Removal of Oil From Wastewater Using Walnut-Shell

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Abstract

The ability of pulverized walnut-shell to remove oil from aqueous solutions has been studied. It involves two-phase process which consists of using walnut-shell as a filtering bed for the accumulation and adsorption of oil onto its surface. Up to 96% oil removal from synthetic wastewater samples was achieved while tests results showed that 75% of oil can be removed from the actual wastewater discharged from Al- Duara refinery in the south of Baghdad.

Keyword: Wastewater, Oil Removal, Walnut-Shell, Adsorption.

Introduction

Fats, oils and greases (FOG) content of wastewater can cause many problems in both sewers and waste treatment plants. If oil or grease is not removed before discharge of the waste it can interfere with the biological life in the surface wasters and create unsightly floating matter and films [1]. The acute effects of oils on birds, fish and microorganism are reasonably well cataloged. The potentially more harmful is the subtle effect on other aquatic life [2].

The food industry seeks effective technologies to remove fats, oils and greases. Manufactures of oil-containing foods face the problem of reducing the oil containment load to downstream wastewater systems. A large amount of water is used in the refinery processes and a big fraction of it comes out as waste after getting polluted by oil which enters into the wastewater from leaks, spills etc., at various stages [3].

Methods of separating FOG from water include physical and/or chemical separation. In physical separation, free FOG is separated according to differences in specific gravity or in surface tension phenomena. In chemical separation, dispersed water droplets and solids are destabilized through the use of chemicals.

Dissolved air flotation (DAF) is a well-accepted method of FOG removal in the meat and diary industries. Through the addition of coagulants and flocculants, very effective separation is achievable. However, the coagulants and flocculants are fairly expensive and alter the composition of retained fats and solids so that reuse as animal food is sometimes not possible.

Ultrafilteration (UF) membranes work very well on filtering out FOG. Oil in water from can-washing operations also has been removed by membranes. Membrane configurations for FOG separation include flat sheet, tubular, hollow fiber, or spiral wound design [4].

Other techniques have been attempted with less success, including combinations of lignin or halogen with natural or synthetic polymers; have been recently patented as agents to facilitate separation of FOG from food processing wastewater [5].

A new pressurized thermal technology for separating oil/water emulsions can have application to food processing FOG. This technology uses the change in physical properties and surface tension of water and FOG at elevated temperature up to 3000C at pressures of 100 atmospheres to break the emulsion and allow recovery of separate oil and water streams for reuse or recycle [6]. One oxidation system, wet air oxidation, has already reported for olive mill wastewater treatment, but was found satisfactory only in combination with biotreatment. Electro-flotation seems to be an excellent method for obtaining high retention of FOG. In this method FOG emulsions are broken under the effect of electric field.

Most refineries and many chemical plants use oil-water separation devices as API separators, corrugated plate interceptors (CPI), sometimes called titled plate interceptors (TPI). (CPIs) are widely used for oil-water separation in many industries, but have found only limited acceptance in refineries. The reason is that the units cannot take shock loads and high flows as well as a conservatively designed API separator [7].

Walnut-shells were originally developed for cleaning gasoline and diesel engines due to its lack of silicon and toughness. One of the most popular uses is the deflashing of molded plastic parts. A typical pH and moisture content values available for walnut-shells are as follows [8]:
pH: 5.4 - 4.5

Moisture: 4.5%

Activated carbon can be prepared from walnut shell which is chemically activated by zinc chloride. It is observed that a the ratio of activating agent to raw material increases to 100%, a sharp enhancement of surface area and pore volume of activated carbon product results[9]. Walnut-shell filtration was developed as a more suitable method for filtering oil and suspended solids in the applications where sand filters were conventionally used. It is used to treat refinery wastewater, oil field produced water, steel mill direct spray and caster water, ethylene plant quench water, copper concentrate decant and oily water [10].

The main objectives of this research are the following
1-Improves the potential of using natural products in the environmental applications to avoid side effects of using synthetic chemical materials.
2-Study the efficiency and mechanism of oil removal from wastewater using walnut-shell.

Experimental
Materials

Pulverized walnut-shell was used in this study. It was obtained from peeling the walnut fruits which was supplied from the local market. The hard external peels were milled and then sieved into different particle sizes with maximum diameter of 850 µm. The sieved pulverized walnut-shell was washed with distilled water for dust and fine removals, then heated at 105^0C for 24 hours and stored in a desiccator until required for use. The effluent used in this work was obtained freshly from the discharge point of the API unit in the treatment plant of AL-Duara refinery in Baghdad/Iraq. The quality of this effluent is presented in table 2.

