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APPLICATION OF POMEGRANATE PEELS AS AN AGRICULTURAL WASTE FOR REMOVAL OF PETROLEUM HYDROCARBONS FROM WATER

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ABSTRACT

With the increase in population growth, the environmental pollution of surface waters increases, especially with the increase in oil extraction and transportation. Research and studies have tended to use cheap materials in the treatment of pollutants, including PAHs pollutants. The world has turned to water treatment with low cost material (environmentally friendly materials to treat pollutants such as PAHs), used pomegranate peel in treatment produced water from PAHs compounds, Six samples were taken, three of them from the Maysan oil fields and three from the north Basra oil fields (Qurnah). The RE% of the concentrations of PAHs in the fields, the highest RE% were for the mixture, peel and pulp. While PAHs concentration: Gc (Shimadzu.2010) , the concentrations of PAHs (16 compounds) present in the produced water before and after treatment with FTIR analysis was conducted to know the functional groups on the surface of the adsorbent before and after treatment to all sites in current study.

***Keywords* :** Pomegranate peels, Agricultural waste, Petroleum Hydrocarbons, Oil fields

Introduction

One of the main environmental problems that essential to be solved these days is recovering water from pollutants such as pollution of sea, lakes and rivers water with organic compounds and petroleum hydrocarbon compounds, including HOCs. These pollutants include aliphatic and aromatic hydrocarbons, polychlorobiphenyls (polychlorobiphenyls), Polycyclic aromatics hydrocarbons (PAHs), PCDD and some are pesticides. Even if these compounds are very low soluble in water. However, the danger of these compounds lies in the focus on removing them from the existing natural water because of the high toxicity they cause to mammals, animals, and aquatic and surface plants that depend on this polluted water, as they have a high ability to cause mutations in living cells, in addition to being carcinogenic when found in drinking water or Through its entry into the food chain (Oost *et al.*, 2003; Union, 2008).

The extraction of gas and oil from oil fields in several regions of the world are followed by (mainly salt) water called Produced Water (PW). Created water pollution is defined by the US-EPA as the water (brine) produced by the groundwater movement formation structures throughout the gas and oil extraction. It may involve the creation of water that is a natural water level that, being denser, lies beneath the hydrocarbons, the water injection, small amounts of water vapors, and byproducts of chemicals remediation, which were introduced to aid in the extraction of oil/water (PW Facts) to prevent negative impacts. These may involve chemicals or solvents like paraffin inhibitors, deformers, flocculants, coagulants, emulsion breakers, bactericides, corrosion inhibitors, scale inhibitors, dehydrators and hydrate inhibitors (Farajzadeh, 2004). Furthermore, the characteristics of the water produced are much the same as that generated by oil or by normal oil extraction, however its formation could be very dissimilar (Veil *et al.*, 2004), since the presence of water probably seems to have a greater amount of solutes, with the cationic composition normally resembling seawater, and is also more acidic.

The ability of plants to remove the elements and purify polluted water has received great scientific attention, and many researches have been conducted in this field, Wolverton and his collaborators, the United States' National Space Agency (NASA), were pioneers in research in this field in the 1970s. Research has continued in this field until the present time due to the superior ability to absorb PAHs and mineral nutrients from the water environment (Tabbada *et al.*, 1990).

PAHs occupied a great interest in this regard due to their great role in water pollution, especially factory and urban sewage wastes. Many studies have demonstrated the accumulation of mercury as well as other PAHs in the plant root zone to a greater degree than the leaves, and the increase in absorption by increasing the concentration. This element, at a concentration of 1-2 parts per million for a month, was not toxic to the plants, but it reduced the production of fresh matter, the length of the root and the percentage of chlorophyll in the plant. Removing large quantities of that element reduces toxicity indirectly to fish (Abdelhamid *et al*., 2010).

