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Assessment and remediation of contaminated elements in varied car wash stations across Samarra city utilizing pomegranate peels, with comparative analysis against silver nanoparticles

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Abstract: The Department of Life Sciences at Samarra University has conducted a study to evaluate the contamination caused by the car wash plants' tainted effluents. Three stations are located in different parts of the city of Samara provided liquid waste, which is then brought directly to the lab for examination and testing of various contaminated samples. Al, Ca, Fe, Zn, Mn, and Cu are some of the primary constituents in raw water that are investigated prior to treatment. The study of the untreated raw water has produced results that are higher than the World Health Organization's acceptable limits (pollution levels) and the standard values of Iraqi water regulations for every quality that is examined.

Three different processing powders are used to treat the unprocessed water samples from the three car wash stations: TAMARIT3 kernel powder, pomegranate peel powder, and silver nano powder (T1). The powders are applied in five different concentrations at five different levels (250, 200, 150, 100, and 50 ppm), and the results are compared to a controlled treatment that involved applying one treatment per station. Following treatment, analyses are conducted, and the findings indicate that for the three selected vehicle wash facilities, silver nanopowder at concentrations of 250 and 200 ppm has the highest removal values of the characteristics under study (Al, Ca, Fe, Zn, Mn, and Cu). Although the removal of nanosilver from pomegranate peels and date cores is not as great as expected, it is still considerably better than the controled coefficients, which have showed the highest levels of removal

Keywords: Shell of pomegranate, Silver Nanoparticles, Date pits.

1. Introduction

The world's recent drought crisis has been brought on by poor rainfall, changing climatic conditions, low river water levels, and an increase in the rate of population growth, particularly in the Arab world and Iraq. According to international reports, the disparity among these factors has led to growing gaps between the demands for water and its sources and stock, and it is anticipated that these gaps will widen in the upcoming decades due to unfulfilled strategic projects that have aimed at addressing water scarcity and the absence of quick treatment solutions [1] and [2]. Although Iraq has a reasonable amount of water compared to the other nations, there is still an urgent need to supply water sources that encourage water consumption in all aspects of life. A shortage of surface and groundwater resources is quite possible[3] and [4].

Due to the release of large amounts of human and industrial waste into rivers and the lack of law enforcement to regulate these practices, the percentage of pollution in rivers has increased significantly and dangerously in recent times. One of the main sources of pollution in rivers is the sewage and industrial waste found in cities, which is highly toxic and harmful chemical, biological, and physical substances that are difficult to decompose. These wastes enter rivers and groundwater through public drainage networks or seep into the ground. Water from residences, hotels, hospitals, restaurants, and water used for road and vehicle wash stations is among these pollutants. Additionally, car wash facilities are thought to be one of the main causes of water pollution [5].

The number of cars has increased significantly in recent years due to the noticed rising in industrial activity, city expansion, and population density. As a result, this has led to a need for multi functioned service stations of all kinds, including car washes, to meet the growing demand from car owners seeking high-quality auto care. In the city of Samara, there are now over 70 stations spread throughout the city, none of which is neither authorized to operate nor had a pre-existing specialized raw water treatment unit. Therefore, there are not dedicated to supply the public health treatment standards.The primary source of effluent from vehicle washes is the usage of chemicals like

As one of the solutions offered to provide quantities that enhance life-supporting water sources, nanotechnology is one of the new and emerging methods for treating industrial wastewater because it is low-cost, environmental friend, and uses materials of natural origin. Compared to the traditional methods, nanotechnology is used as a way to reduce and remove the sources of basic pollution from water [5].

The purpose of this study is to investigate the issue of contaminated water from car wash facilities located in various parts of the city of Samara that is dumped straight into rivers without any treatment and to implement novel solutions to lessen the harmful effects of this contaminated water.

Earlier within this decade, the study of nanoparticles has flourish due to their effective applicationd in many aspects as opto-electronic devices, clinical settings, and the medical field. Specially as the areas of diagnosis, optical switching, drug delivery, and cancer treatment [6, 7]. More specifically, silver-based nanomaterials that have been made of noble metals. Also, Ag NPs' prominent surface plasmon resonance is the cause of this (SPR) phenomenon [8, 9, 10]. The controlled and methodical changes in geometry of nanomaterial are made possible by the coupling of pharmaceutical advancements with SPR, which is a sensitive function of the nanocomposite structure [11, 12].

