### Study the Individual Performance of Bulrush as a Natural Sorbent to Remove Oil Layer from Simulated Sea Water for Isothermal Batch Processes

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#### Abstract

Petrol is an important power source of energy and used in many industries. Accidents occur during transfer of petrol. That can cause harmful consequences for eco-system. One of the techniques to remove it is sorbents. Bulrush was used in this study as a local natural green material to remove petrol in batch isothermal systems. Two factors were tested (time and Bulrush mass). Bulrush was found sufficient to remove 90% of oil at 6 grams of Bulrush. Maximum sorption capacity was (9) for 1 gram of sorbent. Second order equation was suitable to represent the kinetics of Bulrush sorption. Freundlich model was found more acceptable to represent the equilibrium sorption isotherm.

Keywords: Bulrush, oil spill, isothermal process, sorption.

#### 1. INTRODUCTION:

Many industrial products and goods depend on petrol. Petrol is considered one of the most significant power sources for many applications like turbine plants and cars [1]. Oil reaches water resources due to leakage accidents in oil storage containers, oil transport pipes and oil production from water bodies [2]. Oil existence in water causes a harmful effect in eco-system and undesirable economic consequences [3]. Several ways are followed to remove oil pollution like rasping, burning and sorption process [4].

Sorbents are materials used frequently to separate oil from water [5]. These materials are mixed with oil liquid in water to get wetted by oil to be recovered. Oil either diffuses inside pores of sorbent material or adheres on sorbent surface or both [6]. The repulsion of sorbent from water and its attraction to oil simultaneously, is a good indication for sorbent efficiency [7]. Fibers like Kenaf [8] and Kapok [9] were natural organic sources utilized as a sorbents. Equilibrium state and kinetics of sorption oil were also studied for several researches.

In this research, Bulrush is natural plant was used as a sorbent after preparation. Effect of contact time and weight of used sorbent were studied. Two common equations were used to represent the kinetics of sorption and two equations were used to predict the equilibrium state of sorption for isothermal process in this study.

# 2. MATERIALS, DEVICES, AND PROCEDURE OF EXPERIMENT

#### 2.1 Materials:

Amount of crude petrol (density 710kg/m<sup>3</sup> at 30°C) was brought up from Southern Oil Company in Iraq to be used as a pollutant liquid. Simulated sea water was prepared by adding 35g of pure Sodium Chloride salt for each 1000g of distilled water [10]. A natural plant, Bulrush, Figure beneath, was cut it off from Basra city land in Iraq and tested as a green sorbent material. Bulrush was washed with distilled water then dried under sunlight. It's used as pieces with dimensions (0.7, 0.5, 0.3cm). These steps were found succeeded experimentally.



Figure 1: Bulrush Material pieces.

#### 2.2 Devices:

An electronic sensitive balance was used to measure weights during experiments.

#### 2.3 Procedure of experiment:

0.2L of simulated sea water was polluted using 20gm of crude petrol then 1 gram of Bulrush was added for seven periods (in minutes), (0.25, 5, 10, 25, 45, 75, and 90) to evaluate the sorption ability of Bulrush. Though this mixture was stirring well, water stayed covered by (oil-Bulrush) layer. This non-flow process was followed again using other different weights of sorbent (2, 3, 4, 5 and 6) and all these weights were measured in grams. This method is inspired by standard

experimental method used for testing sorption of materials [11]. To estimate sorption capacity, this equation can be used:

$$S = \frac{X_{\circ} - X_{s}}{X_{s}} \dots (1)$$

Where  $X_{\circ}$ : represents the mass of bulrush after sorption process and  $X_s$ : represents the mass of bulrush before sorption process.

The following Figure; from (a) to (d), including photo pictures represent oil spill removal process using Bulrush.



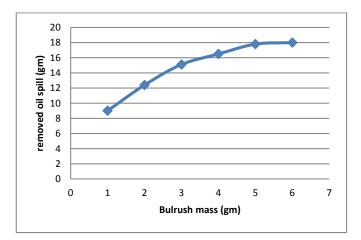
Figure 2: Oil spill removal process.

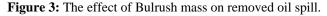
#### 3. **RESULTS AND DISCUSSIONS**

All data obtained in this research were graphically represented to discuss the relationships between all variables.

#### 3.1 The effect of Bulrush amount:

Six amounts of Bulrush were tested with constant oil volume. The maximum value of oil removed was found after 75 minutes of sorption process. According to Figure (3), the highest value of oil spill removal was noticed for six grams of Bulrush because increasing of sorbent amount leads to increase of interfacial area between Bulrush and oil spill [12].





