ANALYSIS OF WATERMELON PEEL AND LEMON PEEL AS LOW COST NOVAL BIOADSORBENTS

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Abstract

Fruit peels are low cost lignocellulosic matter which generated from many food processing industries and household as a organic waste. They have some potential for recycilization. In this paper two fruit peel lemon and watermelon which is easily available in large volume was taken to analysis. There physical, chemical and surface characterization was done. The fruit peel was analyzed by SEM, EDX and FTIR spectra to identify textural structure, chemical analysis of various functional group and element. The pH value and $pH_{pzc}$ was found in the range of 5-6. The water absorption capacity and iodine value was examined higher for lemon peel 11.5 (ml/g) and 122.78mg/g respectively. The micropores were present in higher number in lemon peel and watermelon peel exhibited angular fibrous structure. An FTIR spectrum was strongly associated with the presence of various functional groups like carboxylic acid, ester, amino acid and alcohols. This study provide better results to interpret resources of this two fruit peel and suggest that biomaterial is identified as a novel adsorbent with low cost value.

Keywords – Organic Waste, proximate analysis, Surface Character, FTIR, Iodine Index.

1.INTRODUCTION

In Global Economy, Water plays an important role. Water covers 71% of Earth surface in sea and ocean, distributed as ground water 1.7%, occur 1.7% in glacier and ice form and very small amount as vapors and precipitate form. Only 2.05% of water on the surface of Earth is endowed with the balance in fresh water, lake, river and ground water (1). As Earth population grows and the demand for fresh water increases. Water is used for domestic, industrial water supply and also used in agriculture area for irrigation (2). The major source of water contamination is waste dump, urban sewage, septic tanks, industrial influents, atmospheric deposition and agriculture surface runoff (3). In India, 92% of ground water was used in agriculture area, 5% for industrial operation and only 3% for domestic sector (4). Agriculturesurface runoff is main source of pesticides (5). In urban area pesticide is used not only for irrigation area but also in industrial vegetation control, in Horticulture and plant nursery and domestic plantation. Growing population is associated with extensive usage of pesticides. The substantial worth of pesticides is accountable for organic contamination of water because of their leaching and runoff losses (6, 7). In the last decades the existence of pesticides residue in ground and surface water has turn to be an extensive and burning issue of discussion(7).

There is getting higher interest to find out cost effective, simple, innovative method that will be useful in the treatment of organic contamination in water. In recent year, Activated carbon is commonly used as a adsorbent to remove organic pollutants from water. Activated carbon is amorphous solid with low-volume pore that increases the surface area for adsorption. However, its uses are limited due to its high cost (8, 9).

In present year, different non-conventional adsorbents have been used because of their low cost value. There are five categories of these non-conventional adsorbents – (a)Bioadsorbent (b)Fruit waste
The present work is based on fruit peel waste that is precipitated from the food processing industries and households. Lemon (Citrus Limon (L.) Osbeck) belongs to Rutaceae family. The lemon plant forms an evergreen spreading small tree, 3-6 meter high like shrub that is native to south Asia predominantly North Eastern India. It’s young oval leaves have a decidedly reddish tint later they turn green and its fruit is oval with broad low and form 8 to 10 segment. Lemon peel has exterior yellow peel called epicarp consists flavedo and interior white spongy peel called mesocarp consists albedo is rich in pectin. Another byproducts of lemon are citrate of lime, lemon oil, citric acid and pectan. Lemon peels is very low in calories while high in fiber, vitamin C and D-limonene.

Watermelon (Citrullus lanatus) belongs to flowering plant family cucurbitaceae. It is an annual plant, that is, it can only survive in one growing season. It is type of creeper plant with scrawling and trailing stem which are five- sided angle and long up to 3mm. This plant originated in southern Africa but Now-a–days it has grown in India and as well as in China. Watermelon are popular fruit of summer usually consumed fresh in slices, mix with fruit salad and used for making juices. Watermelon containing 92% water, 6% sugar and little amount of fat 0.16%. Only 50% fleshy portion was consumed and remaining 50% portion consisted rind and peel. Now–a–day’s researcher has interested to find out bioactive compound from fruit waste that used in the treatment of deleterious diseases from Watermelon rind.