2. EXPERIMENTAL

The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

Intervention Ary studies involving animals or humans, and other studies that require ethical approval, must list the authority that provided approval and the corresponding ethical approval code.

2.1. Devices and tools used in this study

Table (1) –Devices and tools used to work in this research

		Origin
	English	
1	Particale Size Analyser	
2	(Sartorius) Balance Sensitive Electrical	Germany
3	Jar Test	
4	Atomic Absorption Spectro	

2.2 processed materials

2.2.1 pomegranate peel powder

-Pomegranate peels are, collected from local markets, dusted, washed with distilled water. Then, they are dried under laboratory conditions with continuous stirring until reaching the complete dehydration. After a week, the dry crusts are ground with an electric mixer and the powder is kept in clean and sterile glass bottles. Finally, an adhesive is fixed on them, on which the sample information is recorded for subsequent uses.

2.2.2 date kernel powder

The date cores are collected from local varieties available in the markets. The cores of the dates are separated from its fruits and washed thoroughly with distilled water . The washed cores are transferred to the laboratory and left with continuous stirring until drying. The cores are ground with a mill after being cleaned well and made sure that they are free of any powdery residues . Then, store the powder in clean, sterile glass jars and fix the adhesive on them without the sample information for subsequent uses.

2.2.3 nano silver powder

The powder uses the processed silver nanomaterials from the American company US Research Nanomaterials Inc and is manufactured according to the corresponding industrial specifications of nanotechnology.

2.2.4 preparation of concentrates for powders

For pomegranate peels, date cores, and silver powder, concentrations of PPM Powder Solutions weight/Volume (1 mg = 1 ppm) are created. A preliminary experiment is then conducted using the Jar Test equipment to ascertain the ideal effective concentrations for use in processing.

2.2.5 collection of samples.

-The first, haphazard set of information is provided to around 70 car wash locations in the city of Samara. These locations are relied on river's water and water purification facilities for the purpose of irrigation and drinking. Three locations have been designated for the collection of samples by car wash facilities; two of them are located on the riverbank and discharge the untreated water directly into the river, while the third one is located in the city center and releases untreated waste into the groundwater. Following their collection in designated basins to gather the station's water and complete washing the automobiles while keeping them stagnant to make sure they do, raw water samples are taken from car wash stations. They are kept in the refrigerator for the second day for the purpose of subsequent transactions and tests. The test is carried out by placing one liter of water from each car wash station in the rollers of the jar test device. Then the silver nanoparticle, date kernel powder and pomegranate peel powder are added according to the concentrations approved in the experiment. After that, the rollers are placed in the said Tester and then the solutions are mixed for 30 minutes separately according to the parameters of the experiment. For the first five minutes, they are at a speed of 100 cycles per minute to homogenize the treated material with water. After that, from the sixth minute the speed is increased to 300 cycles per minute to mix the treated material with water in. Finally, the researchers complete the 24 minutes at a speed of 50 revolutions per minute. Figure.1 shows the procedure of the experiment.

Fig.1 neighbor test equipment

2.3 Factors and design of the experiment

The experiment includs two factors: the first factor includs three types of processing powders such as: silver nanopowder (T1), pomegranate peel powder (T2) and date kernel powder(T3), while the second factor includes the concentration of five levels as illustrated :(250, 200, 150, 100 and 50) ppm for each treatment, which are given codes from C1 To C5, respectively. The final combination has showed 15 resulting transactions between species and concentrations, in addition to the three controlled transactions with a transaction for each station. Table (3.3) illustrats the analysis of three times repetitions for each test and for all samples to reduce the experimental error when collecting samples.

2.4 Statistical analysis

-The results are statistically analyzed for all the qualities that have been studied in the two experiments of the study by using a ready-made statistical analysis system (SPSS, V23) under the Windows operating system, and a complete randomized design is used (R.C.D) according to ?[13]. the arithmetic averages of the transactions are compared according to the Duncan Test at a probability level (0.05)

3. RESULTS AND DISCUSSION

3.1 The study includ two main phases:

The first stage involves analyzing untreated raw sewage from car wash stations to determine the extent of its pollution compared to ordinary water. The second stage examines the efficiency of removing pollutants from wastewater using the treatment methods employed in the study..

