Ass. Univ. Bull. Environ. Res. Vol. 7 No. 2, October 2004

AUCES

ADSORPTIVE REMOVAL OF SOME DETERGENTS FROM WASTE WATER USING FRIENDLY ENVIRONMENTAL MATERIALS

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ABSTRACT :

An activated carbon was obtained from burnt apricot stones. Detergents are widely used by the Egyptian household, they are found in waste water. The most popular detergents that detected were Sodium Lauryl sulfate and dodecyl ß-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 prepared activated carbon was used as an adsorbent for the removal of Sodium Lauryl sulfate and dodecyl ß-D-glucoside compounds from waste water. The related process parameters were investigated. The prepared activated carbon showed a satisfactory adsorption capacity for both detergents.

The factors affecting the capacities of 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 detergents was found to be endothermic.

INTRODUCTION:

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 harmufull and toxic. The accumulation of some detergents in waste water represents a serious environmental problem. The removal of detergents from aqueous solutions is very important from the environmental point of view[1]. Although a number of processes have been developed for detergents removal, adsorption is the leading method, from the economical point of view. The presence of such contaminants in water has undesirable effects. Gamma irradiation is used. Due to the high cost of gamma irradiation, a number of commonly available cheap materials should be investigated. This study was initiated to investigate the ability of preparing activated carbon from apricot stones. It also aims to study its adsorption of some detergents from waste water.

EXPERIMENTAL PROCEDURE:

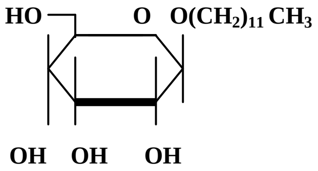
Several adsorbents were, subjected to a prolonged series of preliminary experiments. The preliminary data obtained showed that apricot stones and the activated carbon prepared from apricot stone is quantitatively efficient and has a wide ability to remove the pollutants of concern. A series of experiments

were carried out. In the test series, all the used chemicals and reagents were of analytical grade. 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.

1- Adsorbent:

The raw materials used in this study as an adsorbent is apricot stone collected from EI-Amar twon El-Kalubia Governorate, Egypt. Activated carbon was subjected to a structure characterization using different techniques. The main physical and chemical properties of the investigated detergents were shown in Table (1).

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

Compounds	FW	Chemical Structure	pH
Lauryl sulfate	288.4	$CH_3 - (CH_2)_{11} - OSO_3Na$	0.1M in water at 25 ^{0}C is 5.5–7 in water
Dodecyl ß-D- glucoside	348		0.1M in water at 25 ^{0}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 equation. The volume (V_m) of N_2 gas required to cover the adsorbent surface with a monolayer was calculated using BET equation:

$$\frac{P/P_0}{s(1-P/P_\circ)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_M CP} \quad \text{..... (1)}$$

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

$$\sum = \frac{V_m}{22.4} x 6.02 x 10^{23} x 10^{-20} \sigma_m \quad \text{...(2)}$$

Where:

σ_m is the area (A) occupied by one molecule and has been taken as 0.162 nm^2 for N_2 at 77 °K[2].

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

The chosen adsorbent was prepared by creshing dried apricot stone. They were then sieved into particle sizes (1-2-3-4 mm.) 40 g were impregnated in concentrated solution of ortho phosphoric acid (0.2 M). 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 adsorption 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 rate of 7°C/min. With constant flow of nitrogen. To avoid splashing caused by vigorous evolution of gases, the sample was heated slowly. The sample reached the selected value (500-700°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[3]. It was finally dried overnight in an oven at 105°C. Then it was grinded and sieved to the desired size (1-2-3-4 mm). During the course of experiments, several factors were investigated to optimize the parameters.

The effect of activation temperature on the adsorption capacity of the prepared 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 carbon was investigated. The activation time was from 0 to 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 carbon was tested. Four different particle size ranges (1-2-3-4 mm.) were investigated at optimum values of activation temperature, and activation time.

2-Adsorbates :

Two detergents, that have serious environmental impacts and pose a threat to human health, were selected to be investigated. The technical grade Sodium lauryl sulfate and dodecyl ß-D-glucoside are completely soluble in water. Sodium lauryl sulfate as an anionic detergent which easy to remove by dilution. Dodecyl ß-D-glucoside is an nonionic detergent which useful in the solubilization of membrane –protein[4]. 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[5] using spectro-photometer (Perkin Elmer, German).

3-Adsorption process:

Different amounts 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 detergents (0.05 dm^3) 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 Sodium lauryl sulfate and dodecyl ß-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 detergents.
C_e is the equilibrium concentration of the detergents.
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 and temperature were investigated.

