

# **A STUDY IN THE USE OF SULPHURIZED ACTIVATED CARBON OBTAINED FROM BURNT DATE STONES IN THE TREATMENT OF WASTE WATER**

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## **Abstract**

**An activated carbon** initially prepared using burnt date stones.

**A sulphurized activated carbon** initially prepared using burnt date stones.

**Heavy metals of Iron, Manganese ions and Detergents of Lauryl sulfate and dodecyl  $\beta$ -D-glucoside** were removed using the prepared sulphurized activated carbon that obtained from dates

Since Iron, Manganese and detergents chemical species show a high affinity toward sulphur a tentative method of enhancing the adsorption capacity of activated carbon could be based on the introduction of surface sulphur in the material. Accordingly, the activated carbon was treated with  $\text{SO}_2$  and  $\text{H}_2\text{S}$  under different temperature conditions. Sulphurized activated carbon has been used as adsorbents Iron, Manganese and detergents in aqueous solutions. The adsorption capacity for each adsorbate-adsorbent system has been determined. The uptake percent of Iron, Manganese and detergents using Sulphurized activated carbon was found to be 85 to 90% within the first minutes of contact. The factors affecting the capacities of the date stones and prepared activated carbon were investigated. The activating temperature, the activation time and the particle size range were studied. The thermodynamics analysis of the adsorption of both metals and detergents was found to be endothermic.

## **1. INTRODUCTION**

Most of surface water in Egypt is suffering from existing Iron and Manganese and detergents. Detergents widely used by the **Egyptian** household, they are found in waste water. The most popular detergents that detected were **Lauryl sulfate and**

**dodecyl β-D-glucoside.** They are the most locally used as today's detergents. In addition, they are used in large scales in the manufacture of shampoos.

The date stones and the prepared **sulphurized activated carbon** was used as an adsorbent for the removal of iron, Manganese, Lauryl sulfate and dodecyl β-D-glucoside compounds from wastewater. The related process parameters were investigated. Residues of detergents have been detected, worldwide, in water samples, in human, animal tissues and body fluids causing several diseases. Water pollution with detergents, is of great importance to satisfy the increasing demands for water for various uses. These detergents compounds do not decompose or degrade in aquatic systems. These detergents is very harmful and toxic. The accumulation of some detergents in wastewater represents a serious environmental problem. The removal of metals and detergents from aqueous solutions is very important from the environmental point of view. The presence of such contaminants in water has undesirable effects. Although a number of processes have been developed for pollutants removal, adsorption is the leading method, from the economical point of view.

## 2. Experimental Procedure

Several adsorbents were, subjected to a prolonged series of preliminary experiments.. The preliminary obtained data fit showed that date stones and the **sulphurized activated carbon** activated carbon prepared from date stone is the quantitatively efficient and has a wide ability to remove the pollutants of concern. A series of experiments were carried out. In the test series, all the used chemicals and reagents were of analytical grade purity. Bi-distilled water was used for dissolution, dilution and washing all glassware. It was produced using a distillator of GFL Bi-Dest2104 type from KARLKOLB? Germany. Also, a furnace of HST 3020 type from DENTAL-U LABORBU, (GmbH - Germany) was used for drying purposes.

### 2.1. Adsorbent

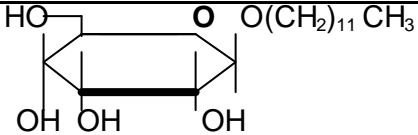
The raw materials used in this study as an adsorbent is date stone collected from Siwa Oasis western desert, Egypt. The date sample preparation can be pointed as follow:

1. The date stone were broken to powder form in an electrical mixer
2. The powder form were put in an electrical oven to a temperature of 45 °c for three days to evaporate the oil from them in-order to increase the adsorption capacity

The **sulphurized activated carbon** were prepared by heating the carbon obtained from date stone firstly at 60 °C in SO<sub>2</sub> and at 900 °C. **sulphurized activated carbon** Activated was subjected to a structure characterization using different techniques The main physical and chemical properties were as shown in figure (1)

