>0.3482</td>
<td>0.8512</td>
<td>70.97</td>
<td>177.33</td>
</tr>
</tbody>
</table>

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

**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 µm 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.

**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**

<table>
<thead>
<tr>
<th>Volume (cm$^3$)</th>
<th>7hr</th>
<th>2hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_0$ (g/L)</td>
<td>$C_e$ (g/L)</td>
</tr>
<tr>
<td>0.1</td>
<td>0.125</td>
<td>0.080</td>
</tr>
<tr>
<td>0.2</td>
<td>0.236</td>
<td>0.093</td>
</tr>
<tr>
<td>0.3</td>
<td>0.346</td>
<td>0.186</td>
</tr>
<tr>
<td>0.4</td>
<td>0.359</td>
<td>0.185</td>
</tr>
<tr>
<td>0.5</td>
<td>0.361</td>
<td>0.163</td>
</tr>
<tr>
<td>0.6</td>
<td>0.623</td>
<td>0.164</td>
</tr>
<tr>
<td>0.7</td>
<td>1.552</td>
<td>0.084</td>
</tr>
</tbody>
</table>

For varying MB concentration, data were taken at equilibrium times of 7 and 21 hours as can be seen in Table 5. An increase in the initial MB concentration (from addition of the 0.1cm$^3$ to 0.7cm$^3$ 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 Na_2CO_3 for 10mins using particle sizes of 250 and 500µm. 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>
<thead>
<tr>
<th>Samples 0.5M Na_2CO_3(10mins activation)</th>
<th>C_0 (g/L)</th>
<th>C_e (g/L)</th>
<th>C_a (g/L)</th>
<th>%RE</th>
<th>q_e (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250µm 60mg</td>
<td>1.199</td>
<td>0.0883</td>
<td>1.1905</td>
<td>99.2</td>
<td>79.37</td>
</tr>
<tr>
<td>500µm 60mg</td>
<td>1.199</td>
<td>0.1414</td>
<td>1.0579</td>
<td>88.2</td>
<td>70.53</td>
</tr>
</tbody>
</table>

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 (Na_2CO_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 Na_2CO_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...
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 Na₂CO₃ before MB adsorption (after activation)
**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).
From the plot in Fig. 2, the value of $1/n = 0.2541$, $K_r = 7.050$ 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 watermelon 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 watermelon using $Na_2CO_3$ as the activating agent at 0.5M can remove up to 99.27% methylene blue in an aqueous solution. The activated watermelon 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.

**References**