RESULTS:

1- Preparation of 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.

A-Effect of temperature:

The effect of temperature of carbonization of apricot stone on the adsorbed detergents, are presented in Fig. (1). The effect of the operating temperature on the adsorption capacity of the prepared activated carbon from apricot stone was studied. The maximum capacity for lauryl sulfate and dodecyl ß-D-glucoside is achieved at 600°C for the selected raw materials. Tar materials blocked the pores created during the carbonization process at law temperature.

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 apricot stone.

C-The effect of particle size range :

The effect of particle size range on the adsorbed detergents was investigated. It was obvious, from Fig. (3) that the quantity of detergents adsorbed by activated carbon prepared from apricot stone increases by increasing particle size.

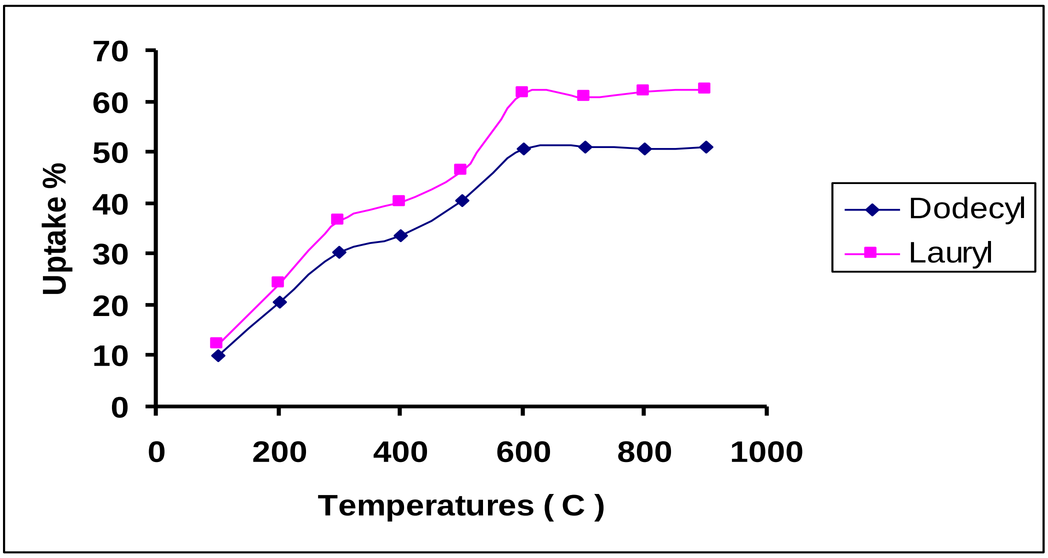


Fig (1): The effect of temperature of carbonization on uptake percent of the detergents on activated carbon