**Table (1) The physical and Chemical Characteristics of the investigated detergents**

Compounds	FW	Chemical Structure	PH
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Lauryl sulfate	288.4	$\text{CH}_3 - (\text{CH}_2)_{11} - \text{OSO}_3\text{Na}$	0.1M in water at 25 °C is 5.5 – 7 in water
Dodecyl β-D-glucoside	348		0.1M in water at 25 °C is 6.5 – 8 in water

The **chemical and elemental content** of the adsorbents was quantified at Micro analytical Centre, Cairo University, The traced elements are carbon, hydrogen, nitrogen, sulfur and phosphorus. The amount of oxygen, in percent, was calculated by subtraction calculations for the adsorbents

The specific **surface area and porosity** measurements were achieved using BET technique as an adsorption phenomenon of nitrogen gas on the adsorbent surface at 77 °K (temperature of liquid nitrogen). The volume ( $V_m$ ) of  $\text{N}_2$  gas required to cover the adsorbent surface with a monolayer was calculated using BET equation:

$$\frac{P/P_0}{s(1 - P/P_0)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (1)$$

Where: P is the equilibrium pressure.

$P_0$  is the saturated vapor pressure of the gas at experiment

Temperature.

S is the total gas adsorbed amount.

C is a constant related to the heat of a adsorption.

The specific surface  $\sum (m^2 g^{-1})$  is related to  $V_m$  by the equation:

$$\sum = \frac{V_m}{22.4} \times 6.02 \times 10^{23} \times 10^{-20} s_m \quad (2)$$

where:  $s_m$  is the area (A) occupied by one molecule and has been taken as  $0.162 \text{ nm}^2$  for  $\text{N}_2$  at 77 °K (**Faust and Aly, 1983**).

The measurements were performed using Pore Size Micrometer - 9320, USA.

The chosen adsorbent was prepared by crushing dried date stone. They were then sieved into particle sizes 0.5 – 4 mm. 40 g were impregnated with concentrated solution of ortho phosphoric acid ( $0.2 \text{ dm}^3$ ) of pre-adjusted concentrations. This amount of acid solution was found to be sufficient to cover the whole mass and to give a paste of soft consistency. The mixture is left overnight in an oven until the excess water completely evaporated. This was done to facilitate the absorption of phosphoric acid by the raw material. The resulting material was transferred to a stainless steel reactor placed inside the tubular furnace attached to the thermocouple for temperature control. The furnace was switched on and the temperature was increased at about  $7^\circ\text{C}/\text{min}$ . at constant flow of nitrogen. To avoid splashing caused by vigorous evolution of gases, the sample was heated slowly. The sample reached the selected value ( $500\text{-}700^\circ\text{C}$ ) in 100-120 min. The sample was allowed to cool at room temperature in nitrogen atmosphere. The product was washed thoroughly with hot water until the pH

attained a value of 6.5. It was finally dried overnight in an oven at 105 °C. Then it was grinded and sieved to the desired size. During the course of experiments, several factors were investigated to optimize the parameters.

The effect of **activating** on the adsorption capacity of the prepared activated carbon was studied. The tested temperatures were 200, 400, 600, and 800°C. A constant activation time and particle size range were used.

The effect of the **activation time** on the adsorption capacity of the prepared **sulphurized activated carbon** activated carbon was investigated. The activation time was 0-200 min at optimum values of activation temperature and particle size range.

The effect of **particle size** range on the adsorption capacity of the prepared activated carbon was tested. Three different particle size ranges 0.5 - 4 mm were investigated at optimum values of activation temperature, and activation time.

## 2.2.Adsorbates

Two metals iron and manganese as a heavy metals and **detergents**, that have serious environmental impacts and pose a threat to human health, were selected to be investigated. The technical grade lauryl sulfate and dodecyl β-D-glucoside are completely soluble in water. Lauryl sulfate as an anionic detergent which easy to remove by dilution. Dodecyl β-D-glucoside is a nonionic detergent which useful in the solubilization of membrane – protein **Shinoda, et al., (1961)** The physical and chemical properties of the investigated detergent are tabulated in table (1). The stock aqueous solutions of the studied detergents (10ppm) were prepared The desired concentration of the studied detergents were obtained. Fresh stock solutions were daily prepared for each experiment to avoid microbial decay The equilibrium concentration of the studied detergents was determined from Amrya petrochemical Co. Amrya , Egypt. The detergents were analyzed {**JOHN WILEY(1990)**} using spectrophotometer of type Perkin Elmer Germany.