3.2. Characteristics of raw car wash water (first stage)

The analysis's findings regarding the washing plants' raw wastewater are presented in Table (1) When car wash facility effluent is compared to control water. The high concentrations of Ca, Mg, Na, and W all have showed values above allowable limits. High elements in wastewater can be attributed to variations in chemical composition depending on the source of pollutants in wastewater. These findings align with a study by [14]. That has found that wastewater quality varies from site to site and that chemical composition varies depending on the effluent source.

Table 2, indicates a noteworthy rise in the amount of heavy metals that is found in untreated wastewater .

-The multiple chemical composition of pollutants in car wash wastewater such as detergents and dust fats and residues of small car parts volatile as a result of washing, which led to their high content [15] .

Table 2 specifications of untreated raw waste water for car wash plants

Measurements	Unit of measurement	Waste car wash stations			General used water measurements	** Iraqi Water Specifications
		St.3	St.2	St.1		
Ca	mg/L	18.97	18.33	20.35	40	30
Mg	mg/L	12.5	13.84	13.38	60	40

Na	mg/L	420	390	400	200	150
Al	mg/L	7.31	7.41	7.45	5	1
Cu	mg/L	1.73	1.62	1.55	0.4	0.05
Zn	mg/L	29	24	26	2	0.5
Mn	mg/L	17	15	13	0.3	0.2
Fe	mg/L	36	34	33	5	3

Iraqi effluent standards for disposal to water bodies

3.3 Removal of contaminated elements Macro and Micro Elements

3.3.1 Aluminum element Al

Table 3 shows that there are significant differences between the types of materials are used in raw water treatment and control treatment. The silver powder treatment gives the highest average decrease in aluminum concentration for all stations, with decreases of 7.054, 6.994, and 7.350. The lowest clearance was observed with pomegranate peel powder, which amounted to 8.026, 7.926, and 7.382 for all stations. This treatment also is differed significantly from the control treatment, which yielded values of 8.24, 8.89, and 8.77 for stations ST1, ST2, and ST3, respectively, when compared with the average values of other treatments and the control treatment.

Stations	**Type**	**CONC. ppm**					**Mean of Type**	**Normal**
		250	**200**	**150**	**100**	**50**		
S1	**Silver**	7.15	7.11	6.67	7.29	7.05	7.05a	**8.77d**
	Pit	7.02	7.02	7.14	7.2	7.29	7.13b	
	Shell of pomegranate	7.5	7.86	8.35	8.06	8.36	8.03c	

M.C.St1		7.23a	7.33 b	b 7.38	c 7.51	c 7.56		
S2	Silver	6.97	6.75	6.85	6.89	7.51	6.99a	8.89d
	Pit	6.91	7.32	7.4 7	7.38	7.57	7.33b	
	Shell of pomegranate	7.8	7.71	7.52	8	8.6	7.93c	
M.C.St2		7.23a	7.26b	7.28b	c7.42	d7.89		
S3	Silver	7.54	7.25	7.35	7.22	7.39	7.35a	8.24d
	Pit	6.96	7.16	7.33	7.94	7.52	7.38a	
	Shell of pomegranate	7.3	7.38	7.18	7.12	7.93	7.38b	
M.C.St3		7.26a	7.27a	7.29b	7.43c	7.61d		

Table 3 shows how the removal of elemental concentration from the raw water of three vehicle wash stations that are located in various parts of the city of Samarra are affected by varying amounts of silver nanomaterial, powders, pomegranate peels, and date cores.

-The results of the analysis indicate that there are also significant differences between the concentrations used for the controlled treatment. It is noted that the highest clearance rate is recorded with a concentration of 250 ppm in all treated samples at all stations by recording average values of up to 7.22 , 7.22 , 7.26 for terminals St1, ST2 and ST3, respectively. The concentrations of 200ppm and 150ppm have reached a higher rate than the concentrations of 100ppm and 50ppm of Al. Also, they are different from the controlled treatment , which is recorded the highest averages of Al concentration 8.77 , 8.89, 8.24 for the three stations sequentially .