Giordano *et al*. (2005) estimated that the sampling batch reactor (SBR) eliminated about 55 percent of PAHs, whereas the anaerobic and anoxicoxic remediation procedure extracted 0.0 percent to 73.5 percent of PAHs (mainly PYR, NAP and BghiP) from waste-water (Sun *et al*., 2013). Qiao *et al*. (2016) confirmed that the efficacy of low -molecular-weight organic contaminants was considerably greater comparison with high-molecular-weight organic contaminants since the low -molecular- weight organic contaminants may more effectively be biodegraded/biotrans shaped throughout biological remediation. Plants were used to mitigate contaminated water and soil, though phytoremediation would be a cheap and noninvasive process. Phytoremediation seems to be a more ecologically advantageous approach comparison with existing treatments (Mojiri *et al*., 2016).

Alagić *et al*. (2015) stated that PAHs assimilation from vectors into crops could be remedied as a balance process under which the cumulative PAHs seem to be in accordance with the PAHs present in the matrix. Plant absorption of PAHs is stimulated by water supply from the transpiration process and passage of water by symplastic and apoplastic paths into the plant roots. The root absorption is apparent for hydrophobic substances like PAHs and is closely associated with the root lipid amount. PAH absorption is impaired by the properties of both plant organisms and organic chemicals (Li *et al*., 2002). If the organic pollutant enters the plant cell, it is spread through translocation to various sections of the plant; afterwards, any number of reactions can happen inside the current series: hydrolysis, reductions or oxidations (Reynoso-Cuevas *et al*., 2010). In contrast with large molecular PAHs, lower molecular PAHs are key in plants (Tao *et al*., 2006). Al-zawey (2020) used the rice husks as bio removal for Hydrocarbons

This type of pollution is very dangerous to human health. Treatments and methods must be developed to get rid of it. Among these cheap treatments is the use of pomegranate peels and pulp as a sorbent to remove oil compounds, including PAHs (El-Ashtoukhy 2008; Moghadam *et al*., 2013). These peels are inexpensive and make up 70% of fruit waste (MacLean *et al*., 2014). This study aims to prepare the low-cost matter for PW treatment as well as removing of some hydrocarbons compound to release the water to environment by using pomegranate peels to treat and purify water from petroleum compounds, especially those that have a direct impact on human health (PAHs).

Materials and Methods

Study area

Oil produced water, six sites were studied, and three of them in the Amara oil fields and three in the Basra oil fields, which are Site-1 -ALamara Fields (AL-Bazerkan Field), Site-2 ALamara Fields (Al Fakaa Field), Site-3 ALamara Fields (Abu Garb Field), Site-4 ALBasrah Fields (St. 1), Site-5 ALBasrah Fields (St. 2) and Site-6 ALBasrah Fields (St. 3).

Fig. 1 : The Map of Iraq and the location of Oil Fields.

For the purpose of obtaining pomegranate peels and pulp, pomegranate peels were collected from juice shops in the city of Hilla, Babel Governorate, Iraq. The pulp (the inner white spongy substance) was separated from the peels and then washed with distilled water in order to get rid of other materials attached to it.

Pomegranate peels preparation methods

In order to prepare the Pomegranate peels, it should be separated the peels from the pulp and isolate them well, which immersion in distilled water and switching water for 24 hours then drying pomegranate peel. After that washed with double distilled water then dry for 24 hours. The pomegranate peel was ground to particle sizes between 2-3 mm and was extra dehydrated by means of a fluidized bed drier at 60 C. The using n-hexane (95% pure) for peels to remove the hydrophobic soluble organic matter and colored pigments in peel, refluxed for 2 hours in n-hexane. To get rid of hexane, the peels is washed with double distilled water, then quick drying. A grinder was used to form the peel, use sieves to get 500-1000 size powder. Wash the powder with distilled water and then dry the powders (peel powder) in a heat oven at 80 °C for 24 hours. The manufactured pomegranate peels was stored in air tight sealed glass containers (Gulistan, 2014).

Procedure

Initially, Pomegranate peels was tested in Oil produced water treatment to know the removal efficiency of the material, and more than one test was done for polluted water using concentrations of, (Pomegranate peels) (1) g/l00 ml respectively, and the mixing time and sedimentation period was which is (15, 15 min) respectively, after which the precipitate was separated from the treated water and the following tests were performed (Temp, pH, TDS, E.C,).