Another set of experiments were performed with oily aqueous solutions prepared by adding cooking oil (sun flower oil) in potable water to obtain synthetic oily aqueous samples of oil content 50 mg/l as a stock solution, subsequent concentrations of 40, 30, 20, 10 mg/l were made by dilution. All the materials used in this research are supplied by Iraqi locally market. Oil specifications as represented the Turkish manufacturer (Trade mark c*ezer*) of the sun flower oil are shown in table1.

Table 1 Specifications of sun flower oil given by the Turkish manufacturer

constituents	Average composition / 100 grams
Energy	884 Kcal
Protein	0 g
Unsaturated	87.5-91.3 g
Saturated	8.7-12.5g
Carbohydrate	0 g
Cholesterol	0 g
Sodium	0 g
Vitamin	3 mg

Analysis

Table 2 represents the quality of the freshly collected actual samples. All measurements were carried out in accordance with the quantitative analysis methods described in the *Standard Methods for Examination of Water and Wastewater* [11].

Table 2 Average composition of the freshly collected actual samples.

Constituents	units	Concentration range	Average concentration
pH	-	7-7.5	7
COD	mg/l	200-600	400
Suspended solids	=	40-100	75
Oil & grease	=	8-12	10
Phenol	=	0.9-1.5	1

pH and suspended solids measurements were done by the researcher, whereby COD and phenol analysis were carried out in the service laboratory / Department of chemistry / Faculty of science / University of Baghdad. Oil and grease contents were performed in the laboratories of ministry of Environment. Shimadzu Model UV-160 spectrophotometer was used to determine the concentrations of phenol which absorb ultraviolet radiation at λ_{max}= 270 nm [12]. All reagents used in the analyses of wastewater samples were of analytical-reagent grade. The pH of solutions was measured by a pH meter of Swiss made (type: Methrihm 605).

Experimental procedure

Three sets of batch tests were performed in this study with oily samples each of 100 ml volume. The first set of experiments were conducted with the laboratory prepared samples containing 10 mg/l initial concentration of cooking oil (sun flower oil) were introduced into Pyrex stoppered bottles containing accurately weighed amounts of pulverized walnut-shell (1, 2, 3, 4 and 5 g). The bottles were shaken at room

temperature (25 ± 2° C) and allowed sufficient time up to 48 hours to reach equilibrium. By the end of each run, the reaction mixtures were filtered and the filtrate was analyzed for determination of equilibrium concentrations. Control solution was similarly treated, without walnut-shell as a blank solution. Residual concentration of the blank solution was taken as the initial one. Another set of experiments were conducted with freshly collected oily samples from Al-Duara refinery effluent. The third set of the laboratory batch tests carried out by mixing and shaking the laboratory prepared samples of different initial concentrations of cooking oil (50, 40, 30, 20 mg/l) with fixed amount (4 g) of pulverized walnut-shell and allowed to reach equilibrium.

Adsorption isotherm was obtained by plotting the amount of oil adsorbed per mg pulverized walnut-shell verses the corresponding equilibrium concentration.

Results & discussion
Quality of the treated samples

Table 3 represents the quality of the treated oily samples and percentage removal of the pollutants. It can be seen that the maximum percentage adsorption of oil in synthetic solution is 96%. This occurs when the initial concentration of oil is 10 mg/l.

Table 3 Specifications of the treated effluent samples

Constituents	Units	Average concentration	Percentage reduction of pollutants %
Prepared samples			
Oil & grease	mg/l	0.4	96
Actual samples			
pH	-	7	-
COD	mg/l	75	81.25
Suspended solids	=	30	60
Oil & grease	=	2.5	75
phenol	=	0.1	90

For the freshly collected actual samples of wastewater the percentage adsorption of oil decreased to 75%. This may be attributed to the existence of other pollutants like phenol rather than oil that could be adsorbed by the walnut-shell particles. As represented in this table the phenol, chemical oxygen demand (COD) and suspended solids show good percentage reduction in their concentrations of 90%, 81.25% and 60% respectively. Oil molecules may be arrested due to physical adsorption represented by electrokinetic forces which seems to be the most governing mechanism in this process. The space between the walnut-shell grains act as a sedimentation tank in which the suspended matter settles upon the walnut-shell particle.