3.3.2 Element calcium

Stations	**Type**	**CONC. ppm**					**Mean of**	**Normal**
		250	**200**	**150**	**100**	**50**		

							Type	
	Silver	1.83	2.23	2.48	2.43	3.32	a 2.45	
S1	**Pit**	2.24	2.26	2.35	3.1	3.35	b 2.66	4.16d
	Shell of pomegranate	3.24	3.16	3.28	3.09	3.49	c 3.25	
	M.C.St$_1$	2.43a	2.55a	2.70b	2.87b	3.38c		
	Silver	2.25	2.13	2.68	3.1	3.24	.68a2	
S2	**Pit**	2.19	2.31	2.56	2.92	3.34	2.66a	4.81c
	Shell of pomegranate	2.55	2.52	3	3.13	3.26	2.89b	
	M.C.St$_2$	2.33a	2.32a	2.74b	3.05c	3.28d		
	Silver	2.73	2.9	3	3.52	3.8	3.19a	
S3	**Pit**	2.80	2.9	2.98	3.31	3.17	3.03 a	4.33c
	Shell of pomegranate	2.72	3.31	3.87	3.3	3.3	3.30b	
	M.C.St$_3$	2.75a	3.03b	3.28c	3.37c	3.42d		

Table 4 *shows that there are significant differences between the treatment and control coefficients, such as the silver powder treatment excelled in recording the lowest concentration of element Ca in the treated water samples of the first station and recorded an average of 2.45. As for the second and third stations, there is no significant difference between the silver and pomegranate peel treatments in reducing the concentration of the CA element, which differs significantly from the treatment of date nuclei and the control coefficient, the latter of which recordes the highest concentration rates as 4.16, 4.81 and 4.33 for the three stations, respectively .*

The results of table 2 also shows that there are significant differences between the transactions, as they recorde a decrease in the concentration of CCA with an increase in concentration in general. The highest clearance rate is recorded with the concentrations of 250 ppm and 200 ppm in the St1 and ST2 stations with average values of 2.43, 2.55 and 2.33, 2.32, respectively. In contrast, it in turn differes from the control transaction, which recordes the highest values for CCA .

3.3.3 Iron element Fe

As for the concentration of the Iron element in all stations, it is significantly affected by the variety of treatment and decreased using the treatment of silver powder in all samples collected from the stations. As indicated in Table 3, and the treatment of silver powder gives the lowest averages for the concentration of the Fe element in the treated water samples, reaching 6.54, 8.29, *9.24 for stations St1, St2, St3 sequentially . The rest of the transactions such as (pomegranate peels and date cores) indicate significant differences among themselves in terms of the effect with the highest averages of the values of the treatment with silver nanopowder. In contrast , they record a significant difference from the control treatment.*

Stations	**Type**	**CONC. ppm**					**Mean of Type**	**Normal**
		250	**200**	**150**	**100**	**50**		
S1	**Silver**	6.30	6.53	6.73	6.33	6.8	6.54a	9.3c
	Pit	6.77	6.73	6.87	7.57	7.2	7.03b	
	Shell of pomegranate	6.83	7.6	7.29	9.5	10.4	8.32c	
M.C.St1		a 6.63	b 6.95	b 6.96	7.80c	8.13d		
S2	**Silver**	8	7.88	8.58	8.18	8.8	8.29a	10c
	Pit	9.32	8.86	9.32	8.31	9.54	9.07b	
	Shell of pomegranate	9.94	11.57	10.83	10.18	12.74	11.05c	
M.C.St2		a 9.08	9.43b	9.57b	8.89c	d10.36		
S3	**Silver**	9.02	9.82	9.17	9.2	8.98	9.24b	10.37c
	Pit	8.98	9.2	9.48	9.82	9.97	9.49b	
	Shell of pomegranate	10.83	10.37	11.83	12.37	14.1	11.90c	
M.C.St3		9.61a	9.79a	10.16b	10.46c	11.02d		

-Table 5 shows how various amounts of date cores, powders, pomegranate peels, and silver nanomaterial affected the elimination of the FE element from the raw water of three vehicle wash stations located around the city of Samarra.

