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Application of Pomegranate Peel Waste in Descaling of Stainless-Steel Water Boilers

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ABSTRACT

Pomegranate peel, has traditionally been considered agricultural waste. However, recent research studies have revealed its potential as a rich source of bioactive compounds with diverse biosorbent and pharmacological effects used in diverse industries. Pomegranate peel is a rich reservoir of antioxidants, polyphenols, dietary fibre, and vitamins, which contribute to its remarkable bioactivity as biosorbent. Furthermore, pomegranate peel has the potential to be used to develop bioactive reagents used in the food industry, and biosorbent reagents to be utilized and water purification industry. Traditionally, limescale build-up is one of the main causes of stainless-steel kettle and boiler failure. This is due to the elements in stainless steel constantly being exposed to water. Chemical descalers are available to buy, some designed specifically for metal kettles and others for plastic models and the user should check if they are suitable for the appliance. Promoting the use of environmentally friendly descalers is our target for this research, where we can use fruit peels in the form pomegranate peel (PGP) to descale stainless steel kettles and boilers, subsequently decreasing the pollution level in our environment. This publication describes how the variety of phenolic substances in pomegranate peel (PGP), which includes tannins, flavonoids, phenolic acids, dietary fibre and other bioactive substances such as alkaloids, minerals, can be employed as environmentally-friendly active reagents for descaling the limescale precipitated in stainless-steel equipment and appliances. Descaling from natural products is a process where components act as scavenging or antioxidant species. The waste of the pomegranate peels also can be better reused for diverse industrial applications.

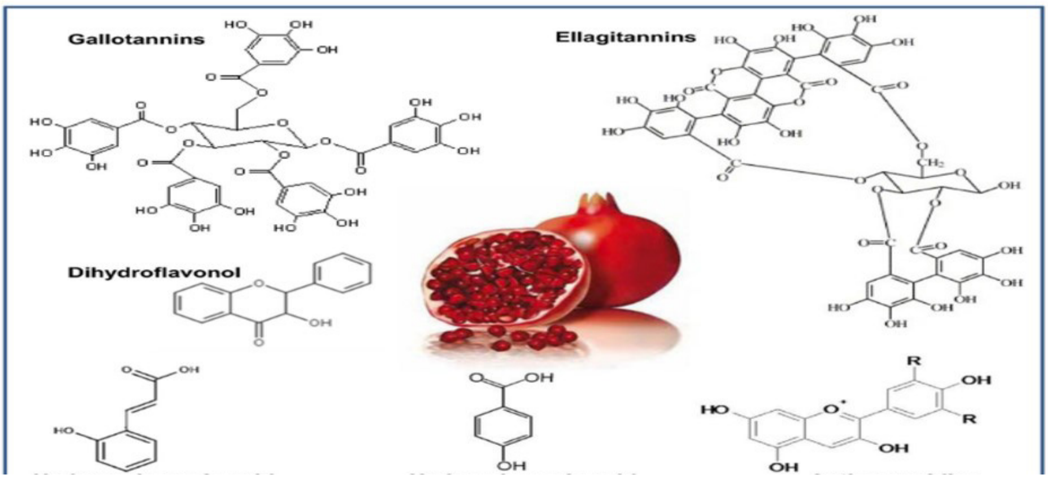
INTRODUCTION

Pomegranate Peel as Eco Friendly Biowaste

The terms eco-friendly corrosion inhibitor or green inhibitor refer to the substances that are of biological origin and biocompatible and biodegradable such as plant extracts. Recently there is a growing interest in the use of natural products such as leaves, fruit waste or seed extracts. Due to the currently imposed environmental requirements for eco-friendly corrosion inhibitors, researchers studied biological active products such as fruit waste, for their corrosion-inhibition efficiency potential with a lower risk of environmental pollution (Ahmad, 20141).

Pomegranate peel, a biowaste known traditionally for its ethnos-medicinal properties, mainly used for boils, rheumatic pain and digestive disturbances, is also known for invitro pharmacological effects such as antibacterial, antifungal and anti-inflammatory properties.

The current research is an attempt to study the performance of pomegranate peel extract as an inhibitor of lime scale precipitation in stainless-steel equipment used in industry where only hard water is available. The evaluation tests of pomegranate peel inhibition performance were carried out by immersion tests on lime scale precipitate to study rate of scale removing using fresh pomegranate peels or dried peel powder.



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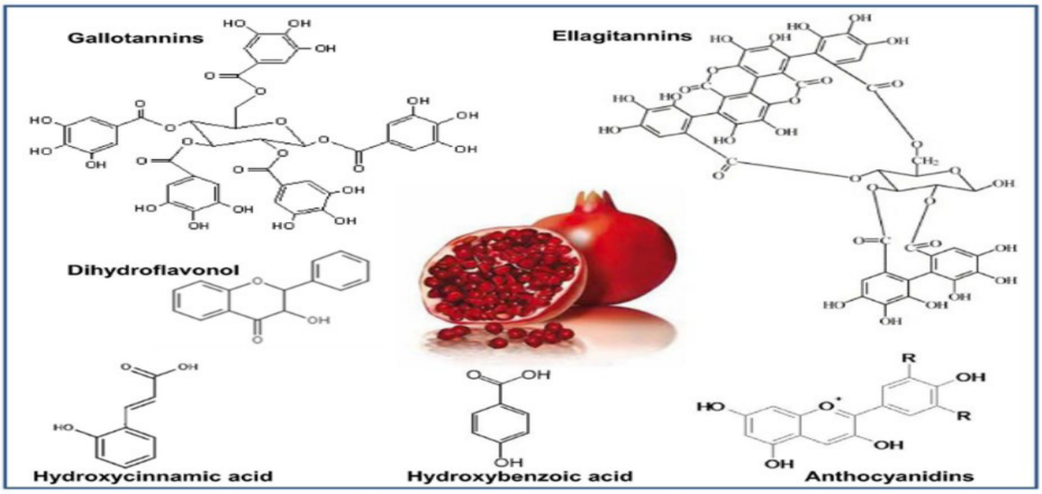