In recent work, we studied about physic-chemical characterization, surface morphology and functional properties of watermelon and lemon peel. Different standard method used to characterized fruit peel as a potentially used as a bioadsorbent. The biomass was characterized by titrimetric, gravimetric, iodometric and instrumental analysis. The result of this study shows various properties of fruit peel and suggest that this biomass should be utilized as novel adsorbents.

2. Material and Method

2.1 Sample preparation for analysis

Watermelon and lemon are collected from local market area. Firstly peel off fruit outer layer and washed with double distilled water. Peel were dried in sun light for 2-3 days then it was further oven dried for 24h at 90° until constant weight was obtained. The dried peels were grinded and sieved through 125µm size sieve. The final product was kept in a clean, airtight, polyethylene bottles.

2.2 Chemicals

All reagents used in methods were of analytical grade and supplied from sigma Aldrich, USA. All glassware was used of borosil.

2.3 Instrumentation

Proximate analysis was done to determine moisture content, ash, volatile matter and fixed carbon percentage. Physic-chemical properties like pH, bulk density, Iodine value and surface charges were determined through standard method. The pH value of the solution was determined using Hanna pH meter with glass electrode. The functional group identified from FTIR (Perkin Elmer, Spectrum-2) was recorded in the frequency range from 450-4500 cm⁻¹ by 16 averaging scan. The Fruit peel powder sample was coated with thin layer of gold coating [Quorum, SC7620 Sputter Coater, Coating time: 120 sec with 20mA]. The microphotograph of these sample were examined using Scanning electron microscope.
(ZEISS EVO 18) equipped with EDX analyzer. Scanning electron microscopy was used to determine surface morphology and EDX (Energy Dispersive X-ray) were used for elemental detection.

2.4 Proximate Analysis

Proximate analysis was carried out according to standard method. To determine moisture content sample was treated at 103°C for an hour in hot air oven without lid. When constant weight was obtained then sample was kept in desiccators till temperature reached at room temperature. Moisture content was calculated from equation (1). To determine volatile matter, sample was heated in silica crucible with lid at 925°C in muffle furnace and after cooling in desiccators weighed and calculated through equation (2). Ash percentage was calculated through equation (3). Firstly sample was inflamed without lid at 250°C for first half an hour and then temperature increased to 580-600°C until all carbonaceous material was burnt. Fixed carbon was determined after subtracting the sum of volatile matter, moisture content and ash percentage from 100 and calculated through equation (4)(17).

\[
\text{Moisture} \% = \frac{\text{Loss in weight of sample after drying}}{\text{weight of initial sample}} \times 100 \ \ldots \ldots \ldots (1)
\]

\[
\text{Volatile Matter} \% = \frac{\text{Loss in weight after heating sample}}{\text{weight of initial sample}} \times 100 \ \ldots \ldots \ldots (2)
\]

\[
\text{Ash} \% = \frac{\text{weight of ash obtained}}{\text{weight of initial sample}} \times 100 \ \ldots \ldots \ldots (3)
\]

Fixed Carbon percentage = 100-(Moisture% + Volatile Matter% + Ash %)………………(4)

2.5 Method to find pH and Bulk density

The pH of the sample was measured by adding 1gm of sample to the 100ml of distilled water in a beaker and continues agitating for an hour. The solution was kept for stabilization and measure final pH value. Bulk density (18) was calculated according to equation (4).

\[
\text{Bulk density (gm/l)} = \frac{M_2 - M_1}{V}
\]

Where \( M_2 = \) mass of cylinder with sample
\( M_1 = \) mass of vacant cylinder
\( V = \) cylinder volume

2.6 Determination of Iodine Index

To determine the iodine number standard method was adopted from Gimba and Musa (19). Iodometric titration was performed with stock solution containing 2.7g of iodine crystal and 4.1g of potassium iodide per liter and standardized with 0.1M sodium thiosulphate. 0.5gm of biomass sample was taken in 100ml volumetric flask and 10cm³ of 5% \( \frac{\text{v/v}}{\text{v/v}} \) HCl was added until sample was wetted. Then 100cm³ of iodine stock solution was added and shaken for an hour in electric shaker. The mixture was filtered and an aliquot (20ml) was back titrated with 0.1M sodium thiosulphate using starch indicator. The concentration of adsorbed iodine was calculated using Equation (5).
\[
I_{mg} = \frac{(B-S)}{B} \times \frac{VM}{W} \times 253.81 \ldots \ldots (5)
\]

B = volume of thiosulphate solution for blank titration
S = volume of thiosulphate solution for sample titration
W = mass of activated sample
M = concentration (mol) of iodine solute
V = 20ml aliquot
253.81 atomic mass of iodine.

