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Removal efficiency of heavy metals from aqueous solutions by albedo of pomelo fruit

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ABSTRACT
The aim of this study was to use low cost adsorbents, which consist of inner peel (albedo) of pomelo fruit as a plant wastes adsorbents for removal of heavy metals from aqueous solutions by packed bed column technique(PBC). The effect of three variables: pH value, contact time and chemical modification were investigated samples of plant waste (albedo) were tested to determine the phytochemical materials that contained in it, and estimate its removal efficiency which gives the best performance in heavy metals removal. Phytochemical investigation of the albedo showed the presence of flavonoids, tannins, coumarin, volatile oils, terpenoids, anthraquinone glycosides, pectin, lignin and cellulose. Adsorption tests of the inner peel (albedo) adsorbents showed the best removal efficiencies: 94% for Co and Ni at pH 4.5 and 98 min. 98.2% for Pb at pH 3.5 and 156 min and 96% for Cd obtained at pH 6 and 98 min. In addition, removal efficiency of albedo was increased in multi ions system than the single ions system. Moreover, results revealed that the chemically modified albedo was better than the raw albedo in multi ions system.

Keywords: pomelo fruit, Inner peel (albedo), Adsorption, Cobalt, Lead, Nickel, Cadmium, aqueous solutions.

1. INTRODUCTION
Industrial wastewater contains high levels of heavy metals that may pollute the water once it is discharged to the nature. These metals include arsenic, chromium, copper, zinc, cobalt, cadmium, lead, boron, nickel, mercury, sulfur and silver. Heavy metals are elements that have more than five times the specific gravity than that of water. They are one of the most toxic types of water pollutants. At least 20 metals are considered to be toxic, and approximately half of these metals are released to the environment in amounts that are hazardous to the environment and harmful to the living organisms, in addition to the human health [1]. Some of the treatment processes for removing heavy metals from industrial waste water include precipitation with coagulation and flocculation, ion exchange, complexing of dry biomass and adsorption. However, limitations can be found such as: Precipitation produces large amounts of heavy metals rich waste sludge; ion exchange and biomass methods are costly and cannot be readily applied to large scale applications [2].

Adsorption process is a low cost effective, applicability on large scales, relatively quick method of heavy metals removal from industrial waste water regardless of the concentration of the heavy metals or the volume of water that it is dissolved in [3]. Different materials were used as adsorbents which collect or adsorb the heavy metals from the industrial waste water. These materials include plants and agricultural wastes such as: cashew nut shells [4], olive cake, date pits and fruits, tea factory waste, maize cobs, and wood saw dust to name a few [5].Plant waste products and other natural products are readily used as adsorbates, hence, allowing for an inexpensive and feasible method of removing solids from industrial waste water [6]. Plant and agricultural wastes have many physicochemical characteristics properties including: Chemical composition (primary and secondary metabolites), functional groups (chemical groups such as: C-H, C=O, N-H, C-OH, C-O-C, O-H and C-N), surface texture, surface area, porosity and type of electrical charges. The secondary metabolites of plant wastes often refers to the cellulose, hemicellulose, lignin, pectine, silicates, phenolic compounds, essential oils, Glycosides, alkaloid and coumarins that considered major active components of plant and agricultural wastes[7]. On the other hand, type of surface electrical charges effects on pH value of the reaction medium and thus the adsorption and removal process , when pH value increases, the overall surface electrical charge on the adsorbents become negative and adsorption process decreases, while if pH value decreases, surface electrical charge become positive and adsorption process increases [8].This work is aimed to use low cost adsorbents, which consist of pomelo fruits albedo (peel pith) as plant waste adsorbents for removing heavy metals from aqueous solutions by packed bed column technique (PBC)technique as well as study the effect of two variables (pH value and contact time) on adsorption process.

2. MATERIALS AND METHODS

2.1 Collection and Preparation of pomelo albedo samples

Pomelo fruits samples were collected from local markets during December – 2016. The external peels of all samples were removed and albedo was taken and cut by a knife, all samples washed with deionized water by mixing inashakerfor24hrs. After that,water was decanted and the process was repeated three times until color removed from the samples. Then, the clean pomelo inner peels placed in a large glass dish and dried at room temperature.

