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Short Articles

Preview / Index /Next

Treatment of wastewater introduced in oil refineries by using Sugarcane beads

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ABSTRACT

The study assesses the wastewater treatment process in the oil refinery by using an agricultural plant (sugarcane beads) to remove crude oil-contaminated water. Experiments were carried out at different periods by using different concentrations of oil-contaminated water in a continuous process system, which has been established in our laboratory. Results show the efficiency of these beads in reducing the Turbidity, TDS and TSS by 68%, 21%, and 12%, respectively. The amount of hydrocarbons also decreased significantly proportional to the time of the adsorbent process due to the physical and chemical properties of these beads, making them an excellent adsorbent agent.

Keywords: sugarcane beads, wastewater, refinery, total organic compounds, adsorbent process

INTRODUCTION

The United Nations Environment Program defines pollutants as any organic, chemical, or radioactive substance present in wastewater that degrades the quality of this water. Pollutants are any physical, chemical, or biological change in water quality that negatively affects living organisms or makes the water unsuitable for the required uses. Numerous sources can pollute water sources, rendering them unfit for drinking, irrigation, and other services and causing environmental harm. The sources of water pollution vary according to the various aspects of water use: [1]

-Waste that does not require spatial treatment but is collected and sorted according to its nature (plastic, paper, and glass) to be disposed of using established methods.

-Polluted waste that must be treated before disposal is classified into two types:

- Environmentally friendly waste, defined as materials that can be removed or destroyed using traditional wastewater treatment methods such as sedimentation, flotation, and filtering, may include aerobic biological processes aimed at oxidizing and destroying most organic matter. The treatment's success is typically measured and expressed in terms of (BOD) biological Oxygen Demand or (COD) Chemical Oxygen Demand.

- Environmentally inappropriate wastes, which can be defined as pollutants incompatible with previous treatment methods because they contain toxic substances such as heavy metals, oils and oil derivatives, considered organic compounds that are difficult to decompose when using traditional methods.

Water-contaminated crude oil contains a high concentration of hydrocarbons, including saturated, aromatic, and other organometallic hydrocarbons, which pollute the environment. Some of the hydrocarbons found in contaminated water are carcinogenic and genotoxic to humans and other organisms [2]

This could be because the waste crude oil contains polyaromatic nuclear compounds (PAHs). Light PAHs have up to four rings, such as naphthalene, pyrene, anthracene, phenanthrene, and fluoranthene. In contrast, heavy PAHs have more than four rings because (PAHs) known for their carcinogenic and mutagenic tendencies have been found to accumulate in significant amounts in these petroleum products [2].

Remediation of such oil-contaminated water has become a problem in oil-producing countries such as Iraq, and more attention is needed. This waste is typically treated with physical, chemical, and biological techniques in oil refinery water treatment units before being disposed of in the environment, as illustrated in Figure 1.

A study of the status and harmful impacts of oil refinery effluents and pre-treatment of pollutants of Iraqi oil refineries have been recently done by researchers [3]. Many studies that dealt with using nanotechnology to treat water polluted with hydrocarbons resulting from refinery activities have been applied [4].

In South Refineries Company, for example, (6000 – 8000) m^3/ sec. of industrial water polluted with hydrocarbons are pumped into the East Basra Canal, which affects the water environment [5].