Effect of walnut-shell doses on adsorption

The percentage adsorption of oil at different walnut-shell doses is shown in figure 1. It can be seen from this   figure that the percentage adsorption of oil increases and reaches a maximum value of 96% at 4 g of

walnut-shell particles and rem
constant for synthetically prepa
waste samples; whereas the percent
adsorption of oil in actual wa
samples increases with the increase
adsorbent doses and reaches
maximum value of 75% since
initial oil concentration was 10 r
reduced by adsorption to 2.5 mg/
the treated effluent samples as sho
in table 3. The increase in percenta.
adsorption may be related to the fact
that the number of available adsorption
sites increases by increasing the
adsorbent doses and that results in the
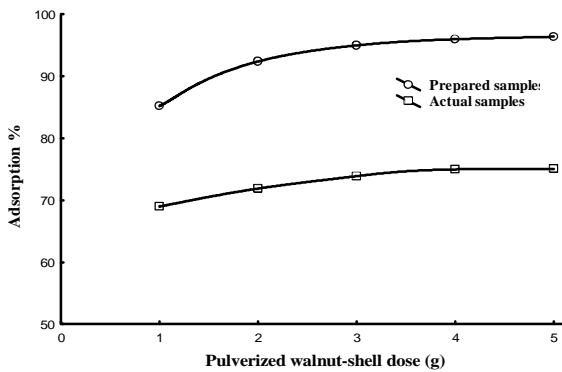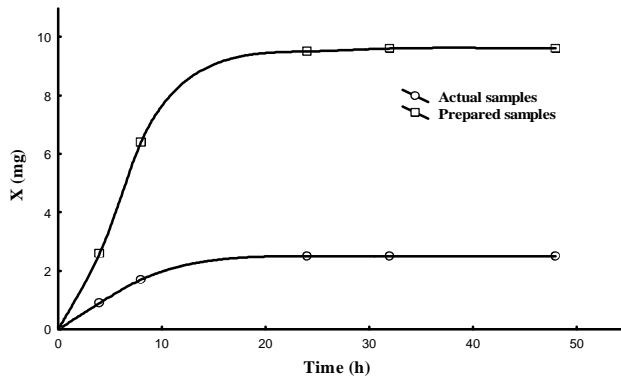increase of the oil removal
efficiency.

Figure 2. Effect of time on the
adsorption of oil in actual samples

Adsorption isotherm

Figures 3 and 4 represent the
adsorption isotherm of oil on
pulverized walnut-shell and the
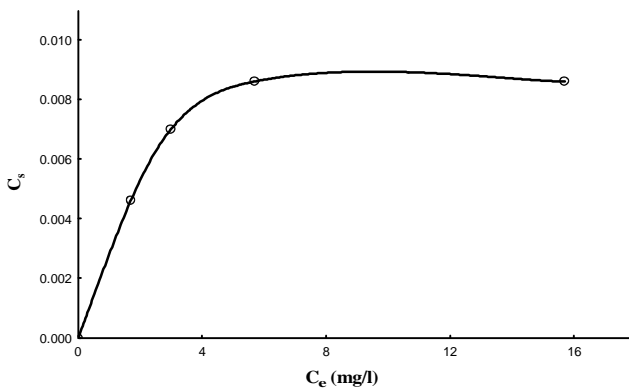linearized plot of Langmuir isotherm
respectively.

Figure 1. Percentage adsorption o
in synthetic and actual waste samp
of initial oil concentratio
10 mg/l with different pulverize
walnut-shell doses

Figure 3. Adsorption isotherm of oil on
pulverized walnut-shell at 25° C

Effect of time on adsorption

Figure 2 represents the effe
time on the adsorption process for
synthetic and actual samples.
represented by these plots, adsorp
at equilibrium conditions were atta
after a contact time of 24 hours
both types of samples.
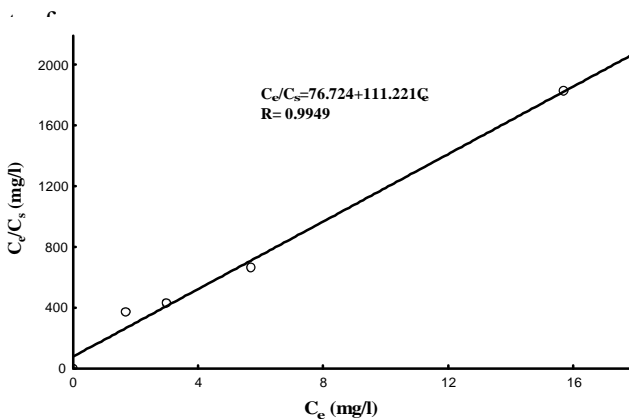
$C_e/C_s = 76.724 + 111.221 C$
R= 0.9949