#### **3.2** The effect of contact time:

Sorption capacity was estimated for each mass of sorbent during the whole periods as shown in Figure (4).

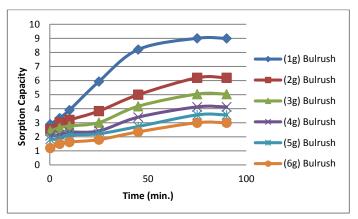


Figure 4: Variance of sorption capacity of Bulrush with time.

Sorption capacity of Bulrush for oil is reversibly proportional with Bulrush mass and sorption capacity increases with increasing of residence time. The maximum value of sorption capacity was found (9) at (1gram) of Bulrush.

#### 3.3 Kinetics of sorption process:

To choose the typical conditions for oil spill removing by sorbent, two empirical equations were investigated. These equations are useful to study and represent the recovery mechanism of oil graphically [13].

#### 3.3.1 First empirical equation:

This equation belongs to Lagergren and can be written as below:

$$\ln(q_{\mathbb{Z}} - q) = -k_{ad,1}t + \ln(q_{\mathbb{Z}}) \dots (2)$$

Where:

q°: the sorption capacity of Bulrush at equilibrium point (g removed oil/g sorbent).

q: sorption capacity at any time of process (g removed oil/g sorbent).

t: time calculated in minutes.

 $k_{(ad,1)}$ : rate constant for sorption kinetics (1/min).

This relationship was applied for the whole experimental data and presented graphically as shown in Figure (5).

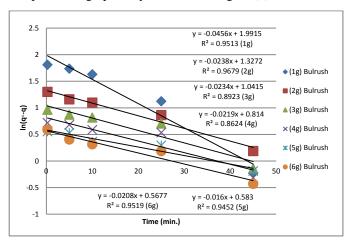


Figure 5: 1<sup>st</sup> order kinetics for six weights of Bulrush.

#### 3.3.2 Second empirical equation:

This equation can be expressed mathematically as:

$$\frac{t}{q} = \frac{1}{q_{\mathbb{Z}}}t + \frac{1}{k_{ads,2}q_{\mathbb{Z}}^2} \dots (3)$$

 $K_{ads,2}$  is the sorption rate constant for second order equation. The mechanism of sorption, correlation coefficients and the equation of linear relationship were estimated for the six weights of Bulrush and illustrated in Figure (6).

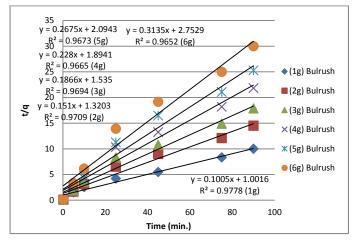


Figure 6: 2<sup>nd</sup> order kinetics for six weights of Bulrush.

**Table 1:** Summary of sorption rate constant, R<sup>2</sup> and equilibrium sorption capacity.

| Bulrush<br>(g) | First Order Kinetic |                |       | Second Order Kinetic |                |       | Experimental |  |
|----------------|---------------------|----------------|-------|----------------------|----------------|-------|--------------|--|
|                | $\mathbf{K}_1$      | $\mathbb{R}^2$ | q°    | $K_2$                | $\mathbb{R}^2$ | q∘    | q°           |  |
| 1              | 0.0456              | 0.9513         | 7.326 | 0.01                 | 0.9778         | 9.95  | 9.0071       |  |
| 2              | 0.0238              | 0.9679         | 3.77  | 0.0172               | 0.9709         | 6.622 | 6.20045      |  |
| 3              | 0.0234              | 0.8923         | 2.833 | 0.0226               | 0.9694         | 5.359 | 5.036833333  |  |
| 4              | 0.0219              | 0.8624         | 2.256 | 0.0274               | 0.9665         | 4.385 | 4.1258       |  |
| 5              | 0.016               | 0.9452         | 1.791 | 0.0341               | 0.9673         | 3.738 | 3.56028      |  |
| 6              | 0.0208              | 0.9519         | 1.764 | 0.0357               | 0.9652         | 3.189 | 3.000433333  |  |

All relationships obtained from Figure (5) and (6) were linear relations with root mean square ( $\mathbb{R}^2$ ) for the different weights of Bulrush. Sorption rate constant for first and second order kinetics besides root mean square were mentioned in the summary of Table (1). These results reveal that the relations of second order kinetics are stronger compared with first order kinetic due to ( $\mathbb{R}^2$ ). ( $\mathbb{R}^2$ )<sub>second order kinetic > ( $\mathbb{R}^2$ )<sub>first order kinetic.</sub> The values of  $q^\circ$  estimated by 2<sup>nd</sup> order kinetics are closer to the experimental values.</sub>

## **3.4** The ability of sorption for isothermal process of Bulrush-oil mixture:

Study the ability of Bulrush to remove oil spill and specify the nature of sorption for this process was determined using two empirical models Langmuiar and Freundlich isothermal models. These two models are widely used to represent the transfer operation of liquid to solid [14]. These models are applied for investigations of oil pollution and heavy metals.