Figure 1: structural and chemical composition of pomegranate peels (Ajmal, 2014)

Pomegranate peel is obtained from the pomegranate juice industry as a byproduct and is known to be one of agricultural waste materials that is efficient as bio absorber for pollutant removal. Pomegranate is a popular middle eastern fruit for its pleasant taste, high nutritional value, and having a variety of medical benefits due to containing antioxidant phenol molecules in the fruit part of pomegranate consumed as juice, jams, vinegar and wine. Pomegranate peels form 30% of the fruits total weight, which is usually abandoned as a waste. It contains two important hydroxybenzoic acids, gallic acid and ellagic acid. It also contains hydroxycinnamic acids, derivatives of flavones and ellagitannins are also present, such as Punica line, punicalagin, corilagine, (Ben-Ali, 2021), and granatine. (Shartooh, 2013) Tannins that can be used for anti-inflammatory, antimicrobial, and antioxidant treatment (Rowe, 1988; Saad, 2012) representing up to 28% of pomegranate peel. PGP constituents can be extracted for medicinal (He & Xi, 2017), dyeing (Ajmal, 2014), and adhesive applications (Hasnaoui, 2014), and the solid waste can be used as low-cost renewable energy source of biowaste (Ahmad, 2014; Saad, 2015; El-Ashtoukhy, 2008).

The world annual production of pomegranate is approximately three million tons. The most productive countries of pomegranate are India, Iran, Iraqi Kurdistan, north Africa, south Europe (Mediterranean region), southern united states and China are also considered to be one of the biggest producers (Ben-Ali, 2021; Rowe, 1988; Lansky & Newman, 2007).

Few studies have been carried out on the potential of untreated pomegranate peel for wastewater treatment (Ben-Ali, 2021). The pomegranate peels were used by researchers in its different forms (fresh, dried small pieces and powder) and tested under different environmental factors such as pH, temperature and contact time to study the capacity of the peels for removing heavy metals like zinc, chromium and nickel from industrial wastewater (Saad, 2012).

The purpose of our study is based on using untreated pomegranate peels on removal of scale from stainless steel containers and boiler which precipitate due to using hard water in industry.

The chemistry of removing the limescale using pomegranate peels (PGP) is based on the reaction between the Ca^{+2} with oxygen of carbonyl functional groups in the structure of the peels see Figure 1. The proof of this reaction is shown in the analysis results and explained in more details in the results and discussion section.

Physical and Chemical Properties of PGP

Harvested pomegranate fruits were chosen randomly; the peel and the pulp were separated manually after fresh fruit juice was extracted. The pomegranate peels (PGP) were dried in shade at 40°C, it was processed by grinding each batch into a fine powder.

Unfortunately, we could not carry out any physical and chemical analysis on our PGP samples due to unavailability of instruments for this analysis in our university. The only data for peel analysis we obtained was from literature for Tunisian pomegranate peel (Ben-Ali, 2021). The only analysis we could carry out on our PGP samples was FTIR before application and after its application in the experimental process. The chemical analysis which obtained from literature for PGP's obtained from Tunisia, Turkey and India.

Chemical analysis information of pomegranate peel which was obtained from literature, showed that its major constituents are carbon, oxygen, and hydrogen. The elemental analysis of Tunisian PGP showed to have the following composition: 43.13% of carbon, 48.15% of oxygen, 7.17% of hydrogen, 0.66% of Nitrogen, and 0.89% of sulphur (Stephen Lower, 2007-10-08)

Composition is comparable to the Turkish PGP, which has 43.94% of carbon, 49.55% of oxygen, 4.73% of hydrogen, 1.23% of nitrogen, and 0.55% of sulphur (Ververi & Goul, 2019).

Whereas Indian PGP composition is different, it has 35.96% of carbon, 58.38% of oxygen, 58.38% of hydrogen, 0.65% of nitrogen, and 0.09% of sulphur (Ay *et al.*, 2012)

Moisture contents obtained from PGP is very high compared to the average literature value, and it may be probably related to fresh PGP while other encountered values are related to dried PGP (Ay *et al.*, 2012)

Table 1, summarizes, from literature the PGP approximate and ultimate analysis. The principal surface functional groups are carboxylic acid, phenol, and carbonyl. (Ben-Ali, 2021)

Table 1: Pomegranate peel proximate and ultimate analysis (Ben-Ali, 2021)

BET (m^2/g)	Po rosity (%)	Pa rticle density (g/ cm^3)	Mosture (wt %)	Ash (wt %)	C	H	S	0- N	N	O	References
-	-	0.38	8.12	9.68	43.13	7.17	0.89	48.81	0.66	48.15	[17]
1.28	30.88	0.89	10.43	3.63	4.92	0.09	35.96	59.03	0.65	58.38	[22]
10	-	-	-	-	43.94	4.73	0.55	50.78	1.23	49.55	[21]
3.36	42	-	-	36.11	-	-	-	-	-	-	[18]

FTIR Analysis

The FTIR spectrum of analysed PGP is shown in Figure 2, obtained from the literature, where absorption bands corresponding to functional groups are interpreted in Table 2:

Table 2: interpretation of FTIR spectrum of Tunisian pome garnet peel obtained from literature (Ben-Ali, 2021).

Absorption band	Assignment
3280 cm−1	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols).
2935 cm−1	Stretching vibration bond of aliphatic C-H groups
1727 cm−1	C=O stretching of the carbonyl group
1617 cm−1	Stretching vibration bond of C=O and C=C
1320 cm−1 and 1020 cm−1	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups
1446 cm−1	Ring vibration

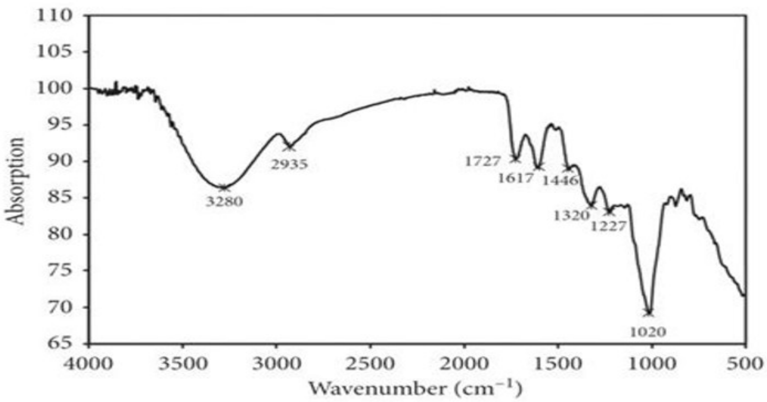

Figure 2: FTIR for Tunisian pomegranate peel (Ben-Ali, 2021).