2.7 Determination of surface charge

According to acid-base titration method surface acidity and basicity were determined (20).

2.7.1 Surface Acidity

To determine surface acidity 500mg of sample was added to 50ml of 0.1N NaOH and took the solution in thermostatic shaker at 30°C for 24 hour. After some time mixture was processed to filter and take an aliquot and back titrate with 0.1N HCl using phenolphthalein indicator. To the end point amount of acidic group available was determined in mmol/g.

2.7.2 Surface Basicity

Basicity of biomaterial was determined by put together 500mg of sample and 50ml of 0.01HCl solution. The solution was kept in thermostatic shaker for 24 hour at 30°C with continues stirring. The residual solution were filtered and back titrated against 0.01N NaOH solution to determine the end point and no. of basic sites available is showed in terms of mmol/g. The amount of HCl that reacted with the absorbent was then used to calculate the number of surface basic sites while the amount of NaOH reacted with the absorbent was used to calculate the number of surface acidic sites (27). The acidity and basicity was calculated from equation 6.

\[
\text{Acidity/ Basicity} = \left( \frac{\text{Normality} \times \text{Volume consumed}}{\text{Molecular weight}} \right) \times \frac{\text{Initial volume}}{\text{selected volume for titration}} \ldots \ldots (6)
\]

2.8 Determination of point zero charge

The determination of pH_{pzc} has been following salt addition method (21). To determine pH_{pzc}, 0.01M NaCl was used. Took 50ml of this solution and adjust the pH of solution at 2, 4, 6, 8, 10 and 12 by used HCl and NaOH solution. When pH value was stabilized then 150mg of material added to the series of bottles of different pH value and kept the bottle for shaking at room temperature for 24 hours in air tight condition. After 24 hours the final pH value was measured. When a graph of final pH verses (initial – final) pH was plotted and where the curve cuts X axis, these point is defined as pH_{pzc}.
3. Results and Discussion

3.1 Physicochemical analysis of fruit peel

Table 1 shows proximate analysis result of watermelon and lemon peel. Very low moisture content of watermelon and lemon peel (3%) is resistant to microbial growth and increases combustion yield. It is easy to store this material for long period and no need to extra precaution. This peels are contains few organic matter like lipid, protein, carbohydrates due to volatile matter content. They are good source of nutrients. Lemon peel has more volatile content (31%) with compare to watermelon peel (28%) due to sulfur monoterpenoid, aliphatic and olefin non-terpenoid aldehyde, ester, ketone and also aromatic compound. The Ash content has found in lemon (3%) and watermelon peel (4%) in the form of incombustible solid material. Low ash content causes low cost of transport, handling and management cost. High yield of fixed carbon obtain from lemon (63%) and watermelon (65%) peels. They are good raw material for charcoal (carbon) production. Activated charcoal is a great adsorbent because of its huge surface area; due to very big surface area per unit of mass it can absorb a lot of particles. Actually, process of ‘activating’ charcoal is designed to maximize the surface area to mass ratio.

Table 1 – Proximate analysis of peel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Watermelon peel</th>
<th>Lemon peel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Ash</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>65</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 2. Physico-chemical properties of peel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Watermelon peel</th>
<th>Lemon peel</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.63</td>
<td>6.46</td>
</tr>
<tr>
<td>Bulk density(g/ml)</td>
<td>0.52</td>
<td>0.36</td>
</tr>
<tr>
<td>Iodine Index (mg/g)</td>
<td>122.78± 0.3</td>
<td>103.54± 0.5</td>
</tr>
<tr>
<td>Water absorption Capacity (ml/g)</td>
<td>11.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Table-2 represents physico-chemical properties of peel such as pH, bulk density, and iodine value and water absorption capacity. When a known amount of peel included to the water, few chemical changes occurred due to some compounds discharge from peel to the water that’s result with pH change. This property provides information about surface pH of the final solution. Final pH of watermelon peel and lemon peel 6.63 and 6.64 respectively. Bulk density of watermelon peel (0.52g/ml) is greater than lemon peel (0.36g/ml). Bulk density of both peel are different due to various factor like air between the individual powder particles, particles size and shape. For most of the adsorbent biomass have low bulk density accompanied by high porosity. Increasing porosity is accessed the volume of trapped air. When hydration process is occurred protein and other starch mineral create hydrogen bond and hydrophilic reaction with water molecule, this are responsible for high water absorption capacity. Water absorption capacity of watermelon peel (11.5ml/g) is found higher than lemon peel (6.6ml/g). High
absorption capacity and low density has being the primary cause of problems as transporting, storage and heating.