Figure 4. Linearized plot of Langmuir
isotherm

As shown in figures 3 and 4, adsorption isotherm of oil particles shows a good agreement with the typical Langmuir isotherm plot and those encountered in the adsorption of most organic compounds from dilute aqueous solutions. This plot shows that, as the concentration of oil is increased in the liquid phase, proportionality more of the adsorbent surface is covered with oil at higher concentration of the material in the solution phase, the adsorbent is completely based on the assumption that a single monolayer of oil accumulates at the solid phase. The Langmuir data demonstrates that walnut-shell is an effective adsorbent for oil. The results indicate a good positive applicability of the Langmuir model. The correlation coefficient was found to be 0.9949. The equation that describes the Langmuir system is represented by equation (1) and its linearized form equation (2) [13].

$$C_s = \frac{X}{M} = \frac{abC_e}{1+bC_e} \qquad \ldots\ldots\ldots (1)$$

$$\frac{C_e}{X/M} = \frac{1}{ab} + \frac{1}{a}C_e \qquad \ldots\ldots\ldots (2)$$

To obtain the sorption characteristics of the system, the laboratory study was followed by best-fit analysis of the sorption isotherm model. The empirically determined Langmuir equation given by equation (3), was used to find the isotherm constant (a) and the saturation coefficient (b) of oil as a relevant adsorbate as follows:

$$\frac{C_e}{C_s} = 76.724 + 111.221C_e \qquad \ldots\ldots (3)$$

$$a = 0.009$$
$$b = 1.45 \text{ l/mg}$$

The effect of isotherm shape effect on whether the adsorption is favorable or not the following formula has been used [12]:

$$r = \frac{1}{1+aC_o} \qquad \ldots\ldots\ldots (4)$$

It is a favorable adsorption for values of r less than 1. For values greater than 1 it is unfavorable. For this system including both synthetic and actual oily samples with initial oil concentration of 10 mg/l, the adsorption was found to be favorable since the separation constant r is equal to 0.9.

Conclusion

This study shows the potential of walnut-shell application for the oil removal from wastewater. The results revealed that during the filtration process, adsorption was taking place on the active surfaces of walnut-shell particles. The Langmuir constants and the constant separation factor have been determined. The percentage removal of oil from synthetic and actual wastewater was 96% and 75% respectively. The beauty of the walnut-shell application for oil removal from wastewater is that it is ecologically sound and environmentally desirable treatment technique. In large scale application of this technique it is recommended to use a complementary scrubbing system to improve the backwashing process. Further work is recommended to study the column tests system.

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Nomenclature

C_e= equilibrium concentration of pollutant in solution after adsorption (mg/l)

C_o= initial concentration of pollutant (mg/l)

X = adsorbed contaminant concentration

C_s= X/M contaminant concentration adsorbed per unit weight of adsorbent(mg/mg)

a = empirical constant

b = saturation coefficient (l/mg)

R = dimensionless constant separation factor

ازالة الزيوت من المياه الملوثة بها باستخدام قشور ثمار الجوز

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الخلاصة:

تم في هذا البحث دراسة قابلية مسحوق قشور ثمار الجوز في إزالة الزيوت من المياه الملوثة بها. تتضمن عملية الإزالة وجود طورين هما الطور السائل الملوث بالزيت والطور الصلب (مسحوق قشور الجوز) الذي يتم تراكم وامتصاص الزيت عليه. تم استخدام مجموعتين من النماذج المائية الملوثة بالزيت في التجارب العملية. المجموعة الأولى محضرة مختبريا وقد بلغت نسبة إزالة الزيت من هذه النماذج ٩٦%. أما المجموعة الثانية فهي نماذج حقيقية تم جمعها من مياه الصرف الصناعية في مصافي الدورة جنوب بغداد وقد بلغت نسبة إزالة الزيت منها ٧٥%