These results agree with surface functional groups determined by the Boehm titration method and are presented above (Figure 2), thus, pomegranate peel is rich in oxygenated surface groups (Ben-Ali, 2021; Uzel, 2012).

Chemistry of Limescale

Limescale is calcium carbonate ($CaCO_3$), which deposits as a hard chalky precipitate mainly inside kettles or hot water boilers and pipework. Hard water contains calcium (and often magnesium) bicarbonate or similar ions. Calcium, magnesium, and carbonate ions dissolve from rocks through which rainwater flows before collection. If hard water flows, plumbing and heating components can get seriously damaged or their functioning impaired by limescale, especially when it precipitates on the inner surfaces of pipes and other surfaces where hot water flows regularly (Pradeep Kumar, 2014).

Descaling agents are commonly used to remove limescale. Prevention of damage by scale build-up depends on the technologies of water softening or other water treatment.

Water softening plants in the water treatment industry such as sewage treatment plants, can effluent flow from the re-generation process can deposit scale that can interfere with sewage systems (Baran, 2019; Rajitha, 2020). When water is softened, a slippery feeling will appear when washing caused by the weaker attraction of the soap particles to the water ions, this is due to stripping of mineral contents of water particles during the softening process.

Figure 3: Limescale in pipes

Figure 4: Lime scale on boiler heaters

Figure 5: Lime scale on a water tap

There are a number of products available in shops, some more expensive than others, that contains acids suitable for dissolving limescale from the internal parts of domestic household pipes, domestic equipment (kettles washing machines, taps). These products are usually harmful chemicals such as sulphatic acid or citric acid. The acid dissolves the limescale, which is then washed away in the drain.

The application of softening products is simple and usually involves adding the relevant dose into the drum and running an empty load on a hot wash.

Therefore, in our research project we wanted to remove limescale using environmentally-friendly products such as sour fruits byproducts such as pomegranate peel PGP which showed to be highly acidic (approx. pH was 2.5-3) and an ideal replacement for the expensive chemicals or citrus acid obtained from fruits (lemon juice) or vinegar obtained from expensive industrial processes. Also using PGP helps to reduce the waste obtained from Pomegranate juice factories and helps to reduce pollution in the environment.

Many industrial systems that use water in their applications, such as cooling systems, condensers, heat exchangers and engines, find limescale is major problem. The maintenance of these systems is very expensive, unless the water is treated with softening reagents to prevent the systems from precipitating limescale.

Using organic inhibitors are a good method to protect iron, steel and stainless steel from lime scale deposition. Recently, modern organic inhibitors that have been discovered by researchers have shown significant results in neutral solutions or salt solutions (Baran, 2019).

The existing organic inhibitors are highly toxic in nature and expensive, these reasons have prompted scientists to develop Lime scale inhibitors that are more acceptable and less expensive. Natural products of plant origin contain many organic compounds such as pigments, tannins, alkaloids and, finally, organic and amino acids. These substances contain a suitable inhibitory molecule that act as a natural product inhibitor can be considered a good source for this purpose (Siedah, 2014).

Numerous studies have demonstrated that these pomegranate peels (PGP) have a wide range of biological activities and health advantages, including antioxidant, anticancer, and anti-inflammatory properties (Mo, 2022). The current studies not only focus mainly on the pharmacological effects of bioactive substances found in pomegranate peel. Focuses are also recently active on development the methods for extraction of bioactive compounds of pomegranate peel to be utilised in the other industries like water purification for removal different types of pollutes. Our research study has added value- to this biowaste products in PGP to be used in descaling had water boilers and its pipe line.

MATERIALS AND METHODS

Pomegranate Peel Preparation

Pomegranate peel PGP we used in our experiment were obtained from fruit that were harvested from pomegranate orchards, located in the Kurdistan region of Iraq in the districts such as 'Choman', 'Soran', 'Hawler', 'Sidakan, 'Barzan, 'Raniyeh', 'Halabja', 'Kerkuk', 'Harir' and 'Balakayati'.

Samples of pomegranate peels were dried at 40°C in shade, then the dried peel was grinded by an electric grinder to fine powder. In some of the experiments fresh peels were used. The pulp obtained from pomegranate juice extraction were also used in another experiment.

Experiment and Results

Materials and Equipment

Equipment

Weighing balance (KERN-PFB 1200-2, serial No.. WF18013928, d0.01g, Kern &Sohn GMBH, D72336 Ballngen, Germany), stainless steel container, gas cooker for water heating (fresh and dried), PH strips, timer. FTIR spectra were recorded using IR-Affinity-1, Shimadzu CORP-A21375003225 Spectrophotometer in the range of 400-4000 cm-1 using KBr Disc.

Materials

Fresh Pomegranate (PGP) peel obtained from Iraqi Kurdistan pomegranate field, dried peel powder (it was in shade at about 40°C, the dried PGP grided into fine powder), pomegranate pulp after the juice extraction, hard water obtained from MRF residential tower water supply (Location Erbil Iraq) (hardness scale =280 ppm).

Experiment 1

Removal of Lime Scale Using Fresh Pomegranate Peel (PGP)

Preparation of Lime Scale Precipitate from Hard Water Supply

A stainless-steel container was used to collect limescale by boiling the water to dryness where layer of white scale was collected.

Weight of lime scale = total weight of lime scale with container (M2) – weight of empty container(M1).