After drying, clean plants wastes were crushed by binder and sievedthrougha3mmsieveto separate and remove the fine particles. Samples of albedo adsorbents were then divided into two groups (Figure 1): The first group, albedo absorbents were left as raw materials for experiments. The second group, adsorbents were treated with (0.1M) HCl for 3 hrs at 30°C for conducting chemically modification, and washed with double distilled water. After that, The adsorbents were treated with (0.1M) NaOH for 3 hrs at 30°C, and washed by double distilled water. Then, the samples were dried at 60°C [9].

All samples (Raw and Modified albedo adsorbents) were kept in precleaned plastic bottles with air tight to avoid absorption of moisture from the atmosphere [10].

Figure 1: Plant adsorbents after configuration for studies.

2.2 Phytochemical Investigation for Albedo of Pomelo

For the phytochemical investigation, hydro methanolic solvent (methanol 80%) was used for extracting the albedo by soxhlet apparatus [11] and then analyzed the extract for the determination of presence or absence of different plant constituents (secondary plant products) by usual qualitative tests of phytochemical constituents such as flavonoids (Alkali test), alkaloids (Dragendroff reagents) and Tannins (Ferric chloride test) [12], Coumarin (Alkali with Fluorescence test), Saponins (Olive oil test), Resins (acetic anhydride test) and Volatile Oils (Fluorescence test) [13], Terpenoids (Salkowski test) [14], Gum and Mucilage (Swelling test) [15], Anthraquinones glycosides (Borntrager's test) [16], Cardiac glycosides (Liebermann's test) and Pectin (Alkali test) [17], Lignin (Aniline test) [18] and Cellulose (Iodin- zinc chloride test) [19].

2.3 Preparation of aqueous Solutions

1-Standard solutions of heavy metals (single ion system)

Standard solutions of heavy metals were prepared as mentioned in [20] based on the atomic and molecular weight and the concentrations of metals

A standard solution of Cobalt, nickel, Lead and Cadmium were prepared with concentration of 50 mg/l for each of them separately by using Co $(NO_3)_2$, NiCl2, 6H2O, (CH3COO)2.3H2O and CdCl2 respectively. These solutions was passed through 0.45µm membrane filter to prevent the passage of any insoluble particles and saved as standard solutions for experiments.

2-Standard solution of Multi-ions solution (Multi-ions system)

A standard solution of multi-ions system with concentration of 50 mg/l of each cobalt, lead, cadmium and nickel was prepared by using same quantities that were used previously but in same volume of DDW. The heavy metal ions concentrations of samples of standard aqueous Solutions were measured before and after treatment by atomic absorption spectroscopy.

2.4 Experimental Design
In general, the purpose of an experimental design is to determining the optimum operation conditions through analyzing and simulating of a process with the objective of optimizing a response which is affected by several independent variables [21].

In this work, an experimental design was carried out according to the Box–Wilson design with two variables: pH value at range (3-6) and contact time at range (15-180 min.). This experimental design was chosen because it considered a suitable design for this study [22].

2.5 Laboratory Scale Design (Columns set-up)
The schematic representation of experimental column "packed bed column (PBC)" is shown in figure (2). The adsorption studies were carried out in six transparent glass columns, Each column had 2.0cm internal diameter and 30cm in height. The adsorbents (albedo) were confined in the column by fine Teflon (PTFE) filter (No. 1) at the bottom and a glass beads layer was placed at the top of the adsorbents to ensure a uniform distribution of influent through the adsorbents.

The influent waste water from plastic feed container (5 Liters) was introduced to the column through a rubber stopper fixed at the top and controlled by a valve at the lower end.