## 2.3.Adsorption process

Different masses of adsorbent (0.005 – 5.0 g ) were used. The adsorbents with particle size that ranged between 0.2 to 4.0 mm was added to the studied adsorbates (0.05dm<sup>3</sup>) with initial concentration between 0.2 and 10 mg/l. The samples were shaken (100 rpm) for a sufficient period of time (4 hr). The sample was then centrifuged. The concentrations of the studied detergents were determined.

The amount of metal or lauryl sulfate and dodecyl β-D-glucoside were computed from the following equation:

$$q_e = (C_0 - C_e) V / m \quad (3)$$

Where:  $q_e$  is the adsorption capacity

$C_0$  is the initial concentration of the adsorbates

$C_e$  is the equilibrium concentration of the adsorbates

$V$  is the aqueous solution volume

$m$  is the weight of the adsorbent

The factors affecting the sorption of the concerned ingredients from aqueous solutions was studied. The adsorbent weight, contact time, pH of the solution solution and temperatue were investigated.

## 3. RESULTS

### 3.1 Preparation of sulphurized Activated Carbon

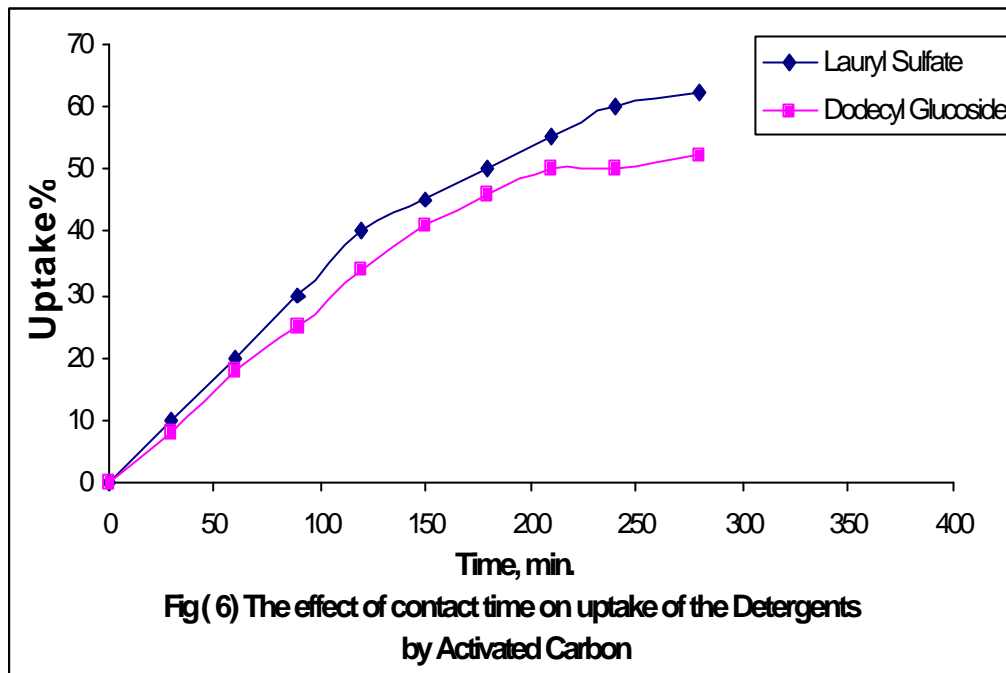
Several things were investigated. Among them are:

The effect of the measured parameters

The characterization of the prepared activated carbon

The measured parameters were analyzed, plotted and presented.