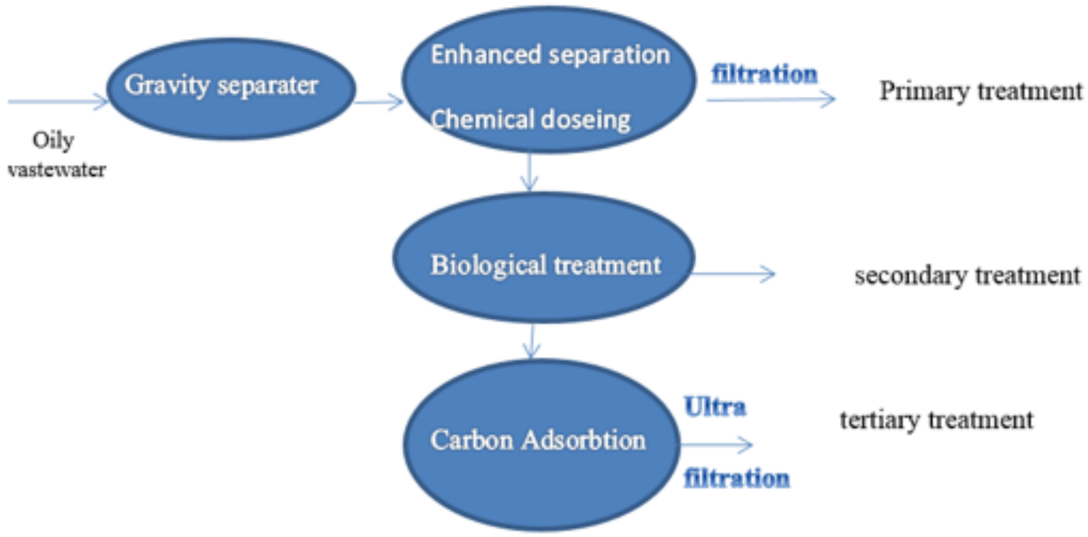

Figure 1. Typical wastewater treatment of Refinery

One of the treatment techniques for oil separation from wastewater is using agricultural plants such as sugarcane beads, which are good bio-sorbents of oil. Sugarcane stalks have one of the highest lignocellulose concentrations or agro-industrial residues, which are composed of several functional components such as cellulose, hemicellulose, lignin, ash, and a small number of extractive lignocelluloses matter, and which, due to their numerous and varied functional groups, provide a solid, attractive force for the binding of pollutants ions. Sugarcane bio-adsorbents contain several functional groups acting as adsorptive sites, such as –OH and – COOH. These sites enable bio-adsorbents to attract and bind pollutant ions by replacing them with hydrogen ions (ion exchange adsorption) or by donating electron pairs or adsorbents [6,7].

Adsorption

It is the accumulation of a gaseous or liquid adsorbate in the form of molecules, atoms, or ions on the surface of another solid adsorbent material using the weak Van der Waals forces. There are two types of adsorption (physical and chemical). Numerous studies have shown that the type of adsorption can be inferred depending on the connection between the adsorbent and the adsorbent and the heat accompanying the adsorption.

-Physical adsorption: It is also called Van der Waals adsorption because it occurs as a result of strong bonding between molecules, ions, or atoms of the adsorbate substance on the surface of the adsorbent so that it occurs on inert solid surfaces and causes the electronic saturation of its atoms. The physical adsorption is either single-layer or multi-layer. The layers are also non-local; that is, it does not depend on the nature of the chemical adsorbent.

-Chemical adsorption: It occurs when the adsorbent material tends to form different chemical bonds associated with the adsorbent material, whether atoms, molecules, or ions. Another under the same conditions.

It is well known that both types of adsorption may co-occur; physical adsorption occurs first, as it requires low temperatures, and then chemical adsorption occurs with high temperatures, such as hydrogen adsorption on the surface of nickel.

Factors influencing the adsorption process:

The most important factors that influence the adsorption process are [8]:

Temperature: the adsorption capacity is proportional to the temperature.

Acidity function: The adsorption efficiency depends on the surface of both the adsorbent surface and the adsorbent material.

Adsorbent surface nature: The efficiency of adsorption increases as the surface area of the adsorbent increases because it increases the number of active adsorption sites, as adsorption efficiency is dependent on the surface area of the adsorbent, the physical and chemical properties, and the size of the pores.

Adsorbent nature: Adsorption efficiency is determined by the adsorbent's chemical and physical properties, the size of the adsorbed particles, the steric chemistry and the number of aromatic rings in the adsorbents, the molecular weight, and the ion size.

MATERIALS AND METHODS

Sugarcane beads were collected from the marshes of Basrah. 5kg of washed sugarcane was chopped into smaller sizes with a kitchen knife, then crushed and squeezed to extract the sugar-rich juice. The crushed beads were treated with 0.01M sulfuric acid and dilute sodium hydroxide before being washed with distilled water.

The colorless beads were dried in a vacuum oven at 100°C before being kept for batch adsorption [9]. Then, the different concentrations of water contaminated with crude oil were prepared of (100,300, 500,1000, 7000) ppm and treated at different times (1,2 and 5) min. The treatment method was carried out as in Figure 2.