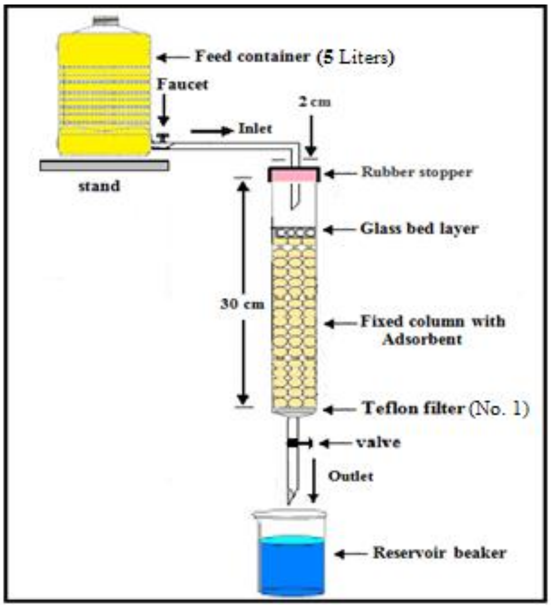

Figure 2: Experimental column (packed bed column).

2.6 Adsorption experimental procedure
All the six glass columns were washed with de-ionized water before the adsorption experiments. Columns were filled with plant wastes samples for standard aqueous solutions treatments .

Four columns were used individually for each type of heavy metal adsorption (single ion system) in order to determine and estimate the efficiency of adsorbent for treatment and removal of heavy metals.
The efficiency of adsorbent was determined according to certain parameters that were: pH value, contact time and adsorbents modification.

The fifth column was used for the treatment of multi-ions system with suitable condition (pH and contact times). Furthermore, the sixth column was used for treatment of mixture of heavy metals (multi-ions system) with modified albedo adsorbent. Finally, the experiment of regeneration of adsorbents were carried out with the same design and approach of fifth and sixth column.

2.7 Factors affecting adsorption of heavy metals
The main investigated parameters that may influence heavy metals adsorption were; pH value, contacting time andadsorbents modification**.**

1- pH value effect
The experiment was carried out according to Box – Wilson design at a range of pH from 3 to 6 for waste water contained of Co, Cd, Pb and Ni,with different contact timevalues . The acidic and alkaline pH of the solution was maintained by adding the required amount of HCl and NaOH solutions [22].

2 - Contact time
The effect of contact time for heavy metals removal by adsorbent was determined according to Box – wilson

design at different periods from 15 to 180 min., with differentpH values [22].

3 - Adsorbents modification

The activity of modified albedo adsorbents for heavy metals removal was used for the treatment of mixture of heavy metals (Multi-ions system) with suitable condition (pH value and contact time) according to the previous experiments results.

2.8 Fourier transform infrared spectroscopy (FTIR) analysis

This technique was employed to determine the functional groups responsible for metals uptake, befor and after using the adsorbents (albedo of pomelo) for water treatment[23, 24].

2.9 Calculations of Removal Efficiency

The following equation was used to calculate the removal efficiency of adsorption process [25]:

$$\text{Efficiency of Removal}(Er)\,\% = \frac{C_0 - C_f}{C_0} \times 100$$

❖ *Where:*

C_0 = the initial metal concentration (mg/l).

C_f = the final concentration (mg/l).

2.10 Statistical analysis

All data of experimental designed were analyzed statistically by using statistica program(Anova test).

3. RESULTS AND DISCUSSION

3.1 Phytochemicals investigation

The results of qualitative phytochemicals analysis for hydro methanolic extract of pomelo albedo showeda presence of flavonoids, tannins, coumarin, volatile oils, terpenoids, anthraquinone glycosides, pectin, lignin and cellulose. While, alkaloids, resins, gum and mucilage, saponins and cardiac glycosides were not found (Table 1).