3.3.4 Manganese element Mn

-The results of the statistical analysis in Table 3-4 show that there are significant differences in reducing the concentrations of the MN element for the type of substance and its concentrations for all transactions. Which illustrates a difference between them from the control transaction .The

transaction using silver powder has recorded averages of 0.140, 0.037. 0.034 while the Mn averages in the control transaction are 1, 0.75, 0.68 respectively.

Stations	**Type**	**CONC. ppm**					**Mean of Type**	**Normal**
		250	**200**	**150**	**100**	**50**		
S1	**Silver**	0.11	0.12	0.14	0.15	0.18	0.140 a	**1d**
	Pit	0.15	0.15	0.16	0.18	0.19	0.166 b	
	Shell of pomegranate	0.14	0.15	0.17	0.19	0.20	0.170 c	
M.C.St1		a 0.133	b 0.14	c0.156	d0.173	e 0.19		
S2	**Silver**	0.02	0.03	0.04	0.045	0.05	0.037 a	**0.75d**
	Pit	0.03	0.035	0.04	0.05	0.06	0.043 b	
	Shell of pomegranate	0.04	0.045	0.05	0.055	0.06	0.050 c	
M.C.St2		a0.030	0.037b	c0.043	d 0.05	e0.057		
S3	**Silver**	0	0.01	0.03	0.04	0.09	0.034 a	**0.68d**
	Pit	0.06	0.08	0.09	0.11	0.12	0.092 b	
	Shell of pomegranate	0.09	0.1	0.11	0.12	0.12	0.108 c	
M.C.St3		0.050a	0.063b	0.077c	0.090d	0.110e		

Table 6 the effect of different concentrations of silver nanomaterial, powders, pomegranate peels and date cores on the removal of the element mn from the raw water of three car wash stations in different locations of the city of Samarra.

The use of different concentrations of substances has shown significant differences among them. The concentration of 250 ppm using silver powder provides the highest reduction percentage, with significant differences from the powders of date kernels and pomegranate. The removal of the element Mn reached 0.133, 0.030, and 0.050 for the three stations, respectively, while the control treatment recorded the highest rates of the element Mn, as shown in the table above.

3.3.5 zinc element Zn

The results of the statistical analysis in Table 7 indicate that there are significant differences between the coefficients in terms of the type of materials used in the processing and their *concentration. The researchers record a significant superiority for the treatment of silver over the treatment of pomegranate peels and date cores in reducing the element zn, giving average values of 0.14 ,0.03, 0.03 for stations St1, St2, ST3, respectively. At the same time, the treatment of pomegranate peels and nuclei has recorded significant differences among themselves 0.16, 0.17,0.04, 0.05,0.9□0.11 for stations St1, St2, St3, respectively. These values differ significantly from the control treatment, which recorded the highest concentration of Zn.*

Stations	**Type**	**CONC. ppm**					**Mean of Type**	**Normal**
		250	**200**	**150**	**100**	**50**		
S1	**Silver**	0.11	0.12	0.14	0.15	0.18	0.14 a	**0.34c**
	Pit	0.15	0.15	0.16	0.18	0.19	0.16 b	
	Shell of pomegranate	0.14	0.15	0.17	0.19	0.2	0.170 c	
M.C.St$_1$		a0.13	0.14b	c0.15	d0.17	e 0.19		
S2	**Silver**	0.02	0.03	0.04	0.04	0.05	0.03 a	**0.07c**
	Pit	0.03	0.035	0.04	0.05	0.06	0.04 b	
	Shell of pomegranate	0.04	0.045	0.05	0.05	0.06	0.05 c	
M.C.St$_2$		0.03a	b0.03	c0.04	d 0.05	e0.057		
S3	**Silver**	0.01	0.01	0.03	0.04	0.09	0.036 a	**0.13c**
	Pit	0.06	0.08	0.09	0.11	0.12	0.092 b	
	Shell of pomegranate	0.09	0.1	0.11	0.12	0.12	0.108c	
M.C.St$_3$		0.05a	0.06b	0.07c	0.09d	0.11e		

Table 7 the effect of different concentrations of silver nanomaterial, powders, pomegranate peels and date cores on the removal of the Zn element of raw water for three car wash stations in different locations of the city of Samara

The concentration coefficients of the three types has recorded significant differences among themselves in reducing the concentration of the Zn element in the treated water, and the concentration gives 250 ppm the highest removal rate of the Zn element and then 200 PMM, which is different from each other from the other coefficients of the plants with values of 0.13, 0.14 , 0.03, 0.03 and 0.05, 0.06 for Terminals 1, 2 and 3, respectively. The two concentrations ppm 50 and ppm 100 give the highest percentage of accumulation of Zn in all samples treated for the control coefficients, which amounted to 0.13, 0.07, 034 .