M1=157.0g, M2 =158.02

Weight of lime scale=158.02-157.0 = 1.02 g

Figure 6: Fresh pomegranate peels

Figure 7: Fresh grated pomegranate peels

Table 3: Data obtained from treatment the lime scale with solution of fresh PGP suspension

Contact Time in minutes	Weight of lime scale (g)	Weight of absorbed lime scale (g)	pH of the solution
0	1.02	0	2.5
10	0.4	0.62	3
20	0.35	0.05	5
40	0.3	0.05	5
80	0.19	0.11	5
140	0.1	0.09	5
190	0.07	0.03	5

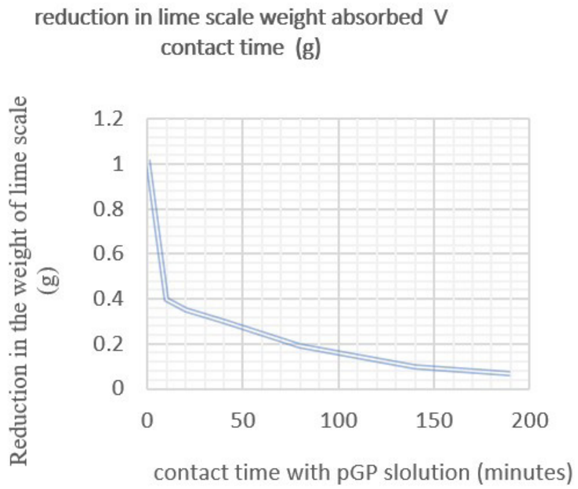

Figure 8: Reduction in lime scale absorbed vs contact time in (min)

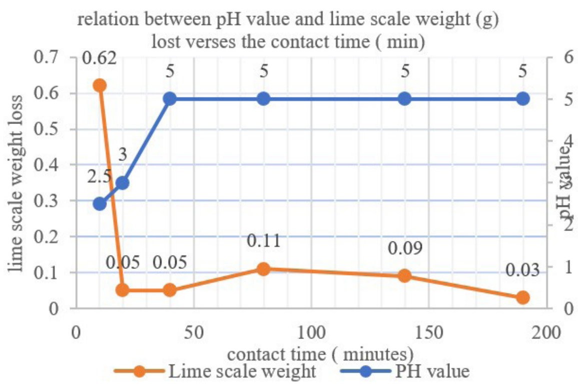

Figure 9: Change in pH value of suspension and limescale weight vs contact time (min)

Preparation and Reaction of Fresh Peel Solution and Lime Scale Precipitate

Freshly peeled pomegranate was grated then (10 g) dissolved in distilled water (500ml).

The fresh mixture (suspension) was added to stainless steel container (contained a layer of lime scale) the mixture Shaked at RT for different periods of times each time the mixture was removed from the container and the container dried to calculate the difference of weight also the PH of the solution was measured.

Experiment 2

Removal of Lime Scale Using the Fresh PMG Pulp Obtained from Pomegranate Juice Extraction

Preparation of Lime Scale Precipitate from Hard Water Supply

A stainless-steel container was used to collect limescale by boiling the water to dryness where layer of white scale was collected.

Weight of lime scale = total weight of lime scale with container (M2) – weight of empty container (M1).

Weight of lime scale= M2 - M1 =158.07-157.0 = 1.07 g

Figure 10: Lime scale precipitate bottom

Figure 11: PGP pulp after juice extraction of juice

Figure 12: Stainless steel pot after the treatment of the lime scale with PGP stainless-steel pot

Preparation of PGP Pulp Suspension

The fresh PMG pulp (10g) was dissolved in distilled water (500ml) and stirred continuously until a suspension obtained.

Procedure

The fresh mixture (suspension) was added to stainless steel container (contained a layer of lime scale) the mixture Shaked at RT for different periods of times each time the mixture was removed from the container and the container dried to calculate the difference of weight also the pH of the solution was measured.

Table 4: Data obtained from treatment of lime scale with PGP pulp suspension

Contact Time in minutes	Weight of lime scale (g)	Weight of absorbed lime scale (g)	pH of the solution
0	158.07	0	5
10	157.21	0.86	5.5
20	157.20	0.01	6
40	157.14	0.06	6
80	157.13	0.01	7
120	157.0	0.00	7

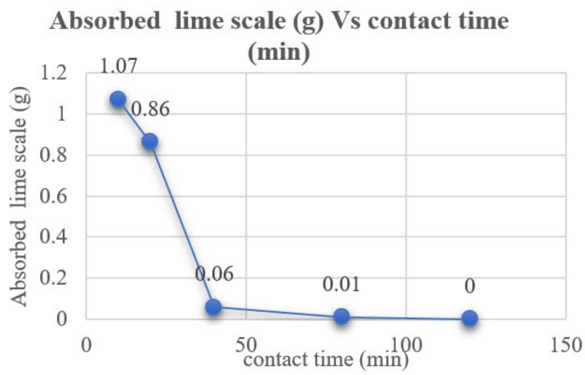

Figure 13: Absorbed lime scale in PGP pulp suspension vs contact time

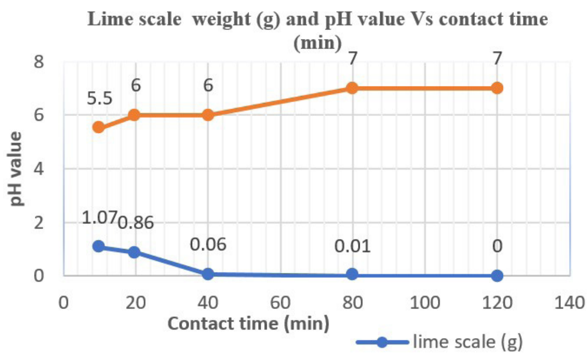

Figure 14: pH value change and lime scale weight change vs contact time

Preparation of Dried PGP Peel Suspension

Pomegranate was dried in the warm room 40oC in shade. The dried peel was grinded to fine powder. The dried powder of Pomegranate peel (PGP) (10 g) was dissolved in distilled water (500ml), the mixture was stirred for 10 minutes.

Figure 15: Dried PGP powder

Preparation of Lime Scale Precipitate from Hard Water Supply

A stainless-steel container was used to collect limescale by boiling the water to dryness where a layer of white scale was collected.