Table 1: phytochemicals analysis of albedo extract

No.	Phytochemicals	Positive Reaction	Results
1	Flavonoids	Yellow colour	+
2	Alkaloids	Reddish brown colour	-
3	Tannins	Greenish black colour	+
4	Coumarins	Yellow fluorescence colour	+
5	Saponins	Emulsion solution	-
6	Resins	Orange to Yellow colour	-
7	Volatile Oils	Pinkish fluorescence colour	+
8	Terpenoids	Reddish brown colour	+
9	Gum and Mucilage	Swelling form	-
10	Anthraquinones Glycosides	Pink – Red colour	+
11	Cardiac Glycosides	Violet – Blue ring colour	-
12	Pectins	White flocculation	+
13	Lignin	Yellow colour	+
14	Cellulose	Blue colour	+

The phytochemicals evaluation of albedo extract is a necessary step for determining the active materials of albedo that play an essential role in the adsorption process depending on functional chemical groups of these materials[26]. Secondary metabolites of plants are considered as an important parameter for plant adsorbents because they help in predicting the efficiency of adsorption process that depends on its chemical structures[27]. Also, the main advantage of plants waste and secondary metabolites of plants (active materials) over other conventional adsorbents is their strong affinity and high selectivity toward heavy metals due to the abundant availability of binding functional groups on the plants waste and secondary metabolites of plant part surfaces[28].

3.2 Adsorption experimental studies

Determining the ability of adsorption process and removal efficiency of the heavy metals according to the Box-Wilson Design.

The adsorbent materials showed different efficiency for adsorption process at different conditions (pH value and contact time),heavy metal residuals (after treatment) ranged from 0.9 to 10.1 ppm (Table 2). Furthermore, different removal efficiency (E.R) of heavy metals (Co, Pb, Ni and Cd) was observed removal efficiency ranged from 80% to 98.2%(Table 3).

Table 2: Residual concentrations of heavy metals (after treatment) at different pH value and contact time.

Parameters			Heavy Metals (Residuals) PPM			
No.	**pH Values**	**Contact Time (min.)**	**Co (50PPM)**	**Pb (50 PPM)**	**Ni (50 PPM)**	**Cd (50PPM)**
1	3.5	40	10.1	2.5	8.5	5
2	3.5	156	9	0.9	7	4.5
3	5.5	156	7	1.1	4	4.8
4	5.5	40	7.5	1.4	6	4.7
5	3	98	6	1.5	5	3
6	6	98	5	1.5	4	2
7	4.5	15	4	1.6	7	2.1
8	4.5	180	4.5	1.7	3.5	2.1
9	4.5	98	3	1.9	3	2.2

Table 3: Different removal efficiency (E.R) of Heavy metals (after treatment) at different pH value and contact time.

Parameters			Removal Efficiency of Heavy Metals (%)				
No.	**pH Values**	**Contact Time (min.)**	**Co**	**Pb**	**Ni**	**Cd**	**The Means**
1	3.5	40	80	95	83	90	**87**
2	3.5	156	82	98.2	86	91	**89.3**
3	5.5	156	86	97.8	92	90.4	**91.55**
4	5.5	40	85	97.2	88	90.6	**90.2**
5	3	98	88	97	90	94	**92.25**
6	6	98	90	97	92	96	**93.75**
7	4.5	15	92	96.8	86	95.8	**92.65**
8	4.5	180	91	96.6	93	95.8	**94.1**
9	4.5	98	94	96.2	94	95.6	**94.95**

3.3 Factors affecting adsorption of heavy metals

According to the results that obtained from studied the effects of parameters (pH values and contact time) on heavy metals removal efficiency by inner peels of pomelos in packed bed column(PBC)(Table 3), the adsorbents showed high removal efficiency of metals with little differences on the ability of adsorbents for heavy metals removal.

3.3.1 pH values

It seems clearly removal efficiency of all adsorbent materials for removal of Co, Pb, Cd and Ni was affected with increasing pH value. According to the arithmetic means of removal efficiency, highest removing was occurred at pH 4.5 and 6 that were 94.95 % and 93.75 % respectively,while removal efficiency was decreased with decreasing the pHvalue, lowest removal efficiency was occurred at pH 3.5 which was 87%.pH of the adsorption process is an important controlling parameter in heavy metals adsorption process [29]. This parameter is directly related to the competition of hydrogen ions with metal ions at active sites on the adsorbent surface [30]**.** In a study carried out by Abdullah and Prasad (2010), the adsorption of nickel (II) was increased when pH was increased from 1 to 6 by using tamarind bark. Dong *et al*., (2010) [32] reported that the best pH for the chromium adsorption was 5.5 by amino starch preparation and its adsorption for Cr.