The density of Cued oil was determined according to the method [ASTM D 4052] by using the Anton Par instrument. The analysis of polluted water before and after treatment was carried out by using [pH meter, conductivity meter, flame photometry and oil in water (TOC) instrument supplied by Horiba Comp.] and the results are presented in tables 1 and 2**.** Finally, scanning Electron Microscope analysis(SEM) for the Sugarcane beads before and after treatment are shown in Figures 3 and 4

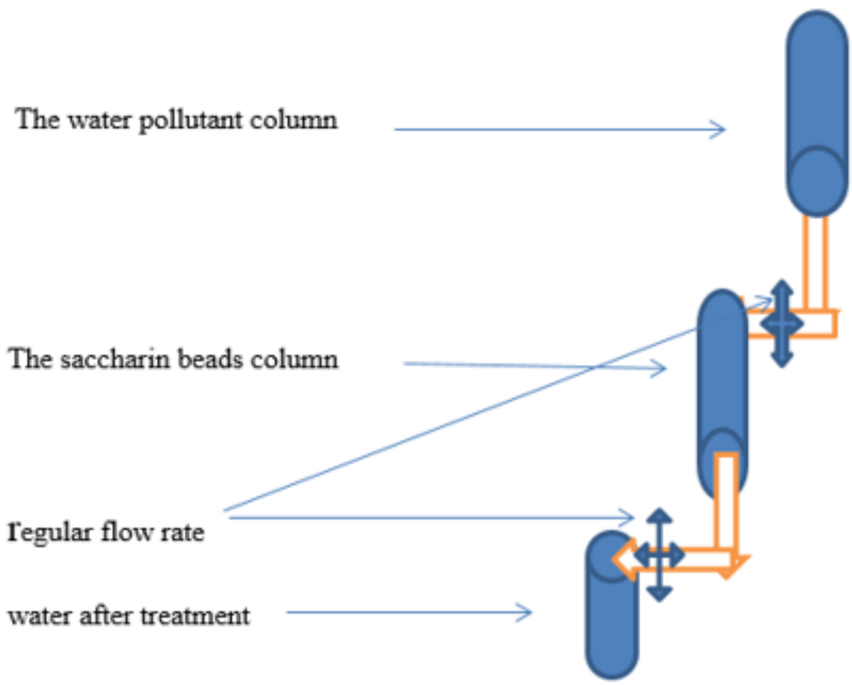

Figure 2. Scheme of the treatment system

Test	Environmental test allowed	Before treatment	After treatment
pH	6.5-8.5	7.28	7.31
T.S.S	Max 40 ppm	23.6	4.1
T.D.S	Max 1500 ppm	5645	1194
Conductivity µs/cm	-	9830	1078
Turbidity (NTU)	-	12.5	3.4
Refractive index	-	1.3235	1.3389
Density @15.6 °C g/cm³	-	1.00767	1.00476
Chloride (Cl^-) ppm	Max 250 ppm	1008.9	790.4
Mg^{+2} ppm	150 ppm	300	91.3
Na^+ ppm	Max 400 ppm	483.7	221.3

Table 1. shows the results of water tests before and after treatment and the permissible environmental limit.

No	Con.(ppm)	Time min.	TOC (ppm)
1	100	1	25.6
2	100	2	14.2
3	100	5	8.3
4	300	1	36.8
5	300	2	19.9
6	300	5	11.2
7	500	1	40.5
8	500	2	22.7
9	500	5	13.3
10	1000	1	45.4
11	1000	2	27.5
12	1000	5	15.8
13	7000	1	78.8
14	7000	2	50.4
15	7000	5	32.7

Table 2. The results of TOC tests for polluted water before and after treatment are shown

RESULTS

The effectiveness of sugarcane beads in improving the specifications of water contaminated with residual hydrocarbons from crude oil produced from Mishref field in Basra Governorate, which has a density of (0.8675 gm/cm^3) measured using a density measuring device as shown in Table 1. It should be noted that the results only represent the treatment of contaminated water by passing it through the reeds for one stage. There is a 68 % reduction in the turbidity of the water before and after treatment, as well as a reduction in the percentages of both TDS (total dissolved solid) and TSS (total suspended solids). Chloride and sodium ions decreased by (78 and 45 %), respectively. The tables also show that the percentage of water conductivity has decreased by 11%. Table 2, on the other hand, shows the activity of sugarcane beads for reducing hydrocarbons as (Total organic compounds) TOC as a result of adsorption. Water-contaminated crude oil contains a high concentration of hydrocarbons, including saturated, aromatic, and other organometallic hydrocarbons, which pollute the environment. Some hydrocarbons in contaminated water are carcinogenic and genotoxic to humans and other organisms. This could be because the waste crude oil contains polyaromatic nuclear compounds (PAHs). Light PAHs have up to four rings, such as naphthalene, pyrene, anthracene, phenanthrene, and fluoranthene. In contrast, heavy PAHs have more than four rings because (PAHs) known for their carcinogenic and mutagenic tendencies have been found to accumulate in significant amounts in these petroleum products.