Weight of lime scale = total weight of lime scale with container (M2) – weight of empty container (M1).

Weight of lime scale= M2 - M1 =158.8-157.0 = 1.8 g.

Procedure

The mixture (suspension) was added to a stainless-steel container (containing a layer of lime scale). The mixture was shaken at RT for different periods of times. Each time the mixture was removed from the container and the container dried to calculate the difference of weight and also the pH of the solution was measured. The results obtained are demonstrated in table 5.

Table 5: Results obtained from treatment of lime scale with the suspension of Dried PGP powder

Contact Time in minutes	Weight of container +lime scale(g)	Weight of absorbed lime scale (g)	pH of the solution
0	158.8	0	5
10	157.32	0.68	5.5
20	157.31	0.01	5.5
40	157.30	0.01	6
100	157.29	0.01	6
220	157.28	0.01	6

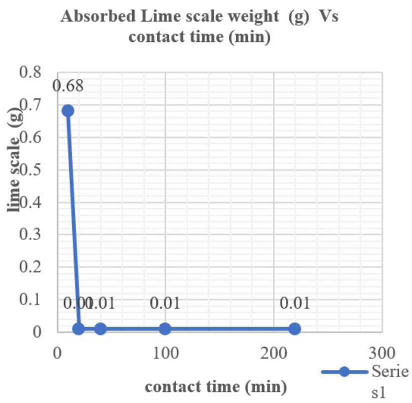

Figure 16: Absorbed lime scale weight vs contact time

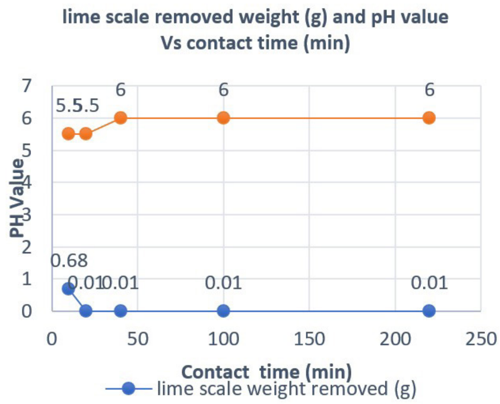

Figure 17: pH value change and absorbed limescale weight vs contact time

RESULTS AND DISCUSSION

Experiment 1

In this experiment, where fresh PGP was used, the PH of the suspension was (2.5) as know from literature information and FTIR analysis that PGP contains several carboxylic group and phenolic functional group.

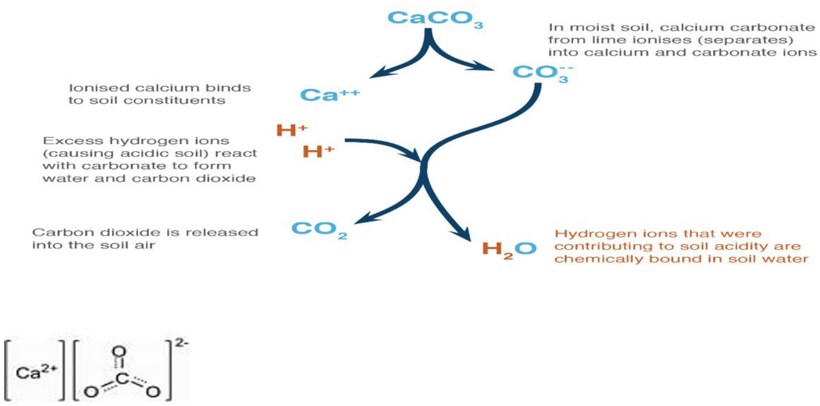

Figure 18: Chemical reaction involved between limescale and PGP solution

During the first stage of experiment, where the contact time was 10 minutes, the pH value dropped from 2.5 to 3 then after 20 minutes to 5. This is due to the reaction of the carboxylic group on the surface reacting with almost 70% of the limescale on the surface of the stainless-steel pot.

FTIR Results

FTIR analysis carried out for the fresh pomegranate suspension before and after using it for lime scale treatment:

The evidence also shown in the FTIR spectrum Figure 19, is FTIR for fresh suspension; the result interpretation is summarised in the table 6:

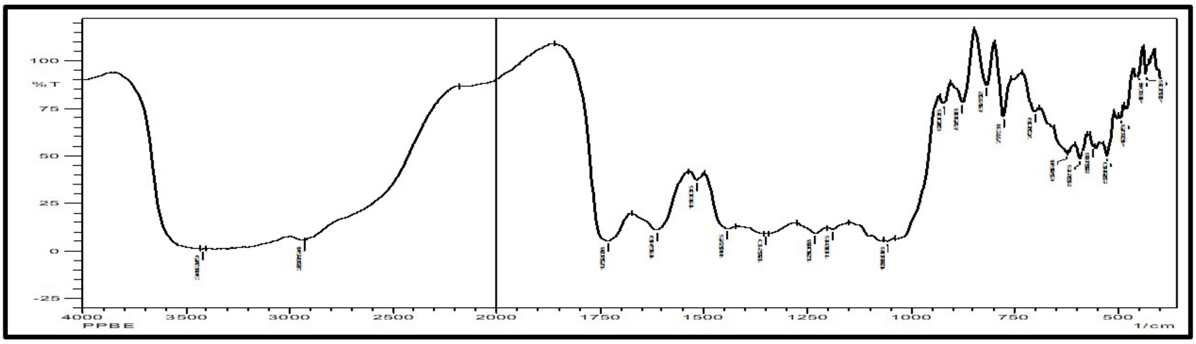

Figure 19: The FTIR spectrum of analysed PGP shown is FTIR from the pomegranate fresh peel obtained from Iraqi Kurdistan area before it was used for treatment of limescale precipitated on the stainless-steel pot

Table 6: FTIR result analysis in Figure 19

Absorption band (cm^{-1})	Band assignment of band with functional groups	%T
3419.79	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols	80
2927.94	Stretching vibration bond of aliphatic C-H groups	80
1732.08	C=O stretching of the carbonyl group.	15
1612.49	Stretching vibration bond of C=O and C=C	5
1362.10	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups.	5
1055.06 cm−1, and 1056.06cm -1	Assigned to the ring vibration	1

