Removal of oil from produced water using biosorbent

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Abstract. The presence of oil in water bodies posses hazards to aquatic life. The essential target of this research is to examine the feasibility using Fish scale as biosorbents to clear up the oil spills in water body. The biosorbent used in this study was fish scale (FS). The effect of absorbent weight, concentration of oil, and pH were investigated using batch system to find the optimum condition. The maximum removal efficiency was 93% at pH 7 and at the concentration of 400 ppm. The equilibrium isotherm data were studied using Langmuir and Freundlich isotherm model and it was found that the data fitted well with Freundlich isotherms.

Key word
adsorption, isotherm, produced water, biosorbent

1. Introduction
Oil is a major source of energy in the world. The extraction of oil and gas is accompanied by the discharge of large amounts of water as a by-product, which is called produced water. The amount of this water produced in oil varies depending on many factors and may reach 98% of the material extracted from oil wells in the case of matured or old fields [1]. This produced water contains a complex mixture of dissolved substances and organic and inorganic compounds such as particulate, inorganic salts, radioactive substances, dissolved gasses, various minerals and a large amount of hydrocarbons such as BTEX (benzen, Toluene, ethylbenzene, and xylene) PAH (polycyclic aromatic compounds) etc. Recently the action of produced water pour out to water bodies and soil has become a serious environmental issue. So it is important to treat this produced water before discharging it into environment or it is used in industrial or agricultural field. In light of the above, several techniques have been utilised to clean up the produced water form oil and other impurities including filtration, emulsification, flocculation, coagulation and adsorption [1]. Among these techniques biosorption is considered an emerging method for cleaning of industrial wastewaters and removal of differen pollutants [1]. Biosorption technology involves the use of low cost biological materials, which can be obtained from agricultural waste. So this technology is economical and environmental friendly. Such materials include clays, agricultural waste etc. Lutfee investigated the ability waste tea for removal of phenol from aqueous solution [2]. A research was conducted to investigate the possibility of Oil bean seed shells as biological material to remove Cd^{2+}, Ni^{2+} and Pb^{2+} [3]. The outcomes of this research showed that the biosorption process was pH dependent and the oil bean seed shell is an efficient adsorbent for the uptake of these metal ions from wastewater. Al-Sharuee and Mohammed investigated the utilized superhydrophobic silica as an adsorbent to absorb Iraqi crude oil leaked in the water of Iraqi rivers [4]. This study included the effect of surface area and the contact angle. Muhammad et. al. utilized expanded polystyrene (EPS) to clean up water from crude oil spill [5]. An experiment shows that eggshell biosorbent could efficiently remove crude oil from produced water and the efficiency reached 100% at the concentration of 1.8 g eggshell/L of produced water and oil concentration as high as 194 mg/l [6]. Another study shows the ability of grounded husk and plantain
peels to removal the crude oil spill from produced water. It was found that the percentage removal of crude oil depends on different parameters such as adsorbent weight, contact time, temperature and particle size [7]. Othman et.al reported that fish scale can be used as inexpensive adsorbent in the uptake of Zinc and Ferum ion from wastewater[8]. Eleta and Ighalo reported a review on removal of pollutants from industrial waste using fish scale as a source biosorbent [9]. In this work, the aim is to investigate the ability of fish scale as a biosorbent for removal of oil from produced water.

2. Material and methods
Fish scales (FS) used in the present work were collected from the local fish market in Baghdad city. FS were washed with hot water and detergent to remove impurities from its surface then these were rinsed with tap water several times. After washing, the scales soaked in 15% HNO\textsubscript{3} for 24 hrs and then in distilled water for 24 hr followed by drying it naturally under the sunlight and then in oven. After drying, the fish scales were ground with miller to smaller size particles. This FS powder was used without any pretreatments. The oil used was crude oil brought from Al-Doura refinery. The pH of solutions was adjusted using analytical reagents grade such as sodium hydroxide (Assay 98.05%) and hydrochloric acid (Assay 35.38%) supplied by Sigma-Aldrich Co. Hexane anhydrous 95% provided by Sigma-Aldrich Company in UK, was used as a solvent for extraction of oil from water for the purpose of concentration measurement.

3. Adsorption experiments
The adsorption study was conducted by batch experiments. The experiments were carried out by putting 50 ml of 400 mg/L of solution in 100 ml conical flasks containing different quantities of FS (0.6-2 g). The flasks were then agitated manually for about 5 minute and then left in contact for about 1 hr at 25°C. The mixture was filtered through screen of fine pore size to separate FS from the solution. The oil in the filtered solution was extracted using extracting technique by hexan. The concentration of oil in extracted solution (mixture of hexan and oil) was determined by using UV- spectroscopy at wave length 350 nm.

Effect of FS biosorbent weight was studied using 400 mg/l oil concentration and different weight of FS (0.6, 0.8,1, 1.5, and 2 g) with contact time for 1 hr. The effect of pH of solution (1, 2, 6, 7, 8, and 9) and the effect oil concentration (200,400, 600, 800, and 1000 mg/L) were studied by using 1 g FS and contact time for 1 hr.