Determination of iodine number is the method to determine the capacity of adsorption of biomaterial. It is a measurement of micropore (0-20Å) content of the solid surface of biomaterial by adsorption of iodine from solution. This method includes the adsorption of iodine in the form of I⁺ complexes. Iodine can be adsorbed on the surface of solid only in the form of the elementary I₂ that results from the oxidation of iodide ions on the surface of carbon (24). Standard determination of the iodine adsorption number consists of the measurement of iodine amount in the adsorption layer of an activated carbon sample (in mg iodine/g adsorbent). As suggested in above table 2 iodine value obtained for watermelon peel (122.78± 0.3) is higher than lemon peel (103.54± 0.5). These values indicated that watermelon peel has higher number of active sites with compare to lemon peel.

3.2 Surface Charges Characterization

The characteristics of surface are associated with the surface group to a very extent. Surface charge appears on the biomass surface when it is placed into acid or base solution, containing H⁺ or OH⁻ Respectively. These ions interact with the object surface. These interactions might lead to the adsorption of some of them on to the surface. From the table 3, it is concluded that both peel has more acidic sites than basic sites. The number of acidic sites for lemon peel and watermelon peel are 0.167 mmol/g and 0.153mmol/g, while the basic sites value is corresponding to 0.042 mmol/g and 0.067 mmol/g. The comparative study between acidic and basic sites suggesting that the more oxygenated functional group like carboxyl, lactone and phenol is present in higher concentration on the fruit peel surface (25, 26). In this case we can say that both peels are good adsorbent for cationic pollutants in compare to anionic pollutant (table 4).

Table 3- Surface charges of fruit peel

<table>
<thead>
<tr>
<th>Adsorbent peel</th>
<th>Acidic sites</th>
<th>Basic sites</th>
<th>pH_pzc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lemon peel</td>
<td>0.1616</td>
<td>0.0425</td>
<td>5.3</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>0.153</td>
<td>0.0675</td>
<td>5.6</td>
</tr>
</tbody>
</table>

3.3 Point Zero Charge (pH_pzc) of fruit peel

Point zero charge is a value of the negative logarithm of the activity in the bulk of the charge determining ions and value of surface charge density is equal to zero. It means particle obsessed equal number of positive and negative charges. When the solution pH reached at this point, particles does not moving in the electric field. pH_pzc value has important characteristics of an adsorbent Adsorption phenomenon of any adsorbent depends on the concentration of proton (H⁺) and hydroxyl ion (OH⁻) that lies on surface and determine pH_pzc value of adsorbent (26). When pH of any solution is low, hydrogen ion should be adsorbed more than other cations (adsorbate) in the case of negatively charged particle. On the other hand when pH is increased, hydroxyl ion concentration also increased then other anion will be less adsorbed. So we can state that from view of an adsorbent if the pH value of an adsorbent is below than pH_pzc (pH<
pH_{pzc}) anion could be adsorbed due to positive surface charge intentionally the pH value of an adsorbent is above than pH_{pzc}, (pH> pH_{pzc})cation could be adsorbed due to negative surface charge(25, 27).

As demonstrated from fig 1 and table 3 the experimental curve (pH versus pH_i-pH_f) of point zero charge following of lemon peel and watermelon peel is in the range of 5-6, this value close to neutral therefore, they can be used for both cationic and anionic pollutants. Table 4 outlines previous work done with this peel for removal of dyes and heavy metals. The presented data concluded that lemon peel and watermelon peel both are given satisfactory result for anionic and cationic impurities.