3.3.2 Contact Times

All adsorbent materials exhibited higher removal efficiency at a variable contact time ranged from 15 to 180 min. for Co, Pb, Cd and Ni, the best contact time for highest removal efficiency were 94.95% and 93.75%at 98 min.(Table 3).While the lowest removal efficiency was 87% at 40 min. Contact time is one of the important parameters for the successful adsorption application. Generally, in a given contact time, there are three primary rate steps in the adsorption of materials from solution by plant wastes. First is the transport of the adsorbate through a surface layer to the exterior of the adsorbent (film diffusion); second is the diffusion of the adsorbate within the pores of the adsorbent (pore diffusion); third is the adsorption of solute on the interior surfaces bounding pore and capillary spaces. For most operating conditions, transport of adsorbate through the 'surface layer' or boundary layer is rate-limiting, if sufficient turbulence is provided, transport of the adsorbate within the porous adsorbents may control the rate of uptake [33]. Kurniawan, et al. (2003) [34] mentioned that the contact time required by all types of adsorbents for metals removal from real waste water was relatively short, ranging from 2 to 6 hrs, suggesting a rapid transport of adsorbate species from the bulk to the surface of adsorbents.

3.4 Multi-ions solution (Multi-ions system)

The removal of heavy metals from multi-ions system shown higher removal efficiency of adsorbents more than single ions system. Pomelo inner peels had the highest ability of adsorption processwith 0.9, 0.3, 0.9 and 0.5 for Co, Pb, Ni and Cd ,respectively (Table 4). At the same time, removal efficiency of Co, Pb, Ni and Cd were 98%, 99%, 98% and 99% respectively. In this context, Husoon (2011) [35] found that the adsorption process was enhanced when heavy metal concentration was increased up to certain values. Also, Dong et al., (2010) [32] reported that the increase of metal concentration caused a significant enhancement in the reaction extent of heavy metals adsorption from aqueous solution. Therefore, the adsorption is highly dependent on the concentration of metal ion especially in multi-ions system. [37].

Table 4: The removal efficiency of albedo adsorbent for metals in single ions system and multi ions system.

Heavy Metals (50 ppm)	Single Ions System		Multi Ions System	
	Residual Concentration	Removal Efficiency	Residual Concentration	Removal Efficiency
Co	3	94%	0.9	98%
Pb	1.9	96.2%	0.3	99%
Ni	3	94%	0.9	98%
Cd	2.2	95.6%	0.5	99%

3.5 Adsorbents modification

The modification by HCl (1M) and NaOH (1M) on the effectiveness of adsorbents of heavy metals removal is illustrated in Table (4and5). High differences were observed between the ability for heavy metals removal by treated and non-treated plants wastes with HCl (1M) and NaOH (1M) (Table 5).According to the results of adsorption process by modified adsorbents, the removal efficiency of pomelo inner peels became best and higher than raw adsorbents. This experiment carried out depending on the best removal efficiency was obtained that were at pH 4.5 and contact time 98 min (table 3). Several studies have mentioned that the Pretreatment methods using different kinds of modifying agents such as organic and metallic acid solutions were for purpose of removing soluble organic compounds, eliminating coloration of the aqueous solutions and increasing efficiency of heavy metals adsorption [38, 39, 40, 41]. Plants waste modification could enhance their natural capacity and increase the efficiency of the plants waste and their active materials (plant secondary metabolites) as natural adsorbents. Also, the prolonged contact with water, natural adsorbent tends to disintegrate, in order to overcome such problems, chemical modification and activation of the raw adsorbents are required and this considered an advantage for natural adsorbents [27]. The basic of modifications is to make changes in adsorbent structure to enhance its properties (capacity, resistance, *etc.*). The researchers have proposed certain modifications for adsorbent backbone to improve its adsorption capacity through grafting reactions [42]. The modification can improve adsorbent's removal performance and selectivity for metals; alter the physical and mechanical properties of the polymer; control its diffusion properties and decrease the sensitivity of adsorption to environmental conditions [43].