Measurement of PAHs concentration using GC device for samples taken before treatment and after treatment with (Pomegranate peels) test was performed to explain the functional groups.

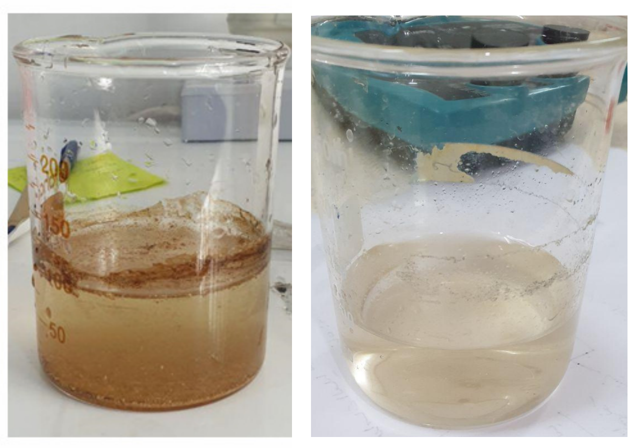

Fig. 2 : before and after treatment PAHs by used pomegranate peels.

LAB Work

Measuring some properties for produced water taken from the three fields of the city of Amara and the three fields of the city of Basra. The following was measured:-

1- Tempertuer, PH, EC, and TDS.
2- Measurement of PAHs (16 compounds) concentration using GC device for samples taken before treatment and after treatment with absorbent (Pomegranate peels) with tree replicates from produced water before and after treatment.

Results and Discussion

Physical parameters

The measurement of some of the physical properties of water is considered a measure of pollution and also gives indications of the nature of the water body, Also, the increase and decrease in some Physical values gives a clear expression of the nature of the pollutants present in the water (Zaghloul, 2019). The process of coagulation-flocculation helps in removing some pollutants with different charges with the surfaces of the used material (Nowacka, 2015), which lead to the interaction of ions and pollutants with the material used in the treatment, which causes a decrease in the compounds that cause the high pH and the compounds that cause the high EC and TDS.

The temperature was examined both in the field and in the laboratory. Laboratory measurement of the physical properties after the treatment process with pomegranate peels and observes the decrease in PH due to the effect of using adsorbent containing surfactants on the functional groups.

Fig 3 show PH value before treatment for example in Sit.1 (7.87) , after use peel in treatment the result was (7.55) This is a result of adsorption of the acidifying ions into the water, the adsorption leads to a decrease in the PH due to an increase H+ on the surface of the adsorbent (Attia, 2010). The contamination in water lead to increase PH in water, used pomegranate peels was reduce contamination in water, the use of pomegranate peel leads to adsorption of polluting compounds with different charges.

The EC test is used as evidence of water pollution from Table 1 we note the EC values of the six sites where the EC value ranges (3.75, 3.51, 3.01, 3.90, 3.10, 4.11) mSi/sm respectively ,after used peel be lowered (1.15, 2.61, 2.31, 1.90, 2.20, 3.80) mSi/sm respectively as shown in figure 4. The high adsorption of the pomegranate peel surfaces, and their containment of active groups, led to a decrease in the negative and positive ions that cause low electrical conductivity. The negatively charged surface contributes to the ability of functional groups to adsorb positively charged ions since it represents the driving force for electrostatic interaction with positive ions (Cui *et al*. 2016). TDS stands for total dissolved solids, and represents the total concentration of dissolved substances in water. Common inorganic salts that can be found in water include calcium, magnesium, potassium and sodium, which are all cations, and carbonates, nitrates, bicarbonates, chlorides and sulfates, which are all an ions.

TDS (2300, 3100, 2180, 3308, 3223, 3166) mg/l respectively for six sites before treatment, fig 5 show variation PH after treatment (1600, 2230, 1765, 1950, 2504, 2801) mg/l respectively for six sites, the high removal rates of total dissolved salts are due to the efficiency of the surface of the crusts and their containment of functional groups that can interact with ions, salts and contaminants present, which leads to their decrease in the water (Abdolali *et al*., 2014).