Solvent Adsorption: The adsorption of the solvent is greatly influenced by the competition between the solvent molecules during the adsorption process, and it is dependent on the interactions between the solute and the solvent, as well as the adsorbing surface. The adsorption force at the surface.

The research represents an attempt to use the modified sugarcane beads for the treatment of industrial wastewater containing a mixture of petroleum hydrocarbons produced from refineries to water sources by using an adsorption process. The positive results of the research (which is known as the first attempt at treatment in South Refinery Company) will shed light on an important issue, which is the exploitation of available plants for the treatment of industrial water so that this water can be reused at the industrial processes without being wasted in water sources.

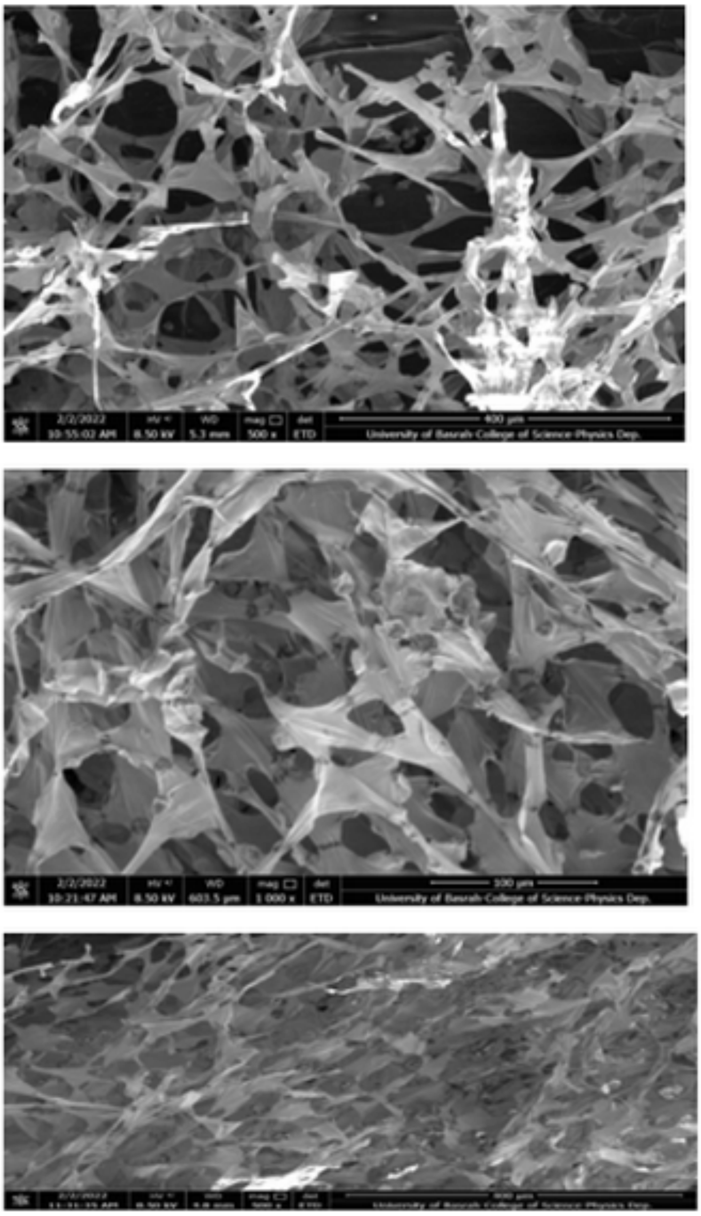

Figure 3. The SEM analysis of sugarcane beads after treatment for con.7000 ppm

(at 1,2, 5 min. respectively)

