Treatment Of Water Hardness Using Activated Carbon Prepared From Libyan Olive Oil Mill Residue

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ABSTRACT

Massive amounts of solid olive mill residues (olive-waste cake) generated every year and disposed of in the environment. Thus, the present work aims to study the preparation of activated carbon (AC) from Libyan Olive-Waste Cakes as a natural source. The solid olive mill residue was carbonized at 200 C^0 and chemically activated with 25% $Zncl_2$ and 25% $Zncl_2$ + 25% H_2SO_4 . The prepared AC was used to reduce total hardness in groundwater. The results showed that the addition of H_2SO_4 increased the treatment efficiency of AC leading to decrease the total hardness concentration. Several parameters affecting the efficiency of AC were investigated including pH, initial concentration of AC, and contact time. The achieved results showed that the optimum values were at pH: 3, AC initial concentration: 2.5 g/L, and contact time 120 min. At these conditions the maximum reduction of hardness was 75%. According to these results the olive- waste cake can be considered as an effective natural source of activated Carbon.

Keywords: Olive mill residue, activated carbon, water hardness

Introduction

Water hardness is the high concentration of dissolved minerals such as calcium and magnesium due to water moving through soil and rocks leading to dissolve amounts of these natural minerals [1,2]. Hard water can cause various issues in daily life including unacceptable taste and ineffective washing of clothes and dishes as well as generating scales in water equipment [3]. Several methods have been used to treat water hardness such as adding a water softener to laundry and the dishwasher or using ion-exchange systems to treat the water before the use. However, ion-exchange can raise the sodium concentration of treated water which may lead to health concerns [4,5]. The de-alkalization process can also soften water using weakly acidic resin, so the calcium and magnesium ions are replaced by hydrogen ions. Then the hydrogen ions react with the carbonate and bicarbonate ions to produce carbon dioxide. Therefore, the hardness of the water is minimised without any increase of sodium ions. However, this method has some disadvantages including anion resins are susceptible to polluting from organics and hardness getting through the softener [6].

Activated carbon adsorption can be effectively used to treat different kinds of water pollution which include the removal of metallic micro pollutants, organic compounds, and pesticides [7]. Activated carbon (AC) is the most promising method due to its safe use, cost-effective, and simple equipment design [8]. However, the cost of using this technique mainly depends on the source of activated carbon used in this process. Therefore, the use of agriculture wastes have been a significant economical solution to this issue [9]. Activated carbon is highly effective for the removal of metal ions such as calcium Ca^{2+} and magnesium ions Mg^{2+} [10,7].

Various sources of natural materials have been widely used for the industrial production of activated carbon such as coal, coconut shell, and wood [11,7,12]. Moreover, other agricultural by-products were used including date stones [13,14], rice husks [15], peach stones [16] and grains of sorghum [17]. Regarding olive-waste cakes as a source of activated carbon there have been a few studies that covered this topic [18,19, 20,21].

In fact, Libya is one of the largest countries in olive oil production so there are massive amounts of olive-waste cakes generated during the manufacturing process every year. In general, the olive oil production process generates about 20% of oil, 30% of solid wastes, and 50% of wastewater [22]. According to [20], the yearly average of olive-waste cakes production is about 200000 tons which can be varied from country to another. Beside the use of these large amounts to produce activated carbon for water treatment purposes it can also contribute to minimise the solid wastes in the environment.

The production of effective activated carbon depends on the nature of raw materials and the preparation method. This method includes physical and chemical procedures as well as key parameters [23,24-30]. Drying, grinding and carbonizing are the most important steps of the physical treatment process that control the porous size and surface area of AC. For chemical procedures different chemicals have been used as dehydrating agents such as $Zncl_2$, ($Zncl_2$ + H_2SO_4), KOH, and H_3PO_4 [31]. The general activation procedures can be categorized as shown in Figure 1 [21].