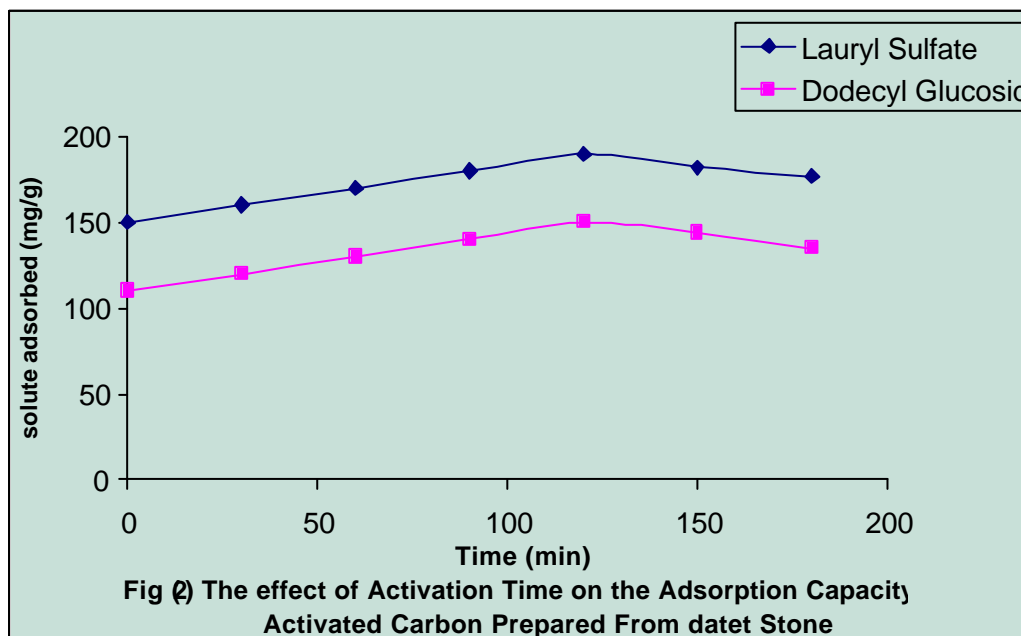
The **effect of temperature of carbonization** of date stone on the adsorbed studied adsorbates, are presented in Figure ( 1). The effect of the operating temperature on the adsorption capacity of the prepared activated carbon from date stone was studied. The maximum capacity for lauryl sulfate and dodecyl  $\beta$ -



D-glucoside is achieved at 600 °C for the selected raw materials. Tar materials blocked the pores created during the carbonization process at low temperature.