3.3.6 Copper element CU

Stations	Type	CONC. ppm					Mean of Type	Normal
		250	200	150	100	50		
S1	Silver	0.010	0.020	0.027	0.035	0.040	0.02a	0.85c
	Pit	0.020	0.030	0.031	0.040	0.048	0.03b	
	Shell of pomegranate	0.025	0.035	0.035	0.050	0.049	0.04b	
M.C.St1		0.01a	0.02a	0.03b	0.04b	0.04b		
S2	Silver	0.022	0.031	0.032	0.043	0.042	0.03	0.81c
	Pit	0.032	0.041	0.040	0.050	0.052	0.04	
	Shell of pomegranate	0.034	0.047	0.048	0.060	0.056	0.05	
M.C.St2		0.029a	0.039b	0.04b	0.05b	0.05b		
S3	Silver	0.018	0.022	0.025	0.033	0.039	0.02	0.70c
	Pit	0.028	0.033	0.033	0.042	0.048	0.03	
	Shell of pomegranate	0.029	0.037	0.035	0.052	0.053	0.04	
M.C.St3		0.02a	0.03b	0.03b	0.04b	0.04d		

The results of table 8 show that there are significant differences between the coefficients that are used in the treatment in the concentration of the element cu in the water .The treatment of silver powder is significantly superior to the powders of date kernels and pomegranate peels. It records average concentrations of the element Cu as 0.02, 0.030, and 0.02 for the three stations, respectively. The powder of the date nuclei does not differ significantly from each other in relation to the impact ratio, but it is not the same as the control treatment, which found that stations St1, St2, and St3 had the highest concentrations of suspended solids, with values of 0.70, 0.81, and 0.85, respectively.

Table 8 shows how various amounts of date cores, powders, pomegranate peels, and silver nanomaterial affect the amount of CU removed from raw water at three separate Samara car wash locations.

The concentration treatment of ppm 250 in all treatment material transactions gives the lowest average concentration of Cu in all stations. Compared with the rest of the transactions and the control treatment with average values of 0.01, 0.02, and 0.02 for stations St1, St2, and St3, respectively. The average concentrations record significant differences between them in the values of Cu concentrations and with the average comparison treatment. [16]. [17] and [18]. Conversely, the control treatment has the least impact on lowering the raw water's CU concentration.

-As a resultAs a result of introducing them to the water, the processes of coagulation and flocculation may have increased the proportion of contaminated elements removed by utilizing nanoparticles and powders, since the contaminants agglomerate through precipitation. Flocculation procedures have demonstrated efficacy in treating wastewater by employing additives and their capacity to effectively precipitate and eliminate soluble components and salts from wastewater.

When compared to the results of earlier treatment studies by [19] and [20], which reported a clearance rate of 50–60% using chemical doses of other chemicals ranging from 100 to 500 mg/L, the current study's results generally showed that treatments using silver nanoparticles and natural powders achieved a clearance rate of more than 60%. Additionally, the results of the current study are consistent with the findings of [21]. [22].

4. CONCLUSIONS

Wastewater from car wash stations in random areas contains pollution levels that exceed the limits allowed by the World Health Organization and Iraqi standards, thus being a major source of pollution for Rivers and groundwater in the city of Samarra . The treatment using natural vegetable powders and silver nanopowder has proven its effectiveness in water treatment and has reduced the percentage of pollution, making it suitable for use . The materials that are used in the treatment recorded a good removal rate and the treatment methods are cheap, easy to use, available and with little damage to the environment and can be an alternative to chemical and physical products that are manufactured and used in the current hazardous treatments that affect the human environment, its negatives and behavior .

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