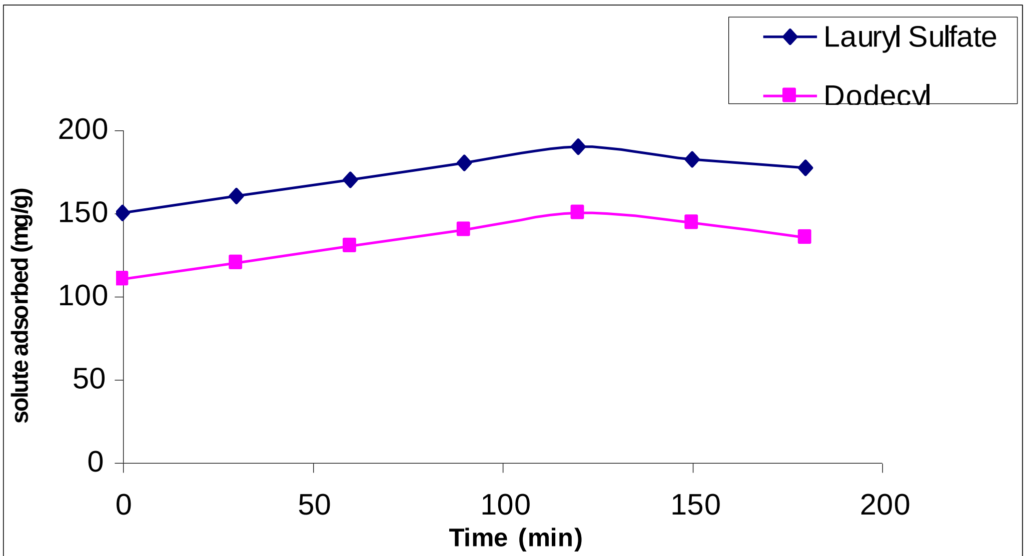
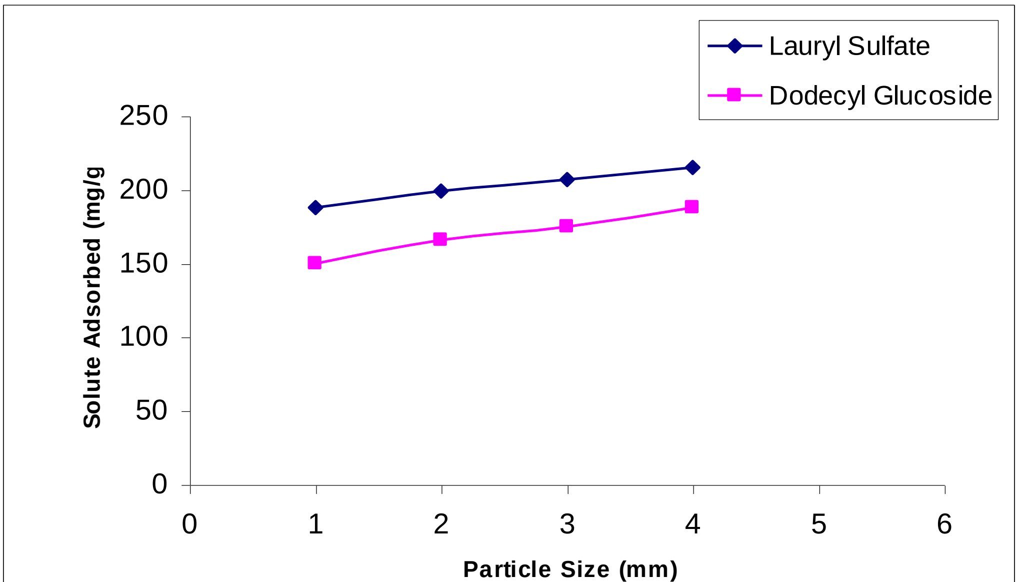


Fig (2) The effect of Activation Time on the Adsorption Capa
Activated Carbon Prepared From Apricot Stone



Fig(3)Effect of Particle Size of Apricot Stones on the Adsorptio
Capacity of the Activated Carbon

2-Characterization of the Prepared Activated Carbon:

A-Elemental Analysis:

The elemental analysis of apricot 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 apricot stone and activated carbon prepared from apricot stone

Items	C%	H%	N_2%	S%	P%	Ash
Apricot stone	45.22	9.34	6.23	1.2	5.3	1.2
Activated carbon from apricot stone	83.01	2.15	2.56	0.32	2.3	4.2

B-Chemical Analysis :

The apricot 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 apricot stone

Component	%	
	Apricot stone	Activated Carbon
a- cellulose	52.52	66.4
Pentosan	10.33	14.6
Lignin	15.25	12.3
Fat and oil	17.20	1.30
Ash	2.71	8.40

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.

C-The adsorption capacity and the factors affecting it :

The values of the maximum adsorption capacities are presented in Table (4).

Table (4): Comparison of the Maximum adsorption capacities for apricot stone and activated carbon

Types of adsorbents	q_{max} (mg/g)	
	Sodium lauryl sulfate	Dodecyl ß-D-glucoside
Apricot stone	110	142
Activated carbon obtained from apricot stone.	256	277

Fig. (4): Representative scanning electron micrograph of the adsorbent

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

The adsorbent weight variation affects the removal efficiency of detergents. The data obtained are represented in Fig. (5).

The effect of contact time on the adsorption of Sodium lauryl sulfate and dodecyl ß-D-glucoside from aqueous solutions at different time intervals using activated carbon obtained from apricot stone is illustrated in Fig. (6). The figure imply that the adsorption extent increases with elapsed time till reaching saturation level where the uptake percentage attains a constant value.