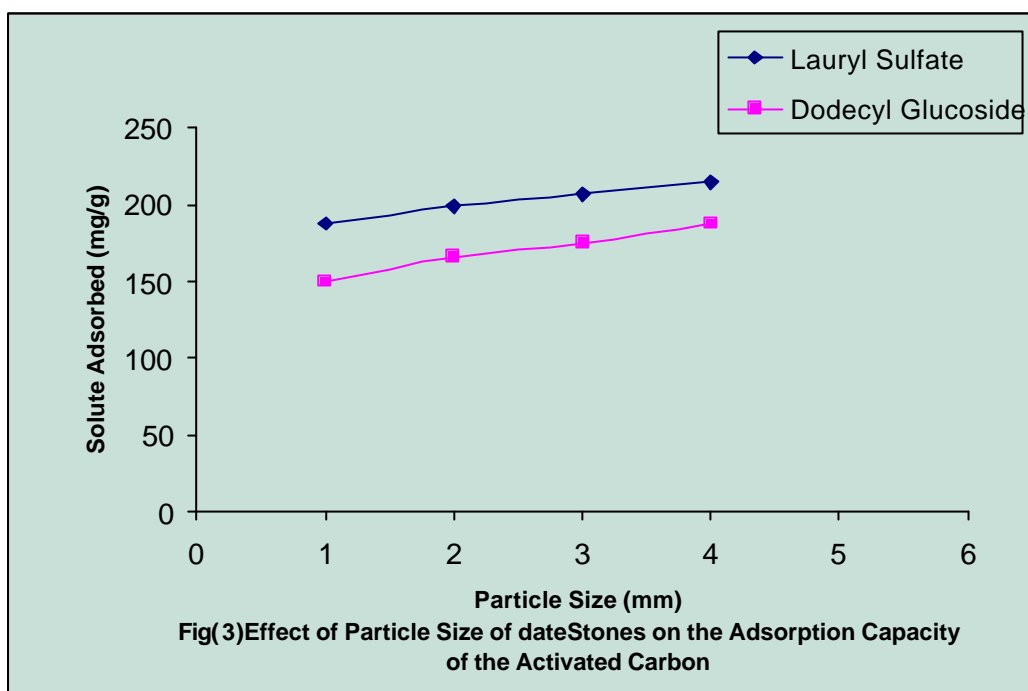
#### 3.1.2.b. Effect of activation time

The effect of the activation time is shown in Figure (2). The optimum activation



time was found to be 120 min. for the date stone.

The effect of particle size range was investigated. It was obvious, from Figure 3, that the quantity of detergents adsorbed by activated carbon prepared from date stone increases with different particle size



### 3.2 Characterization of the Prepared Activated Carbon

#### 3.2.1 Elemental Analysis

The **elemental** analysis of date stone and the activated carbon are listed in Table 2. The results showed that, during carbonization, there is a noticeable increase in carbon content and a decrease in hydrogen. Subsequent activation further increased the carbon content.

**Table(2) Elemental analyses for date stone and activated carbon prepared from date stone .**

Items	C%	H%	N <sub>2</sub> %	S%	P%	Ash
date stone	45.22	9.34	6.23	1.2	5.3	1.2
Activated carbon from date stone	73.01	2.15	2.56	12.3	2.3	4.2

#### 3.2.2. Chemical Analysis

The date stone and activated carbon from it were subjected to **chemical analysis** and the results obtained are listed in Table 3

**Table 3. Chemical analysis of activated carbon prepared from date stone.**

Component	%	
	date stone	Activated Carbon
a- cellulose	52.52	66.4
Pentosan	10.33	14.6
Lignin	15.25	12.3
Fat and oil	17.20	1.3
Ash	2.71	8.4

The representative scanning electron micrograph of the activated carbon is shown in fig (4). It reveals spherical pores with internal diameter that ranged between 1.5 and 4.8 micrometer

Fig(4) Representative scanning electron micrograph of the adsorbent



### 3.3 The adsorption capacity and the factors affecting it were investigated

The values of the maximum adsorption capacities are presented in Table(3).

**Table(3) Comparison of the Maximum adsorption capacities for date stone and sulphurized activated carbon**

Types of adsorbents	$q_{max}$ (mg/g)			
	Iron	Manganese	Lauryl Dodecyl sulfate	$\beta$ -D glucoside
date stone	180	170	110	142
Sulphurized Activated carbon obtained from date stone	320	280	256	277

The adsorption capacity of Sulphurized Activated carbon obtained from date stone was found to be more than date stone. This may be due to the high porosity of activated carbon that formed as a result of fat an oil burning.

The factors affecting adsorption capacity of the detergents onto the activated carbon was found to be affected by the following factors:

Fig (5) The Effect of Activated Carbon Weight on The Removal of Detergents From Aquous Solution

The **adsorbent weight variation** affects the removal efficiency of the studied adsorbates. The data obtained are represented in figure (5a, b).