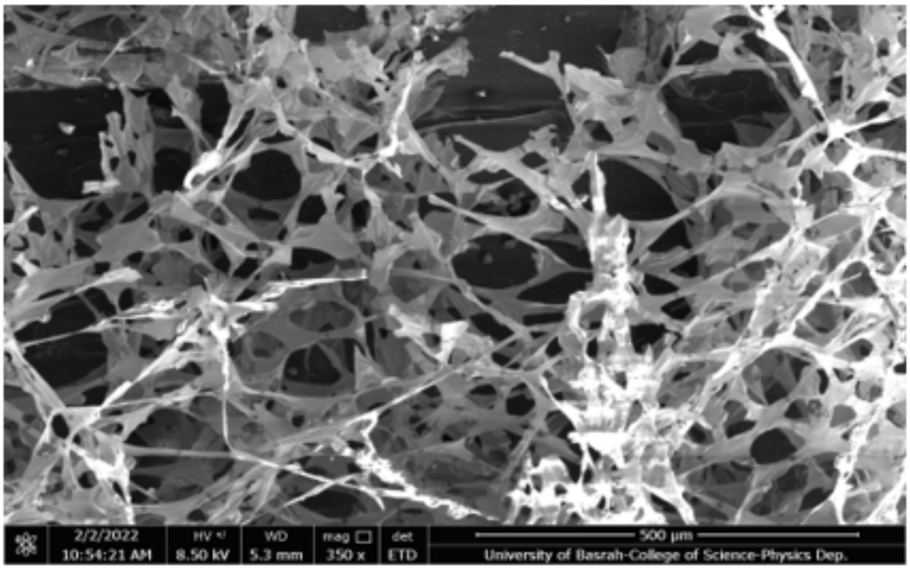

Figure 4. A three-dimensional image of the nanomaterial by AFM

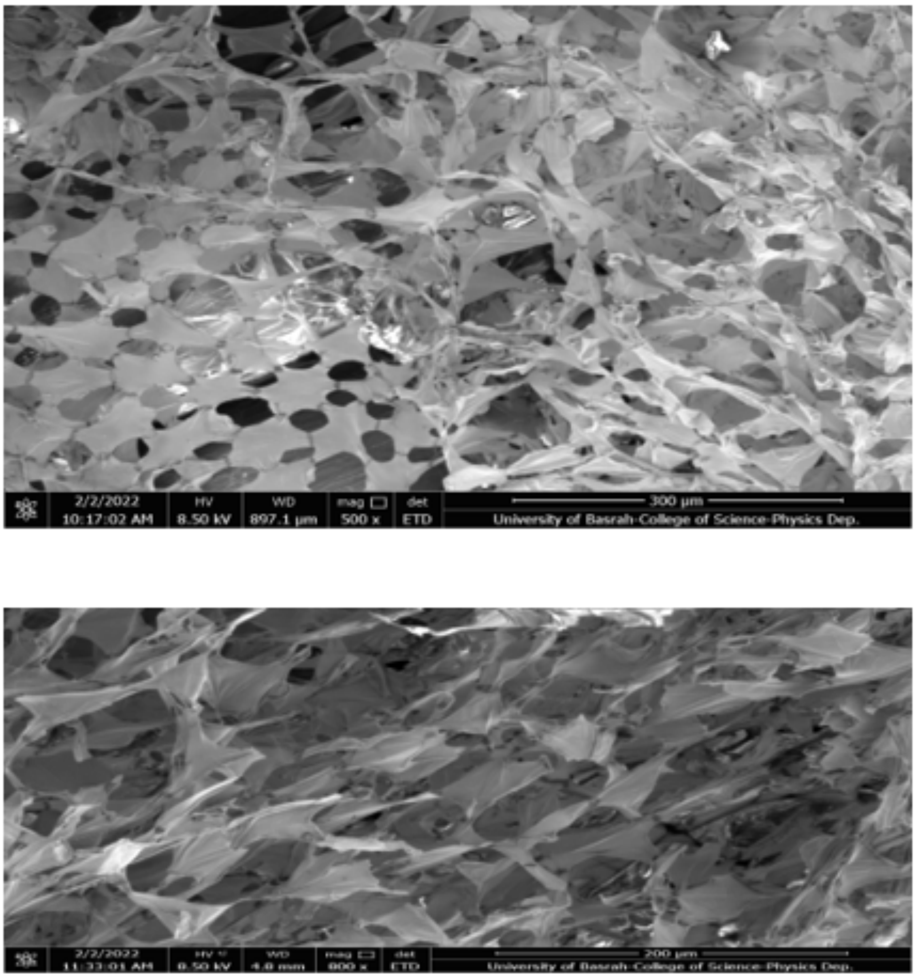

Figure 5. The SEM analysis of sugarcane beads after treatment for con.100 ppm (at 1,2,5 min. respectively)