4. Results and discussion
4.1 The effect of adsorbent weight
The effect of the FS weight was investigated at room temperature (30 °C) by adding 0.6 g of FS in 50 ml of 400 mg/L crude oil-water mixture at natural pH 7 and contact time for 1 hr with 5 min agitation. The step was then repeated using different weights of FS 0.8, 1, 1.5 and 2 g respectively under the same conditions. After that the optimum weight of FS weight was selected. Figure 1 shows the effect of FS weight on the percentage removal of crude oil.
From Figure 1, it can be concluded that the percentage removal of crude oil increases rapidly from 76% to 93% as the weight of FS increased from 0.6 to 1 g, respectively. Then the percentage removal increased slowly from 93% to 95% as the weight increased from 1 to 2 g. So 1 g was selected as the optimum weight of FS absorbents. This can be explained that increase in the adsorbent weight led to increased surface area of the adsorbents and increased the number of adsorption sites available for adsorption [10,11]

The percentage removal of oil was calculated using:

\[
\text{% removal} = \frac{c_a - c}{c_0} \times 100
\]  

(1)

4.2 The effect of pH

pH is one of the basic indicators that affect the biosorption process. The effect of pH was studied using different initial values of pH ranging from 1 to 9, at room temperature (30 °C), and 1 g FS adsorbent weight and 50 ml of 400 mg/L concentration of crude oil in water. Figure 2 shows the effect of pH of solution on the percentage removal of crude oil. From this figure, it can be observed that under the acidic conditions at pH from 1 to 6 the percentage removal increases with increasing pH. As pH value reached 7 the percentage removal reached its maximum value of about 93%. After that, under alkaline conditions at pH more than 7 the percentage removal decreases with increase in pH of the solution. This observation indicates that the acidic and alkaline conditions are not suitable and the optimum pH for the removal was 7.
The same indication was observed by many researchers [9,11]. This indication was explained that under the acidic condition a huge amount of protons was present in the solution which caused saturation of adsorption sites and increased the cationic properties of the surface, while at higher pH greater than 7, there is a huge amount of hydroxyl ions in the solution. These ions and crude oil compete for the active adsorption sites of the adsorbent [10,13].

4.3 Adsorption isotherm

Adsorption isotherm is used to describe the amount of oil adsorbed by per unit weight of solid adsorbent (FS). In this work, the adsorption isotherms was studied under the optimum conditions of 1 g FS adsorbent and pH 7. The initial concentrations used were 200, 400, 600, 800 and 1000 mg/L. Figure 3 shows the effect of initial concentration of crude oil uptake by FS absorbent.

![Figure 3. The effect of initial concentration of crude oil on the adsorption capacity](image)

As shown in Figure 3, the adsorption capacity increased with increasing initial concentration of oil, this may be due to saturation of the adsorption sites on the FS at higher concentration. In the present work two isotherms employed, the Langmuir isotherm [14] and Freundlich isotherm [15], to describe the isotherm data. The non-linear form of Langmuir isotherm is

$$q_e = \frac{q_m K_f C_e}{1 + K_f C_e}$$  

(1)

The linear form of the Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_f}$$  

(2)

where $q_e$ is the unit weight of crude oil uptake per unit weight of FS at equilibrium (mg/g), $C_e$ is the crude oil concentration in the bulk solution at equilibrium (mg/l), $q_m$ is the maximum adsorption capacity (mg/g) and $K_f$ is constant associated to the free energy of adsorption (1/mg).

The non-linear and non-linear form of Freundlich isotherm can be represented by the following equation respectively:

$$q_e = K_F C_e^{1/n}$$  

(3)

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$$  

(4)

where $K_F$ and $1/n$ are Freundlich constants associated with the adsorption capacity and adsorption intensity, respectively, of the bio-sorbent. Figures 4 and 5 represent the applying Langmuir and Freundlich isotherms respectively to experimental data.
The values of isotherm models parameters are represented in Table (1).

Table 1. Coefficient values and parameters of Langmuir and Freundlich

| Isotherm Model | Isotherm Parameters | Values |
|----------------|---------------------|--------|
| Langmuir       | \( q_m \) (mg/g)    | 41.66  |
|                | \( K_L \) (L/mg)    | 0.040  |
|                | \( R^2 \)           | 0.987  |
| Freundlich     | \( n \)             | 2.35   |
|                | \( k_f \) (mg/g) (L/mg)^{1/n} | 4.81   |
|                | \( R^2 \)           | 0.995  |

The Langmuir assumes a homogenous distribution of the active sites on the FS surface with the formation of monolayer coverage of crude oil on FS surface. While the Freundlich assumes formation of multilayer crude oil onto the heterogenous surface of the FS. Figures 4 and 5 exhibit a good agreement between both Langmuir and Freundlich to the experimental data. The values of \( R^2 \) are 0.987 and 0.995 for Langmuir and Freundlich, respectively. This indicated that the Freundlich isotherm described the adsorption of crude oil onto Fs better than Langmuir isotherm and the adsorption occurs in multilayer on the heterogenous surface of the FS adsorbent [11]. The value of \( n \) is greater than unity and less than 10 (\( n = 2.35 \)) which indicates that the adsorption of crude oil onto FS is favorable [13,16,17].
5. Conclusion
The biosorbent used in this study was fish scale (FS). It can be deduced that FS can be used as a biosorbent for oil removal. The effect of absorbent weight, concentration of oil, and pH were investigated using batch system to find the optimum conditions. The optimum conditions are 93% removal efficiency at pH 7 and concentration of 400 ppm. The equilibrium isotherm data were studied using Langmuir and Freundlich isotherm models and it was found that the data fitted well with Freundlich isotherm.

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