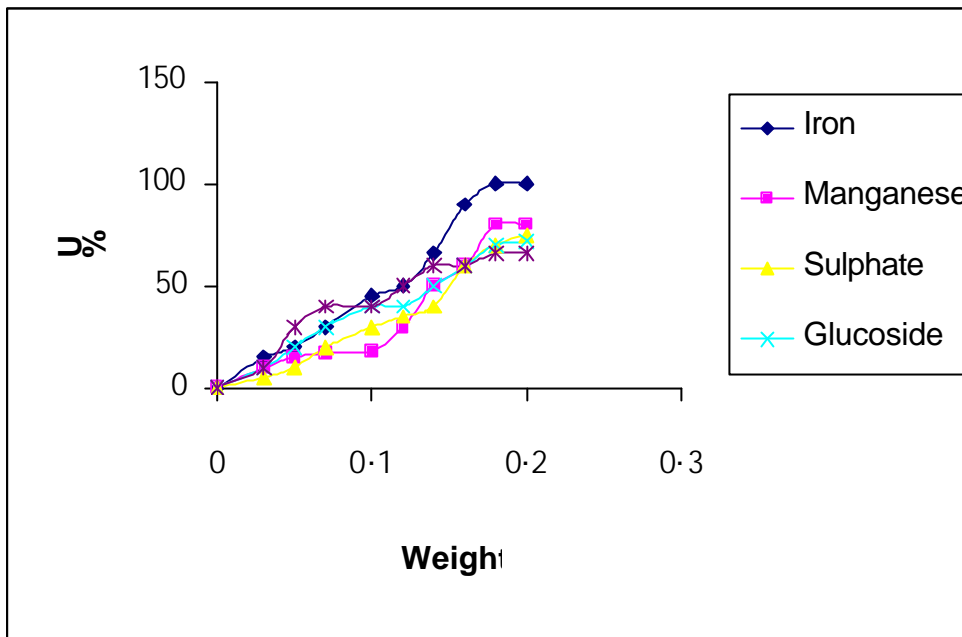


Fig (5-a) The Effect of Activated Carbon Weight on The Removal of adsorbate From Aqueous Solution

**The contact time affects** the adsorption of iron, manganese, lauryl sulfate and dodecyl  $\beta$ -D-glucoside from aqueous solutions at different time intervals using activated carbon obtained from date stone is illustrated in Fig. (6a, b). The figure imply that the adsorption extent increases with elapsed time till reaching saturation level where the uptake percentage attains a constant value.