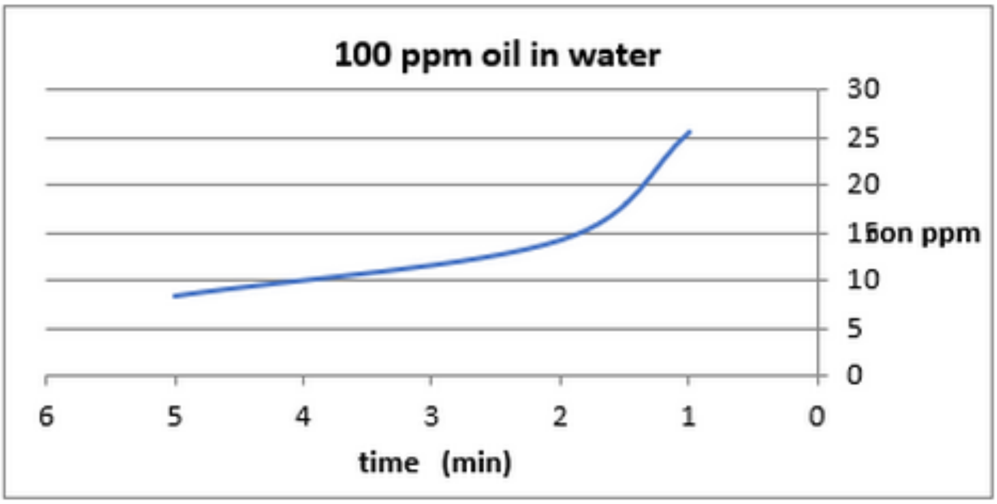

Figure 6. Treatment of a sample of 100 ppm oil in water

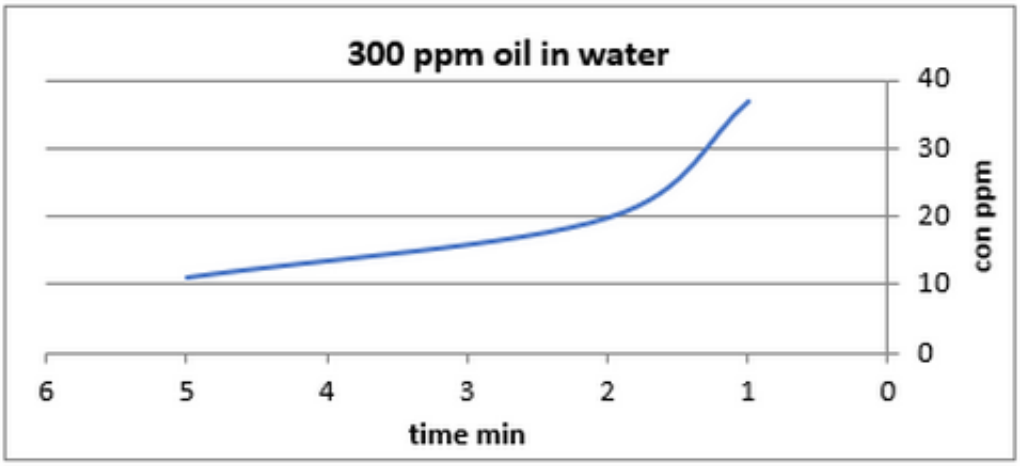

Figure 7. Treatment of a sample of 300 ppm oil in water

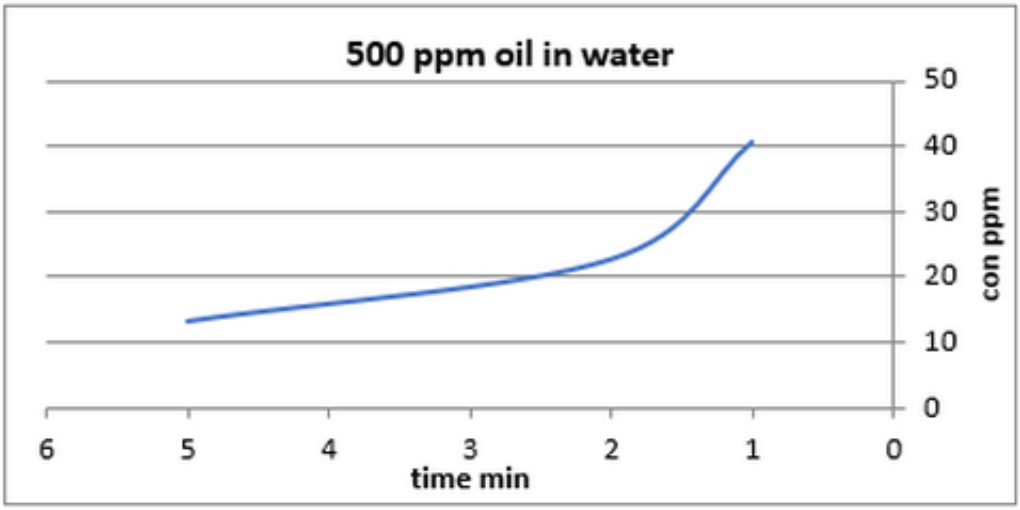

Figure 8. Treatment of a sample of 500 ppm oil in water

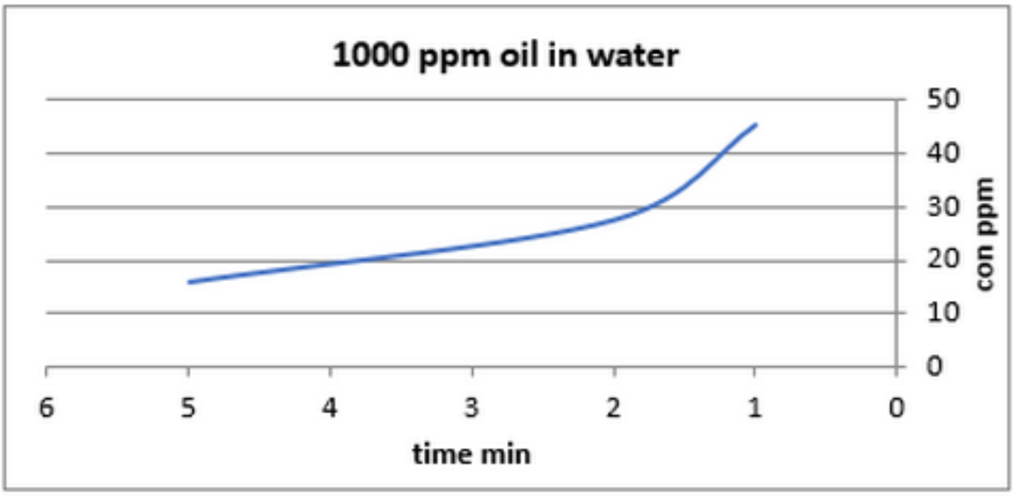

Figure 9. Treatment of a sample of 1000 ppm oil in water

DISCUSSION

The results obtained in this paper were presented in tablet No.1, showing the performance of the sugarcane beads to improve both. Physical and chemical specifications of the water by reducing the amount of turbidity value in the wastewater from 12.5(NTU) before the treatment to 3.4 NTU. According to the results shown in Table 1, the initial concentration of suspended solids in wastewater was 23.6 ppm; this concentration was decreased to 4.1 ppm by using sugarcane beads, which reveals the effect of the cellulose units that provide a robust and attractive force for the binding of pollutants ions. On the other hand, the concentration of total dissolved solutions also decreased from 5645 ppm to 1194 ppm. Due to the activity of functional groups contained in the sugarcane cellulose, the concentration of chloride ions was minimized from 1008.9 ppm to 790.4 ppm. [5,6]

The SEM indicated the results figures 3-8, which illustrate the activity of sugarcane beads towards the hydrocarbons at different times, indicate the useful of using these beads as an excellent adsorbent agent due to their compositions of 50 % cellulose, 25 % hemicellulose and 25 % lignin [9,10]; sugarcane beads compete favorably with synthetic adsorbents in oil removal from crude oil contaminated water [10,11]. Figures 5-8 illustrate the results obtained from Table 2 graphically, which enhance the effectiveness of beads for reducing the amount of oil in wastewater proportional to time; these results indicate the significance of this method for wastewater treatment.

CONCLUSIONS

Sugarcane beads are an excellent agricultural adsorption agent that can be used to treat crude oil-contaminated water and improve the specification of wastewater introduced in oil refineries so that it can be reused rather than discharged into the sources of water.

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