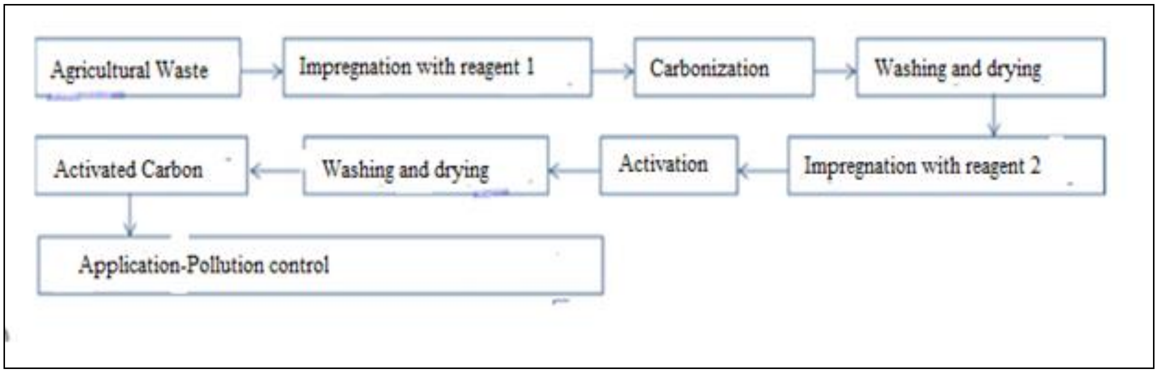

Figure 1 A general method of preparation of activated carbon from a natural source.

The present work aims to prepare activated carbon from Libyan olive-waste cakes as a natural source. Both physical and chemical treatments were performed in order to produce an effective AC. Two chemical activation methods were used including $Zncl_2$ alone and $Zncl_2 + H_2SO_2$. The optimum activated carbon prepared was used to treat the water hardness of the tap water.

1. Materials and Methods

1.1 Materials and Equipment

All chemicals used in these experiments were checked for expiry dates. 25% of sulfuric acid (H_2SO_4) and 25% of zinc chloride ($ZnCl_2$) were prepared. Regarding equipment Spectrophotometer (HACH DR900), pH meter, and DS Meter were used Figure 2.

Figure 2 Chemicals and equipment used

1.2 Preparation of activated carbon

Olive-waste cakes were collected from an olive oil mill located in Gharyan, Libya Figure 3. This solid residue was used as a raw material for the production of activated carbon. The activation method can be defined as physical and chemical processes that enormously increase carbon surface area through removing hydrocarbons [14]. The process of changing the olive-waste cake into coal is called carbonization while the chemical decomposition by heat without oxygen is called pyrolysis [32,33]. First of all, 500 g of olive-waste cake was wished with distilled water and dried at 200 C^0 for 180 min. Then the carbonized sample was crushed till it became homogeneous powder. After that the powder is taken into a thermal frying pan and covered by aluminum foil. This pan was put in the furnace at 300 C^0 for 3hr in order to perform the pyrolysis step. The carbonized material was again crushed to get smaller particles. Chemical activation was performed using 25% of $ZnCl_2$ which mixed with the powder to make a paste. Then the mixture was taken into the furnace at 100C^0 for 30 min for drying. Finally, the prepared activated carbon was washed using distilled water and filtered to get the final form of the activated carbon Figure 4. All above procedures were repeated for the other raw material using 25% of $ZnCl_2$ and 25% H_2SO_4 [34]. Both models were air dried for three days at room temperature.

Figure 3 Study location (Gharyan, Libya)

Figure 4 (a) Olive-waste cake (raw material), (b) Prepared AC

1.3 Use of activated carbon (AC)

Two activated carbons (AC) were used to treat groundwater containing 600 mg/L of total hardness at pH 7. Two grams of AC (25% of $ZnCl_2$) was added to 1L of water sample and stirred for 5 min before taking the first sample for total hardness reading. Then five samples were taken at 15 min, 45 min, 90 min, 120 min, and 150 min respectively.

To study the effect of pH and the initial concentration of AC the above steps were repeated for various values. Furthermore, the same procedures were implemented for AC (25% of $ZnCl_2$ + 25% H_2SO_4).

2. Results and Discussion

2.1 AC (25% of $ZnCl_2$)

Table 1 shows the obtained results and it can be noticed that the maximum total hardness removal was 60% at 120 min then the adsorption was constant.

Table 1*Total hardness (600 mg/L) removal using AC (25% of $ZnCl_2$) & pH 7*

Time (min)	5	15	45	90	120	150
Total hardness removal (%)	16	30	41.66	50.2	60	60.0

The effect of pH was studied and found that the best results in this case was 64 % at pH 3.