The FTIR Figure 20, is FTIR for suspension after treatment limescale showed the absorption bands corresponding to functional groups are attributed band about which was assigned to the has minimised in size and showed as a small peak at 3292.49 cm^{-1}. band observed at about, has reduced to minimum. Peak around 1732.08 cm^{-1} represents C=O stretching of the carbonyl group. The band at 1616.35 cm^{-1} is assigned to the stretching vibration bond of C=O and C=C has reduced or disappeared. The peaks at 1361.74 cm^{-1} and the peaks at 1056.99 cm^{-1} and 1033.85 cm^{-1} are assigned to C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups has reduced to minimized in size and showed as trace at 1369.46cm^{-1} and1049.28 cm^{-1}. The change in FTIR proves the formation of salts of calcium and magnesium due to reaction of calcium and magnesium ions with the chemicals structural components in the pomegranate peel.

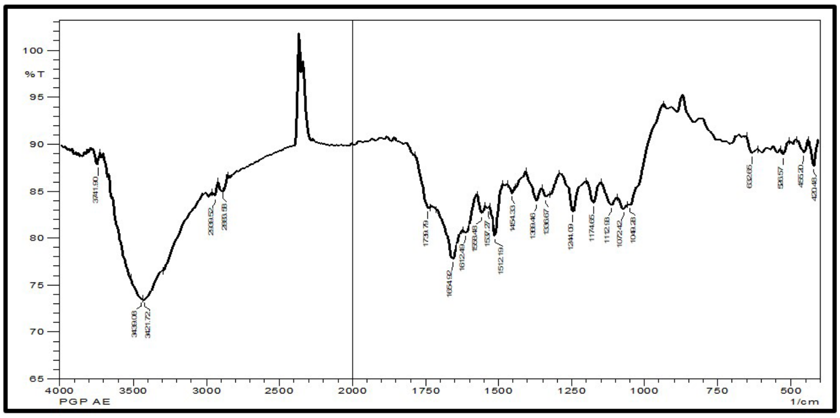

Figure 20: FTIR for Iraqi-Kurdistan pomegranate fresh peel pulp after absorption of limescale precipitate of stainless-steel pot

Table 7: FTIR result analysis in Figure 20

Absorption band (cm^{-1})	Assignment of band with functional group	%T
3439.08	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols)	17
2939.52 and 2883.58	Assigned to the stretching vibration bond of aliphatic C-H groups	2
1739.79	C=O stretching of the carbonyl group.	0.5
1654.92	Stretching vibration bond of C=O and C=C	3
1369.40, 1336.7, 1244.09, 1174.65,	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups.	1
1072.42	Assigned to the ring vibration	1

Experiment 2

In the experiment 2, where fresh pulp (obtained after juice extraction) was used, the PH of the suspension was 5. as it known from literature information and FTIR analysis that PGP contains several carboxylic group and phenolic functional group, there for as during the first stage of experiment the where the contact time was 10minute the pH value dropped from 5 to 5.5 then after 20 minutes to 6, this is due to the reaction of the carboxylic functional groups on the surface reacted with almost 80 % of the limescale exist on the surface of the stainless-steel pot.

The evidence also shown in the FTIR spectrum Figure 21, is FTIR for fresh peel pulp (obtained after juice extraction) suspension, The absorption band around 3419.79 cm^{-1} is assigned for stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols), where band around 2927.94 cm^{-1}, assigned for stretching vibration bond of aliphatic C-H groups. The absorption band at 1732.08 cm^{-1} represents C=O stretching of the carbonyl group. The band at 1612.49 cm^{-1} is assigned to the stretching vibration bond of C=O and C=C. The bands at 1362.10 cm^{-1}, 1056.06 cm-1and 1055.06 cm^{-1} are assigned to C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups. The bands at 1056.06 cm^{-1} are assigned to the ring vibration has reduced to a minimum.

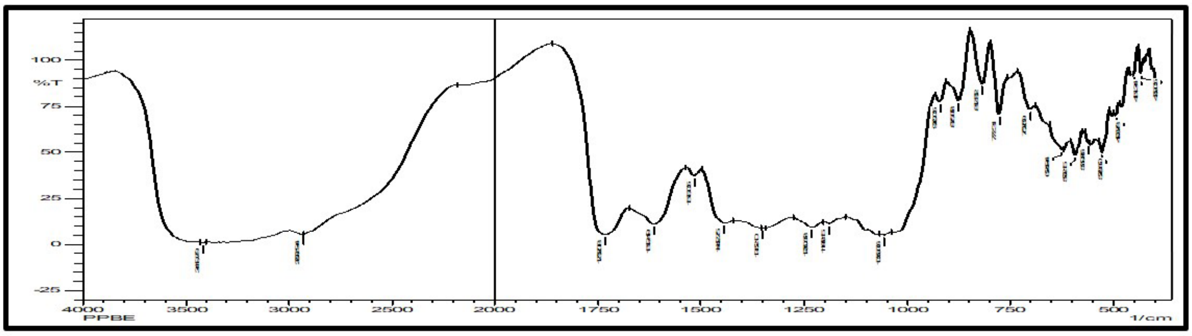

Figure 21: FTIR for Iraqi-Kurdistan pomegranate fresh peel pulp

Table 8: FTIR result analysis in Figure 21

Absorption band (cm^{-1})	Assignment of band with functional group	%T
3419.79	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols)	80
2927.94	Assigned to the stretching vibration bond of aliphatic C-H groups	80
1732.08	C=O stretching of the carbonyl group.	3
1612.49	Stretching vibration bond of C=O and C=C	2
1362.10	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups.	2
1056.06	Assigned to the ring vibration	1

Figure 22, is FTIR for suspension after treatment limescale showed the absorption bands corresponding to functional groups are attributed band about 3439.08 cm^{-1} and 3421.72 that were assigned to the stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols) has minimised in size. The band observed at about 2939.52 cm^{-1} and 2883.58 cm^{-1} assigned to the stretching vibration bond of aliphatic C-H groups has reduced to minimum. Bands around 1654.92 cm^{-1} and 1612.49 represents C=O stretching of the carbonyl group. The band at 1558.49.cm^{-1} and 1512.19 cm^{-1} are assigned to the stretching vibration bond of C=O and C=C has reduced size. The bands at 1369.46 cm^{-1} , 1336.67 cm−1, 1244.09 cm^{-1} ,1174.69 cm^{-1} and 1072.42.99 cm^{-1} are assigned to C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups has reduced to minimized in size. The bands at 1072.42 cm^{-1} and 1049.28 cm^{-1} are assigned to the ring vibration has reduced to a minimum.