Table 5: Comparing the removal efficiency of raw and modified albedo adsorbent for metals in multi ions system.

Heavy Metals Multi Ions System -50ppm-	Raw Albedo Adsorbent		Modified Albedo Adsorbent	
	Residual Concentration	Removal Efficiency	Residual Concentration	Removal Efficiency
Co	0.9	98.2%	0.08	99.8%
Pb	0.3	99.4%	0.002	100%
Ni	0.9	98.2%	0.08	99.8%
Cd	0.5	99%	0.025	99.95%

3.6 Statistical analysis of Adsorption experimental studies by Anova test

Results of this study were analyzed by Anova test to find out the significant effects of parameters on adsorption process and heavy metals removal. It is worth mentioning that the situation which we can choose between one-way ANOVA and other statistical test is when the explanatory variable has exactly two levels. In that case the same conclusions can be reached regardless of which method has been used [46].In statistics, analysis of variance (ANOVA) is a method used to compare means of samples (using the F distribution). This can be used only for numerical data. Typically, however, the one-way ANOVA is used to test for differences among at least three groups [45]. Results of ANOVA were carried out for determining the pH value and contact time that affect the treatment of aqueous solution and heavy metals removal (Table 6).

In all ANOVA statistical tests, the level of significance is $p \leq 0.05$ suggesting that the test is considered to be statistically significant [47]. According to table 7, pH values and contact time did not show significant effect on the heavy metals adsorption and removal from the aqueous solution. While the type of heavy metals showed a significant difference between ability of the plant wastes towards heavy metals adsorption and removal from aqueous solution (Table7).

Table 6: Anova test of pH value and contact time and there effects on adsorption process by raw inner peels of pomelo.

No.	pH Values	Contact Time (min.)	Means of Heavy Metals (PPM)	Standard Deviation (S.D.)	F - Value	P - Value	Comment
1	3.5	40	6.525	2.967	**1.527**	**0.149**	**Not- Significant**
2	3.5	156	5.35	3.024			
3	5.5	156	4.23	2.112			
4	5.5	40	4.90	2.250			
5	3	98	3.875	1.746			
6	6	98	3.125	1.430			
7	4.5	15	3.675	2.118			
8	4.5	180	2.950	1.116			
9	4.5	98	2.525	0.487			

At a probability ($p \leq 0.05$)

Table 7: Anova test of heavy metal types and there effects on adsorption process by raw inner peels of pomelo.

Heavy metals	Means of Heavy Metals (PPM)	Standard Deviation (S.D.)	F - Value	P - Value	Comment
Co	6.233	2.231	**15.719**	**0.000**	**Significant**
Pb	1.566	0.434			
Ni	5.333	1.779			
Cd	3.377	1.262			

At a probability ($p \leq 0.05$)