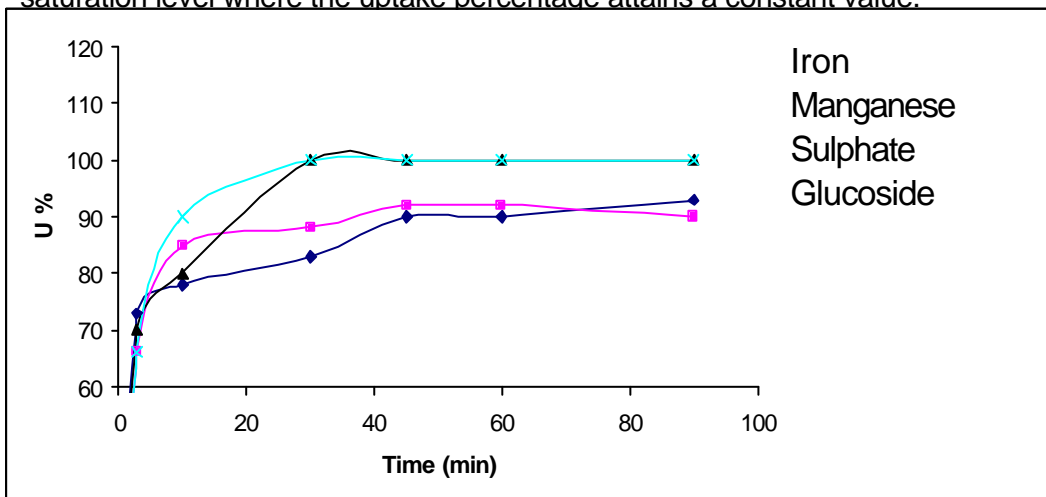


Fig ( 6-a) The effect of contact time on uptake of the adsorbates by date stone

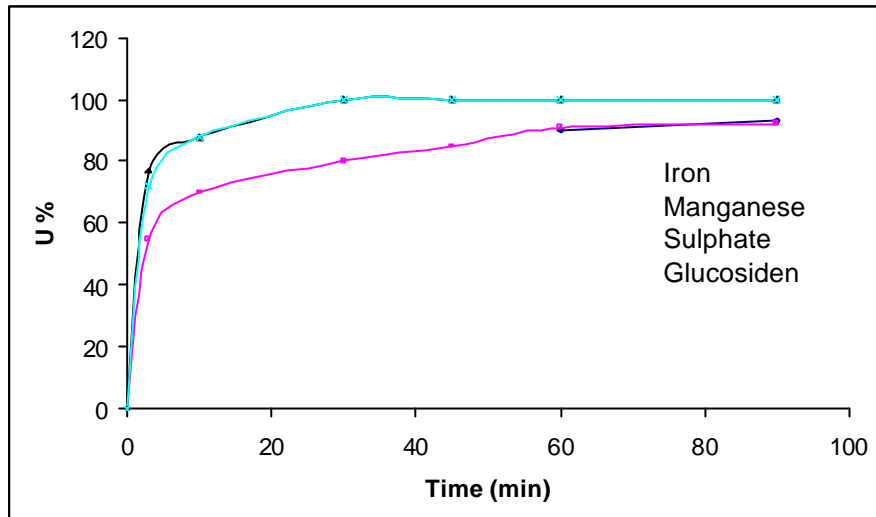
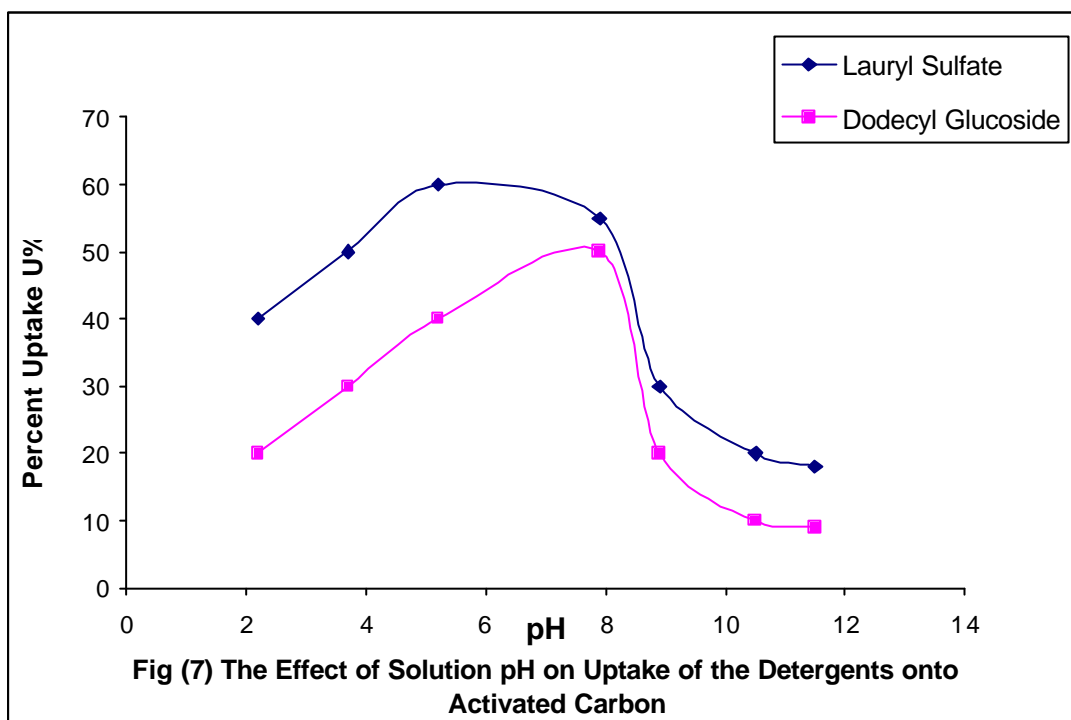