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Fig. 3 : PH variation, before and after treatment with pomegranate peels.

Fig. 4 : EC variation, before and after treatment with pomegranate peels.

Fig. 5 : TDS variation, before and after treatment with pomegranate peels.

Measurement of PAHs

The hydrocarbons present with the water produced with the oil were examined for six sites with a GC device for the produced water before treatment, and also measure the concentrations after treatment with pomegranate peels.

The adsorption process is generally classified as physicsorption (characteristic of weak Van Der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction, the containment of pomegranate peel and pomegranate pulp on functional groups on its surface leading to polarization of contaminants with opposite charges to those of adsorbed surfaces This is called the attractive force that is weak by the forces of weak Van Der Waals (Rashed, 2012).

Absorption is one of the widely used methods as PAHs possess a great absorption ability into the solid media and their low aqueous solubility property (Lamichhane *et al.*, 2016). Figure 6 shows the results of the process of removal and treatment of hydrocarbon compounds (PAHs) by using pomegranate peel, Pomegranate peels were used to remove hydrocarbon compounds, because pomegranate peels have a high porosity to adsorb hydrocarbon pollutants (Gulistan, 2014) and this has achieved high R.E% for most fields, where, for example, the Ace compound in sit.. 1 was the R.E 100% while B (a) Flu the R.E% was 93%.

Fig 7 show the difference shows the R.E of PAHs, where the R.E ranged from 68.835 to100% in some fields and the R.E% ratios are due to the nature of pollutants in the water, such as heavy elements that adsorb on the surfaces of the adsorbent material, which reduces the adsorption process (PAHs) for example B (a) Fluoranthene in sit. 5 was removed from 68% (Seliema *et al.*, 2020).

The R.E% also depend on the molecular weight (LMW, HMW) and the number of rings of the compound itself and also to the strength of the bonds on the surface of the adsorption material as one of the most important elements contributing to the adsorption process, The PAHs in current stady are adsorbed tightly because of the various functional groups on pomegranate waste surface such as hydroxyl (–OH) ,carboxyl (–COOH) and silanol (Si-OH), which are responsible for sorption of (PAHs) from the aquatic environment (Akhtar *et al.*, 2006; Aksu, 2005; Krishnani *et al.*, 2008; Abdolali *et al.*, 2014).

R.E% Phe. in sites 2,5 (94, 60)% respectively, percentages of removal Anth. in sites 1,5 (95 , 74.5)% respectively, the vibration in removal rate fig by used pomegranate peels, lead to difference in the removal rates for the same compound and the same adsorbent material is due to the nature of the contaminant's external environment, meaning that the polluted water contains a group of pollutants such as heavy elements that leads to their interaction with the pollutant and thus the reduction rate of the same compound (Seliema *et al*., 2020; Shartooh *et al*., 2013; Salmani *et al*., 2017, Abdulrazak, 2017; Ben-Ali *et al*., 2017).

R.E% of PAHs LMW more than HMW The high removal efficiency of the compounds is due to their molecular weight, where the low molecular weight compounds are more spread over the pores of the adsorbent surfaces (Dowaidar, 2012). Increase pollution compound in environmental lead to decrease the removal target compound such as PAHs (Ben-Ali *et al*., 2017). The negative charged (functional grops) on the surface of the pomegranate peel lead to the adsorption of positively charged ions (pollutants) through an electrostatic reaction (Cui *et al*., 2016). High usable surface area and a porous structure of facilitate to enhance the absorb capacity (Burchell, 1999)