Table- 4. Reported adsorption capacity in (mg/g) of some anionic and cationic pollutants on fruit peel

<table>
<thead>
<tr>
<th>Fruit peel</th>
<th>Adsorbate</th>
<th>Ion</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lemon peel</td>
<td>Congo red</td>
<td>Anionic</td>
<td>34.5</td>
<td>Bhatnager et. al.</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>Methyl orange</td>
<td>Anionic</td>
<td>50.0</td>
<td>Bhatnager et. al.</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>Cobalt</td>
<td>Cationic</td>
<td>22.0</td>
<td>Bhatnager et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Methylene blue</td>
<td>Cationic</td>
<td>188.68</td>
<td>Jawed et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Cu^{2+}</td>
<td>Cationic</td>
<td>5.73</td>
<td>Liu et. al.</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>Pb^{2+}</td>
<td>Cationic</td>
<td>19.556</td>
<td>Tovar et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Remazol Brilliant Blue R, Remazol Brilliant violet 5R</td>
<td>Anionic</td>
<td>1.046, 1.036</td>
<td>Kanthasamey S et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Remazol Brilliant</td>
<td>Anionic</td>
<td>1.566</td>
<td>Kruger M et. al.</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>Pb^{2+}</td>
<td>Cationic</td>
<td>19.556</td>
<td>Tovar et. al.</td>
</tr>
<tr>
<td>Lemon peel</td>
<td>Malachite green, Pb^{2+}</td>
<td>Cationic</td>
<td>66.67, 90.91</td>
<td>Mohammad et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Cr^{3+}</td>
<td>Cationic</td>
<td>172.6</td>
<td>Reddy et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Cu^{2+}</td>
<td>Cationic</td>
<td>5.73</td>
<td>Liu et. al.</td>
</tr>
<tr>
<td>Watermelon peel</td>
<td>Congo red</td>
<td>Anionic</td>
<td>20.72-26.06</td>
<td>Ibrahim et. al</td>
</tr>
</tbody>
</table>

3.4 Fourier transforms infrared spectroscopy

The FTIR technique is an important approach to distinguished characteristics functional group which is able to adsorbing any heavy metal or organic pollutants efficiently. As demonstrated in table 5 and fig. 2 the ftir spectra of Lemon Peel indicated that at 3288.60 cm^{-1} due to N-H and O-H vibration of secondary amine and alcohols. The band assigned symmetric and asymmetric stretching of methyl group of carboxylic acid at 2937.23 cm^{-1}. The peaks at 1724.15 cm^{-1} and 1607.35 cm^{-1} confirmed that Carboxylic acid, esters, aldehyde group present at the Lemon peel due to stretching vibration of C=O (carbonyl) and C=C stretching that may be conjugated or not. The bending vibration of C-H and O-H of carboxylic acid and alcohol found at 1428.67 cm^{-1} and 1365.18 cm^{-1}. The range of 1232.45 cm^{-1}, 1014.93 cm^{-1} and 603.89 cm^{-1}suggested that primary alcohol and amide group present in lemon peel.
Table 5. FTIR Analysis of Fruit peel

<table>
<thead>
<tr>
<th>Adsorption band</th>
<th>Characteristics Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lemon peel</td>
<td>Watermelon peel</td>
</tr>
<tr>
<td>3288.60</td>
<td>N-H and O-H vibration of secondary amine and alcoholic group</td>
</tr>
<tr>
<td>2937.23</td>
<td>Symmetric and asymmetric stretching mode of –CH3 and –CH2</td>
</tr>
<tr>
<td>„</td>
<td>Symmetric C-H stretching of alkanes</td>
</tr>
<tr>
<td>1724.15</td>
<td>Stretching vibration of C=O (carbonyl) of ester,</td>
</tr>
<tr>
<td></td>
<td>carboxylic acid or saturated aldehyde</td>
</tr>
<tr>
<td>1607.35</td>
<td>May be C=C stretching of amide group or alkenes, phenol group</td>
</tr>
<tr>
<td>1428.67</td>
<td>Bending vibration of C-H of methyl group and deformation of C-H</td>
</tr>
<tr>
<td>1365.18</td>
<td>Bending vibration of O-H and aromatic amine</td>
</tr>
<tr>
<td>1232.45</td>
<td>C-O stretching in esters, Aliphatic amide</td>
</tr>
<tr>
<td>1014.93</td>
<td>C-O stretching in primary alcohols</td>
</tr>
<tr>
<td>„</td>
<td>C-N stretching in NO₂</td>
</tr>
<tr>
<td>603.89</td>
<td>O-H bending with hydrogen bond in out of plane</td>
</tr>
<tr>
<td>527.15</td>
<td>Alkyl halide</td>
</tr>
</tbody>
</table>