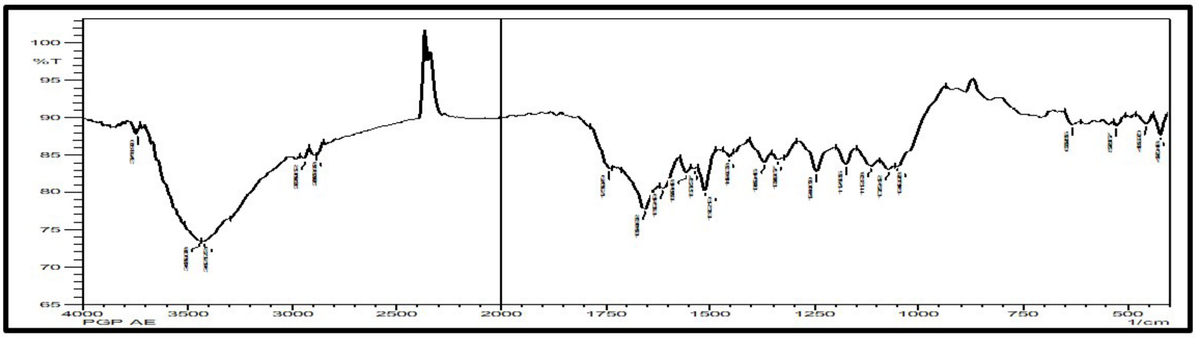

Figure 22: FTIR for Iraqi-kurdistan pomegranate fresh peel pulp after adsorption of limescale precipitate of stainless-steel pot

Table 9: FTIR result analysis in Figure 22

Absorption band (cm^{-1})	Assignment of band with functional group	%T
3439.08 and 3421.72	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols)	16
2939.52 and 2883.58	Assigned to the stretching vibration bond of aliphatic C-H groups	3
1739.79 and 1654.92	C=O stretching of the carbonyl group.	7
1558.49 and 1512.19	Stretching vibration bond of C=O and C=C	1 and 4
1244.09, 1174.65	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups.	4
1072.42 and 1049.28	Assigned to the ring vibration	1

Experiment 3

In the experiment 3, where the suspension of dried PGP powder was used, the PH of the solution was 5 as know from literature information and FTIR analysis that PGP contains several carboxylic group and phenolic functional group. Therefore, as during the first stage of the experiment, with the contact time of 10minutes, the pH value dropped from 5 to 5.5, then after 20 minutes to 5.5. This is due to the reaction of the carboxylic functional groups on the surface reacting with almost 38% of the limescale exist on the surface of the stainless-steel pot.

The evidence also shown from FTIR analysis spectrum Figure 23, is FTIR from the pomegranate peel powder obtained from Iraqi Kurdistan area. The absorption bands corresponding to functional groups are attributed band of about 3392.79 cm^{-1} can be assigned to the stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols). Band observed at about 2935.66 cm^{-1} is assigned to the stretching vibration bond of aliphatic C-H groups. Peak around 1732.08 cm^{-1} represents C=O stretching of the carbonyl group. The band at 1616.35 cm^{-1} is assigned to the stretching vibration bond of C=O and C=C. The bands at 1444.68 cm^{-1} and 1361.74 cm^{-1}, are assigned to C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups. The bands at 1056.99 cm^{-1} and 1033.85 cm^{-1} are assigned to the ring vibration.

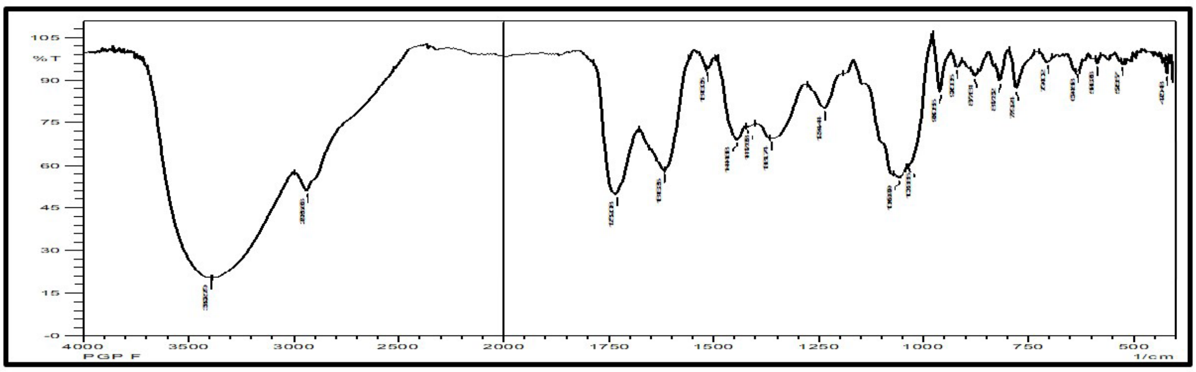

Figure 23: FTIR for Iraqi-Kurdistan pomegranate dried peel powder before extraction of calcification

Table 10: FTIR result analysis in Figure 23

Absorption band (cm^{-1})	Assignment of band with functional group	%T
3392.79	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols)	12

2935.66	Assigned to the stretching vibration bond of aliphatic C-H groups	2
1732.08	C=O stretching of the carbonyl group.	7
1616.35	Stretching vibration bond of C=O and C=C	12
1444.68, 1361.74 and 1234.4	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups.	2, 2, and 4
1056.99 and 1033.85	Assigned to the ring vibration	2 and 1