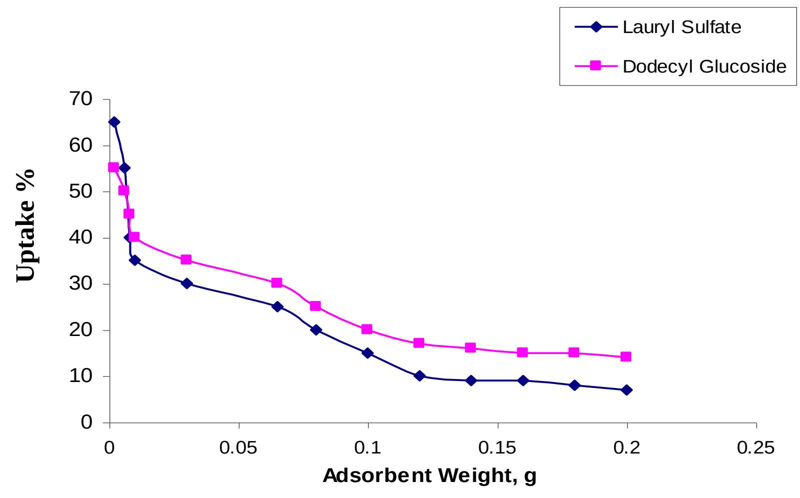
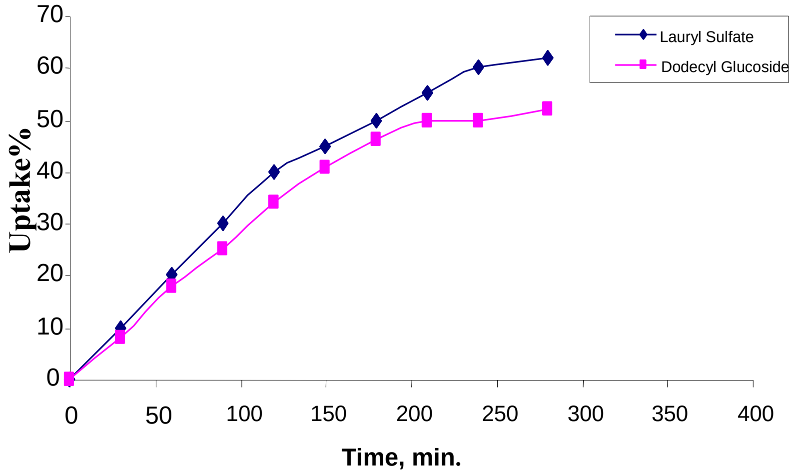


Fig (5) The Effect of Activated Carbon Weight on The Removal of Detergents From Aqous Solution



Fig(6) The effect of contact time on uptake of the detergents by Activated Carbon

The effect of pH values: 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 O.lM NaOH. A constant mass of adsorbent was added to 0.05 dm^3 Sodium lauryl sulfate and dodecyl ß-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 Sodium lauryl sulfate and dodecyl ß-D-glucoside from aqueous solutions on activated Carbon is shown in Fig. (7).

D-Effect of temperature:

Activated carbon obtained from apricot stones. Variations in temperature cause adsorbent rearrangements and also changes in the adsorption equilibrium. The uptake of Sodium lauryl sulfate and dodecyl glucoside compound obtained at 25, 35, 45 and 55°C, is shown in Fig. (8). activated carbon obtained from apricot 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.