2.2 AC (25% of $ZnCl_2$ & 25% H_2SO_4)

All above procedures were repeated for AC (25% of $ZnCl_2$ & 25% H_2SO_4). The achieved results showed that the activated carbon treated with sulfuric acid was more effective than zinc chloride alone. This result might be due to low ash and humidity content of the activated carbon. Acid washed activated carbon is desirable for treating drinking water and food grade applications [34].

2.3 Effect of pH

Influence of pH on the removal of total hardness was investigated. The adsorption of calcium and magnesium ions on the surface of activated carbon is mainly affected by the surface charge, in other words the value of pH. The maximum removal for total hardness was detected at pH 3, meaning the surface has a positive charge due to excess protons in the solution It is known that the decrease of pH value leading to rise in the H^+ concentration in the aqueous solution and the activated carbon surface gains positive charge by absorbing H^+ ions. As a result when the adsorbent surface is positively charged the hardness ions owns a strong attraction with the positively charged carbon surface [10]. However, table 2 showed that the maximum removal of total hardness was 75 % at AC (25% $ZnCl_2$ & 25% H_2SO_4), and pH 3.

Table 2 *Total hardness (600 mg/L) removal using AC (25% $ZnCl_2$ & 25% H_2SO_4) & pH 3*

Time (min)	5	15	45	90	120	150
Total hardness removal (%)	20.32	37.5	45.3	60.5	75	75

2.4 Effect of AC initial concentration

The influence of the initial concentration of activated carbon on the removal of total hardness was investigated as well. In this part the model two was used to study this effect due to its higher efficiency compared to model one. Different initial AC concentrations were used at following conditions involving 600 mg/L total hardness, AC (25% $ZnCl_2$ & 25% H_2SO_4), and pH 3. Figure 5 shows the obtained results and can be clearly seen that the maximum was about 2.5 g/L.

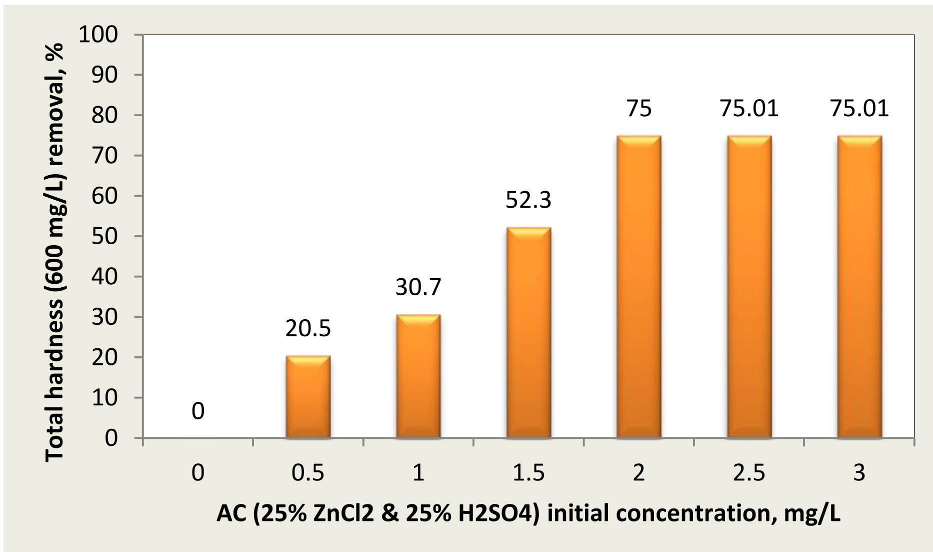

Figure 5 The influence of AC initial concentration at pH 3 & 150 min

After the optimum value of AC (2.5 mg/L) it can be noticed that there is no significant reduction of the total hardness.

3. Conclusions

The obtained results of the present work show that the activated carbon prepared from Libyan olive-waste cake can effectively reduce the water total hardness from aqueous solution. The chemical activation of activated carbon via zinc chloride with sulfuric acid is more effective than zinc chloride alone. The adsorption is significantly dependent on pH and the initial dose of the activated carbon. The acidic medium (pH 3) was found to be suitable for total hardness removal. Olive-waste cake as a natural source of activated carbon is promising to be efficient for other water treatments due to its high adsorption capacity.

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