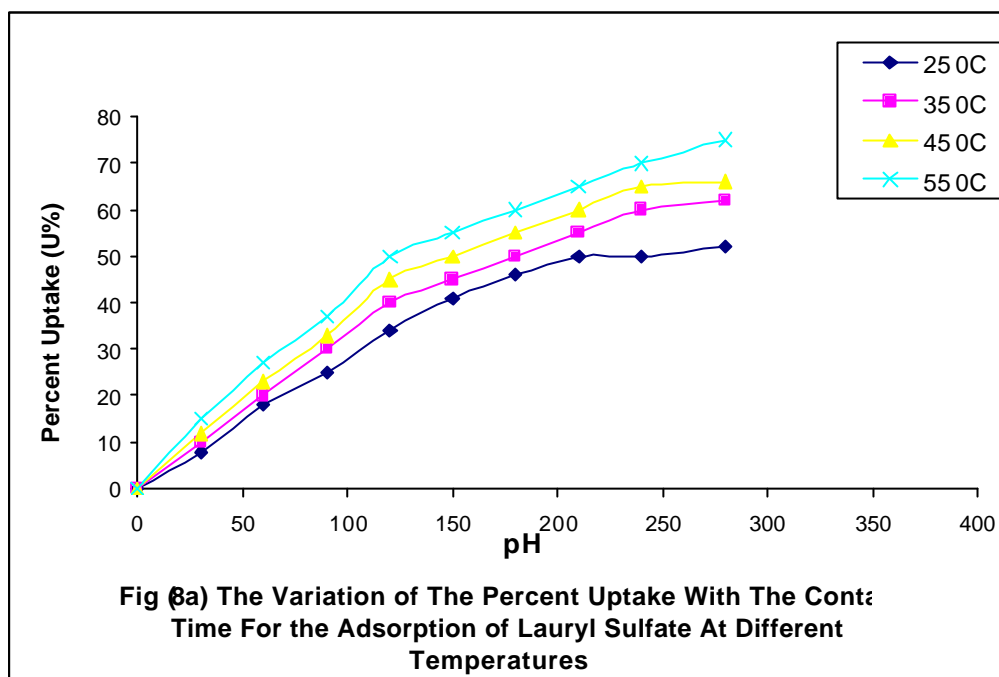
Fig ( 6-b) The effect of contact time on uptake of the adsorbates by Activated Carbon

**The pH values: affects** the sorption process. The pH value of the mother solutions was adjusted to the required values, in the range 2 -12, by adding a solution of 0.1M HCl or 0.1M NaOH using 321990 pH/mv/Temp. Analyzer from EXTECH.USA A constant mass of adsorbent was added to 0.05 dm<sup>3</sup> lauryl sulfate and dodecyl β-D-glucoside solution. The bottles were sealed and placed on a shaker at constant temperature (25 ± 2 °C) for a sufficient period of time to ensure that equilibrium had been reached (2hr). After that time the samples were centrifuged at 3000 rpm for 15min The effect of hydrogen ion concentration on uptake of lauryl sulfate and dodecyl β-D-glucoside from aqueous solutions on AC is shown in Fig. (7).



### 3.4. Effect of temperature

Activated carbon obtained from date stones. Variations in temperature cause adsorbent rearrangements and also changes in the adsorption equilibrium. The uptake of lauryl sulfate and dodecyl glucoside compound obtained at 25, 35, 45 and 55°C, is shown in Fig.(8a, 8b). activated carbon obtained from date stones indicates an inversion trend associated with physical adsorption i.e. an increase in the amounts adsorbed with increasing temperature. Tills observation seems to suggest that, after removal of the solution effect, the process becomes endothermic in nature.



### Conclusion

The following conclusion were reached:

1. Due to the disadvantages of the use date stones (harmful for animal) in animal feed, a new technique using date stones in the inorganic and organic pollution treatment was developed.
2. The cost of the waste water treatment by this methods is not expensive.
3. The adsorption onto activated carbon obtained from date stone attains the saturation level after four hours with uptake percentage of 65 % and 51 % for lauryl di-ethanolamide and dodecyl benzene sulfonate. This time is relatively short if compared to other adsorbents (biological system ).
4. The results exhibit a higher sorption capacity of sulphurized activated carbon obtained from date stone for some metals and Lauryl and dodecyl sulphate. It would be useful to use the carbonized date stone shells for the treatment of hazardous waste solutions enriched with such metals detergents and it can be regarded as one of the promising materials used For the removal of organic pollutants from surface water

## References

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