From the results demonstrated in table-5 and fig.3 it should be concluded that watermelon peel showed a strong peak 3288.79 cm⁻¹ due to N-H vibration of Amide Group. The stretching vibration of C-C at 2917.50 cm⁻¹ and 2765.18 cm⁻¹ and its bending vibration peaks found at 1485.67 cm⁻¹ and O-H bending at 1334.87 cm⁻¹. This band showed that, alkanes, methyl or ethyl group of carboxylic acid and esters and primary alcohol. The peaks at 1795.23 cm⁻¹ and 1611.17 cm⁻¹ observed due to C=O and C=C stretching suggested that carbonyl group of aldehyde, alkenes and phenolic group. The stretching peak centered at 1232.45 cm⁻¹ and 1014.93 cm⁻¹ confirms primary alcohols and aliphatic amide. The strong peak obtained at 527.15 cm⁻¹ confirm alkyl halide compound.

Fruit peel have consisted large quantity of cellulose, lignin and pectin. These compounds are large skeleton of carboxylic acid. FTIR spectrum of fruit peel showed broad spectrum of stretching vibration of –CH₃ or –CH₂ group of carboxylic acid. They are major source of the adsorption of cationic dyes, due to the deprotonation or protonation of surface group. The involvement of hydroxyl and phenol compound with hydrogen bonding responsible for the interaction between anion adsorbent and dye particles (15, 20, 40).

3.5 Electron scanning microscopy

Scanning electron microscopy with energy dispersive X-ray analysis is a combination of techniques which are used to provide both physical and chemical information with sub-micron resolution. Microstructure evaluation ranges from simple determination of certain parameters such as pore size,
coating thickness and topology to full surface characterization of material. The surface of lemon peel is unsymmetrical with highly porous structure and watermelon peel surface is indented and skewed with tiny pores. The particles shape and size are different in both peel as showed in fig.4 and fig.5. Pore size distribution has been used to describe the internal structure and adsorption capacities of activated carbons. The EDX spectra of lemon peel (fig.6) and watermelon peel (fig.7) indicated high content of carbon (16.68% and 75.96%) and oxygen (20.55% and 70.05%) according to weight percentage. The data of various other beneficial elements present in fruit peel showed in table 6. Lemon peel was contained least amount of Mg (0.51%), Fe (0.05%) and Cu (0.44%) and few amounts of K (3.20%) and Ca (3.01%). A small amount of P (0.46%), Ca (0.90%) and Mg (0.58%) examined in watermelon peel. Potassium ion (5.66%) in watermelon peel has showed in table 5 found more than lemon peel. A large number of functional group contains carbon and oxygen is responsible for adsorption of organic contaminant. These results also accompanied with FTIR spectra. Potassium in plant biomass remains in the form of cation where it is neutralized organic acid and other anionic groups. Magnesium and Calcium was found in ionic form as the divalent ion. Copper and iron was done similar in redox enzymes and allowed electron transfer reaction accompanied with valence change from Cu+ to Cu2+. Phosphorus may be present in the form of phosphate anion. These elements in ionic form should be responsible to different types of adsorbent surface in adsorption.

<table>
<thead>
<tr>
<th></th>
<th>Lemon peel</th>
<th></th>
<th>Watermelon peel</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Element</td>
<td>Weight%</td>
<td>Atomic %</td>
<td>Element</td>
</tr>
<tr>
<td>C</td>
<td>16.68</td>
<td>21.96</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>O</td>
<td>75.96</td>
<td>75.06</td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Mg</td>
<td>0.51</td>
<td>0.33</td>
<td></td>
<td>Mg</td>
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<tr>
<td>K</td>
<td>3.20</td>
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<td>P</td>
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<td>Ca</td>
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<td>Fe</td>
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</tr>
<tr>
<td>Cu</td>
<td>0.44</td>
<td>0.11</td>
<td></td>
<td>Ca</td>
</tr>
</tbody>
</table>