3.7 Fourier transforms infrared spectroscopy (FTIR) analysis

The FTIR technique was used to study the main changing in functional groups that present in pomelo albedo before and after removing heavy metals from aqueous solution. Figure 3 shows the FTIR spectra of raw pomelo albedo before removing heavy metals. Generally, the cellular wall of most citrus albedo contains insoluble polysaccharides that composed of pectin, cellulose, and hemicelluloses [52]. The most distinct absorption peak was observed on the untreated spectra (a), with the presence of a peak located at ~1741.8 cm-1 that indicates the presence of C=O and C-O-C stretching of the acetyl and uronic ester groups of polysaccharides, such as pectin, lignin and hemicellulose[35,54]. It is also shown in Figure 3 that all of the samples have peak 3346.78 cm-1, which indicates the presence of O-H stretching vibration and O-H bending of the absorbed water. The absorption peaks in the region of 1644.98 cm-1 and around ~2923.83 and 2853.10 cm-1 correspond to the O-H and C-H groups [55]. The vibration peak around 1454-1518.98 cm-1 related to the bending vibration of the C=C and C-H bonds in polysaccharide aromatic rings, while 1340 - 1205.52 cm-1 related to the carbonyl amide C-N [56]. A band around 1176.40 and 1135.65 cm-1 that represents the C-O and C-H stretching vibration, confirms the structure of cellulose and oleanolic acid. The vibration peak around 1037.62, 1013.65 and 986.76 cm-1 that represents the C=O as ester groups. Furthermore, the increase in the intensity of these groups indicates to the increase of the crystallinity of the samples [57, 58]. Overall, the typical absorption band that appears in the extracted cellulose from pomelo albedo spectra is similar to the characteristic of pure cellulose. Also, the band at peak 3346.78 cm-refers to presence of terpenoids and anthraquinone glycosides [59]. While, figure 4 shows the FTIR spectra of raw pomelo albedo after removing heavy metals that showed there are significantly different on the major peaks, which explains clearly that the binding of these functional groups with heavy metals in adsorption process and removing the heavy metals from aqueous solution.

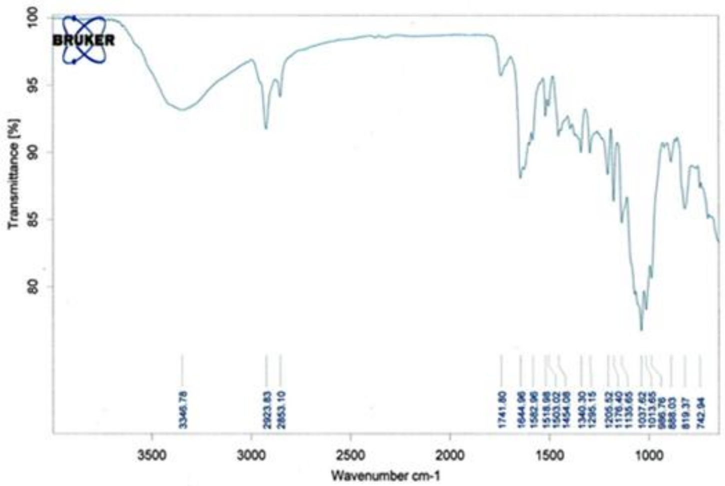

Figure 3 : FTIR of inner peels (albedo) of pomelo fruits before adsorption process

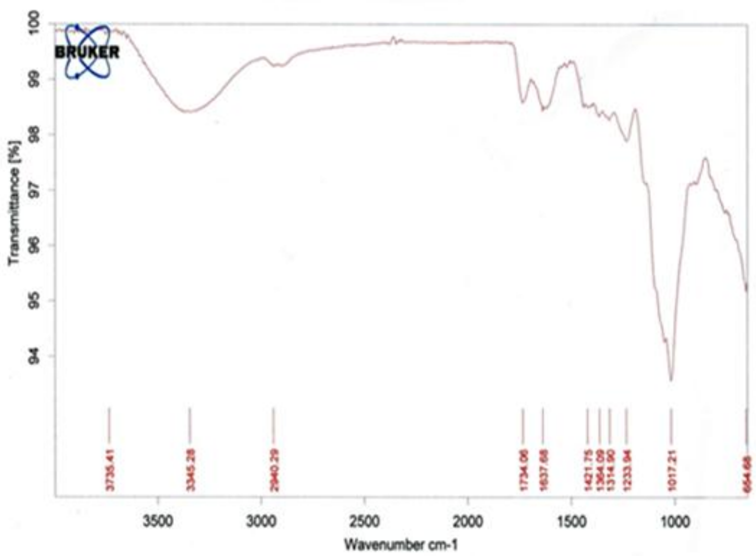

Figure 4 : FTIR of inner peels (albedo) of pomelo fruits after adsorption process

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