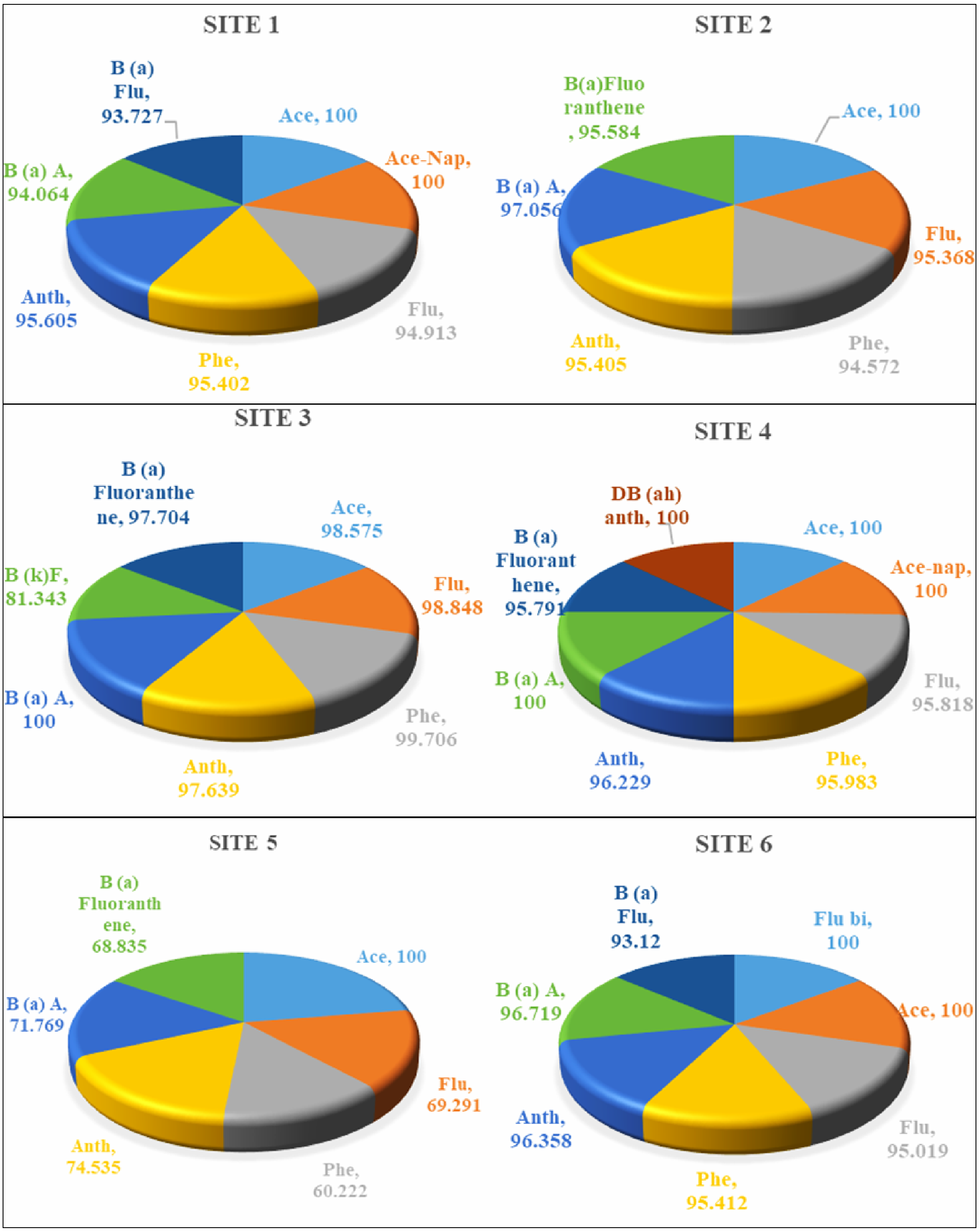

Fig. 6 : R.E% PAHs in select sites after treatment with peel.

Conclusions

1. Used low-cost materiel in water treatment, the use of agriculture waste in treating polluted water is better in terms of health, environment and economics.
2. Pomegranate peel can be used effectively in treating the water produced with oil before putting it to the surface water environment.
3. Pomegranate peel is a natural, environmentally friendly that has no health effect and, It can be disposed of easily.

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