4. Application of fruit peel for future prospective

In global scenario India is second largest fruit producer with a production of 49 million MT and contribute 10% of global value (12). Chhattisgarh is 9th largest and rapidly developing state in India. About 82% of the population is rural and their occupation depends on the Agriculture and Horticulture. In Chhattisgarh total area of fruit crop is 2, 56,776 Ha along with the production of 25, 42,241 MT in the year 2018-2019(Horticulture Statistics Division Department of Agriculture, Cooperation & Farmers
In urban areas, the nutritional intake of fruit is higher compared to rural areas. Figure 6 and 7 represent year-wise area and production of watermelon and lemon in Chhattisgarh state. These data were reported at 110.897 MT production for lemon and 52.13 MT for watermelon peel in 2017-18. This records an increase from the previous number of 89.03 MT for lemon and 32.16 MT for watermelon in 2016. Chhattisgarh data remains active status in 2018 from previous year. It was also showed that utilization of this fruit was also increased parallel to the production (Department of Agriculture, India).

High quantity of this biomass through off to the municipal landfills from food processing industries. They cause a serious problem to the environment due to their high biodegradability. It is mandatory to convert this biomass into value-added products to avoid solid waste handling (15, 12). This fruit peel assigned as adsorbent was also helpful to clean environment through elimination of this solid waste. This biomass also will be utilized potentially for different applications such as low cost biodegradable products and raw material to produce biofuel and bioenergy and the proximate analysis data showed higher quantity of carbon and volatile matter (Table 1). Various types of physicochemical analysis, surface analysis, and spectral data indicate that both peels have shown favorable outcomes in adsorption of different types of organic pollutants like heavy metal, dyes, and pesticides (Table 4).

Ewansiha, J.U. et al. proposed different phytochemical constituents—saponins, alkaloids, flavonoids, anthraquinones, volatile oil, resins, phenols, cardiac glycosides, tannins, terpenes, and steroids were present in the lemon peel extract and distributed among the different extract (42). These constituents have possessed various biological activities against chronic diseases. Citric acid has been used in the treatment of intestinal disorders. It has antioxidant properties and also boosts our immune system (41). Limonene increases enzyme activity that helps reduce oxidative stress. Oxidative stress is associated with tissue damage. Flavanoids may stimulate immune system to protect our health (43). Pectin may reduce cholesterol levels by increasing the excretion of bile acid. D-Limonene has anticancer properties especially for stomach cancer and may help treat gallstones of gall bladder (40).

Watermelon Rind possesses a variety of vitamins like vitamin A, B, C, and K, mineral salts K, Mg, Fe, Ca, and amino acids arginine and citrulline. Polysaccharides which isolated from Watermelon rind has various medicinal properties like antioxidant, antihypertensive, ACE inhibitors and also identified galactose, rhamnose, mannose, arabinose, glucose, galacturonic acid, xylose and traces of glucuronic
acid(44). Recently watermelon waste product have used as a anticorrosive material for mid steel (45). Watermelon peels have some pharmacological importance. It shows significant (analgesic activity due to the presence of flavanoids, tannin, glycosides, saponin and phytosterol (46). Watermelon rind has exhibited antifungal and antibacterial potential against bacterium Escherichia coli and fungus Canelida albican (47). Saponin shows hemolytic activity and cholesterol binding properties and Alkaloids in watermelon rind as anticancer reagent (46).

5. Conclusion

In present paper we studied physic-chemical and surface characterization in detail and dealing with their potential reutilization as a bio-adsorbent. We have discussed their potential use in the environmental and medicinal field. The proximate analysis of lemon and watermelon peel showed higher content of carbon and low content of ash, moisture and volatile matter. It means, it should be used as a good fuel. The pH and pH pzc value of fruit peel is around to 6 is concluded that it can be used for both cationic and anionic pollutants but it contains more acidic sites instead of basic sites. So we can say that they have more efficiency to remove cationic pollutants. FTIR results confirm the presence of types of functional group such as carboxylic acid, amide group, alcohol, halide and alkanes in both peels. Lemon peel surface has more pores than watermelon peel and they both have irregular surface. EDX spectra concluded that they have more nutritional element like Ca, Fe, Mg, P and K play an important role in plant biomass.

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7. References


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Fig. 1 Point zero charge value of lemon peel and watermelon peel for salt addition method for 0.01 NaOH.

Fig. 2 FTIR Spectrum of lemon peel
Fig. 3. FTIR Spectrum of watermelon peel.

Fig. 4. SEM images of lemon peel.
Fig. 5- SEM image of watermelon peel

Fig. 5 EDX spectra of lemon peel

Fig. 6 EDX spectra of watermelon peel