#### 3.4.1 Langmuir isothermal sorption model:

In this model, the attraction of sorbent sites to oil liquid is assumed equal [15]. This model is expressed below:

$$\frac{1}{q} = \frac{1}{q_{max}K_{ads}} \left(\frac{1}{C}\right) + \frac{1}{q_{max}} \dots (4)$$

Where:

q: sorption capacity (removed oil mass/Bulrush mass).

q<sub>max</sub>: maximum value of sorption ability.

C: constant concentration of pollutant in aqueous solution (mass/volume).

K<sub>ads</sub>: attraction measurement parameter of oil to Bulrush.

This model was applied and plotted in Figure (7); between 1/q and 1/C then found  $q_{max}$  and  $K_{ads}$  using fitting line.

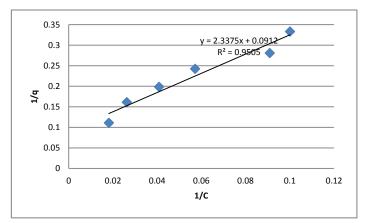


Figure 7: Langmuir model for Bulrush-oil isothermal sorption.

There is a parameter denoted as  $(R_L)$  used to determine the shape of sorption isotherm model which presented in the following equation:

$$R_L = \frac{1}{1 + K_{lang.}q_i} \dots (5)$$

 $K_{lang}$  and  $q_i$  represent the Langmuiar constant sorption isotherm and the initial value of pollutant. The value of  $(R_L)$  is 0.992 occurs in the range  $0 < R_L < 1$ ; it means that shape is favorable [16].

#### **3.4.2** Freundlich isothermal sorption model:

This model describes the isothermal process with more than one layer sorption [14] and can be represented by the following equation:

$$q = KC^{-n} \dots (6)$$

(K) is an ability measurement of sorbent used (adsorbate amount of oil/sorbent amount) and (n) is a measure of relation between oil affinity and sorbent density. If n > 1 it means that attraction decrease with increasing density of sorbent [17]. By taking logarithm for equation (8):

$$logq = logK + \frac{1}{n}logC \quad ... (7)$$

Data of Bulrush were fitted using Freundlich isotherm and presented in Figure (8).

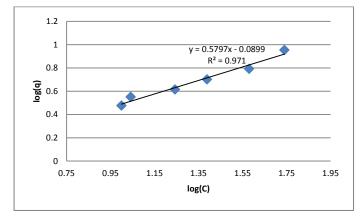


Figure 8: Freundlich model for Bulrush-oil isothermal sorption.

Table (2) includes summary information for Freundlich and Langmuir models to make a comparison between them.

 Table 2: Summary information for Freundlich and Langmuir models for Bulrush

| Sorption Isotherm   | Slope  | Intercept | К         | n         | R <sup>2</sup> |
|---------------------|--------|-----------|-----------|-----------|----------------|
| Freundlich Isotherm | 0.5794 | -0.0896   | 0.8135795 | 1.7259234 | 0.9711         |
| Langmuir Isotherm   | 2.3368 | 0.0913    | 0.0390705 |           | 0.9505         |

According to Table (2), n > 1 for Freundlich model the relation between affinity and Bulrush density is reversible. The correlation coefficient for Freundlich model is larger than

the one of Langmuir model which declares that Freundlich equation is more suitable to represent the equilibrium sorption behavior for Bulrush [18].

#### 4. CONCLUSION

The Bulrush was found as a good sorbent to remove oil spill. The maximum value that was recovered is 18grams of 20 grams oil mass when Bulrush mass was 6grams. The highest value of Bulrush sorption capacity was (9) at 1gram of Bulrush. Increase of time leads to increase in sorption capacity and sorption capacity decrease with increasing weight of Bulrush. Second order equation was found more fitted to represent the kinetics of Bulrush sorption process. Freundlich model is more suitable to represent the ability sorption isotherm of Bulrush which means that performance of this green material in oil remove is due to more than one active layer.

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