Figure 24, is FTIR from the pomegranate peel powder obtained from Iraqi -Kurdistan area after it was used for treatment of limescale precipitate on the stainless-steel pot. The absorption bands at 3439.08 cm^{-1} and 3421.72 cm^{-1} corresponding to functional groups was assigned to the stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols) has minimised in size and showed as a small peak. The absorption bands observed at about 2909.52 and 288.58 cm^{-1} is assigned to the stretching vibration bond of aliphatic C-H groups, has reduced to minimum. Bands around 1654.92 represents C=O stretching of the carbonyl group. The band at 1512.19 cm^{-1} and 1454.33 cm^{-1} is assigned to the stretching vibration band of C=O and C=C has reduced to minimum. The bands at 1369.45 cm^{-1},1336.67 cm^{-1}, 1244.09 cm^{-1} are assigned to C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups has reduced to minimum in size. The bands at 1112.93 a $cm-1$ and 1049.28 $cm-1$ are assigned to the ring vibration has reduced to minimum as well. The changes in the size of absorption band the reduction in their intensity (%T) are attributed to the reaction between the hydrolysed calcium and magnesium ions of limescale precipitate with carboxylic ions, carbonyl ions and phenol or ester groups exist in the chemical structural of the chemical components exist in the pomegranate peels.

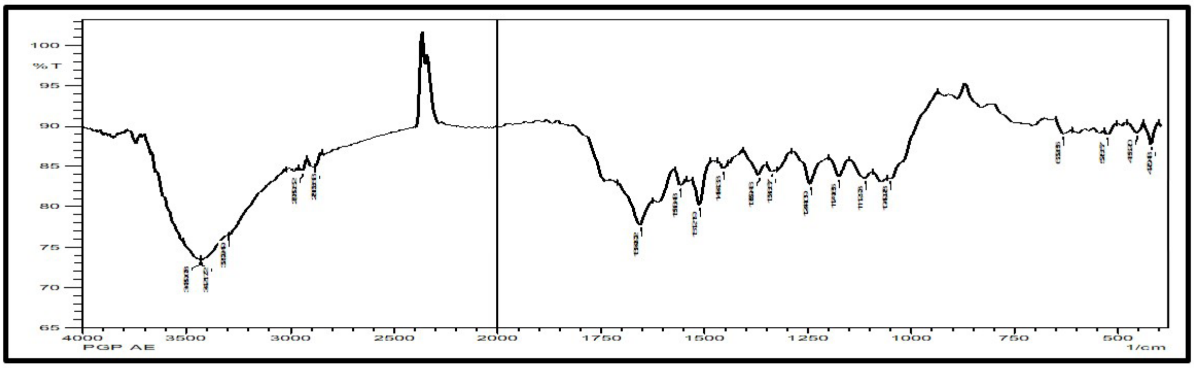

Figure 24: FTIR for Iraqi-Kurdistan pomegranate dried peel powder after absorption of limescale calcified of stainless-steel pot

Table 11: FTIR result analysis in Figure 24

Absorption band (cm^{-1})	**Assignment of band with functional group**	**%T**
3439.08 and 3421.72	Stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols)	17
2909.52 and 288.58	Assigned to the stretching vibration bond of aliphatic C-H groups	3
1654.92	C=O stretching of the carbonyl group.	5
1512.19 and 1454.33	Stretching vibration bond of C=O and C=C	5 and 2
1369.45, 1336.67 1244.09	C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups.	3, 4
1112.93 and 1049.28	Assigned to the ring vibration	1

CONCLUSION

Although pomegranate peel has historically been considered a waste material in the food industry, recent researches have demonstrated its potential as a source of bioactive compounds that offer numerous health benefits. Studies have shown that pomegranate peel possesses many pharmacological properties, including antioxidant, anti-inflammatory, anticancer, and antimicrobial properties, making it a potentially valuable resource for the pharmaceutical and cosmetic industries.

Development in extraction techniques play a crucial role in maximizing the potential efficiently of pomegranate peels specific components for other purposes in industry such as water purification.

The purpose of this work is to demonstrate, for the first time to our knowledge the potential and efficiency of unmodified and un treated PGP as low-cost biosorbent for limescale treatment. Numerous studies have demonstrated the physical and chemical properties of raw PGP. The basic principle of this study was built upon using extraction method was based on green chemistry where the distilled water was used as a solvent for the purpose of preparing the suspensions of pomegranate peels (PGP)as biosorbent.

The main purpose of this study to establish an experimental method and optimum conditions for the adsorption process to remove the limescale that are mainly ($CaCO_3$, and $MgSO_4$). Using pomegranate peels (PGP) as adsorption reagents, the reaction output was analysed to proof if proposed task has been achieved.

It appears from experimental results of this studies that the pomegranate peels constituent as promising biosorbent candidate for limescale removal. In this research three different suspension mixture of pomegranate peels were used. In experiment (1) the suspension was from fresh pomegranate peel (PGP), and in experiment (2) the suspension was prepared from peel pulp obtained from pomegranate juice extraction process While in experiment (3) the suspension was prepared from pomegranate dried peel powder. After the analysis of the obtained results, it was shown that the best absorption result obtained from experiment (2) which gave 80% absorption of limescale within 10 minutes of contact time. The 2nd best result was from experiment (1), where the process showed 70% adsorption within 10 minutes contact time. The third experiment where dried peel powder was used showed about 38% adsorption. Further investigation required to find out about the reason of obtaining different absorption rate despite using the same experimental conditions. The pH of the suspension might have some effect or availability carboxylic carbon on the surface of pulp are more than that of the fresh peel and reduced by drying heat. The FTIR should have taken for the peel before and after drying to proof the changes of functional group existence on the surface.

Nevertheless, the process showed the efficiency raw pomegranate peel in removing the lime scale from water pipe lines and domestic water boiling equipment resulting in minimizing most environmental risks. Contrariwise, raw pomegranate peel is an eco-friendly biosorbent with high adsorption capacity and with low environmental impacts.

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