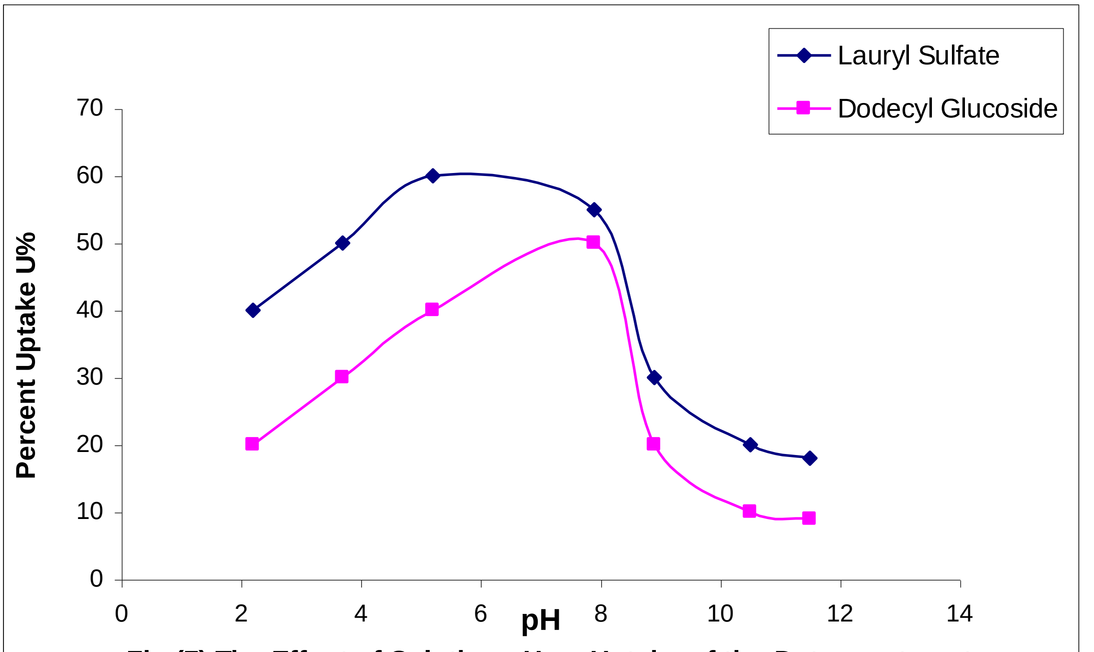


Fig (7) The Effect of Solution pH on Uptake of the Detergents ontc Activated Carbon

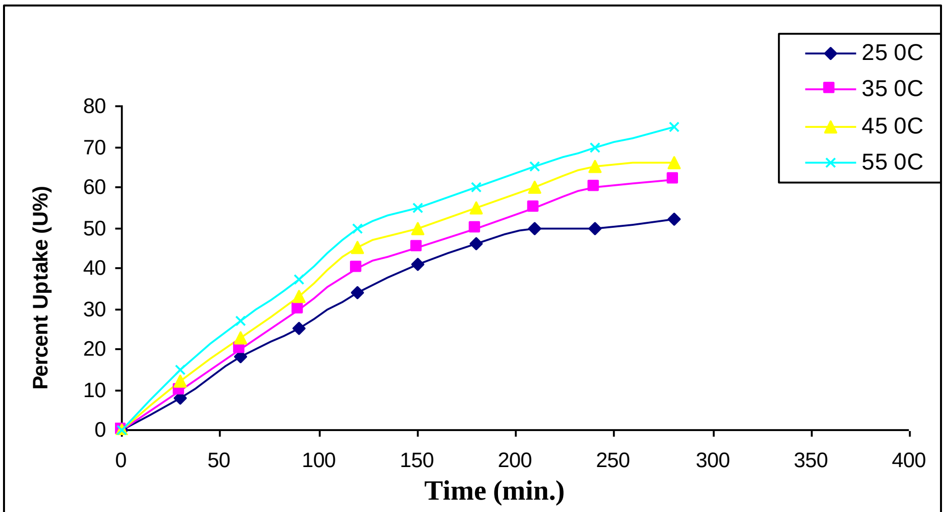


Fig (8) The Variation of The Percent Uptake With The Contact Time For the Adsorption of Lauryl Sulfate At Different Temperatures

CONCLUSION:

The following conclusions were reached:

1-The cost of the waste water treatment by these methods is not expensive.

2-In all cases, the residual concentration decreases with increasing the adsorbent weight upto a certain dose, where the removal curves become steady. The further additions of adsorbent were found to have no appreciable effect on the removal efficiency of lauryl di-ethanolamide and dodecyl benzene sulfonate are completly adsorbed per unit weight of adsorbent decreases with increasing the adsorbent weight. It can be concluded that a 0.09 g of activated carbon obtained from apricot stone is sufficient for the quantitative removal of lauryl di-ethanolamide, while 0.120 g of activated carbon is recommended for the same purpose for dodecyl benzene sulfonate.

3-The adsorption onto activated carbon obtained from apricot 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 activated carbon obtained from apricot stone for Lauryl and dodecyl sulphate. It would be useful to use the carbonized apricot stone shells for the treatment of hazardous waste solutions enriched with such detergents and it can be regarded as one of the promising materials used For the removal of organic pollutants from surface water.

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الإزالة الادمصاصية لبعض المنظفات الصناعية من المياه الملوثة باستخدام بعض المواد الصديقة للبيئة

سعد محمد السيد

معهد البحوث البيئية والتغيرات المناخية – المركز القومي لبحوث المياه – القناطر الخيرية

تم تحضير نوع من أنواع الفحم المنشط، وذلك بحرق نوى المشمش بطريقة معينة مع بعض المنظفات الصناعية التى تستخدم بكثرة فى مصر، وخاصة فى تصنيع المنظفات الصناعية والشامبو، وهى على سبيل المثال كبريتات اللوريل والدوديسيل (بيتا دى جلاكوزيد).

أنوية المشمش والفحم المحضر منها تم استخدامهما فى إزالة المنظفات الصناعية (مركبات عضوية)، وهى تعتبر من المواد السامة للإنسان والحيوانات بصفة عامة. وعند استخدام الفحم المحضر لإزالة هذه المنظفات الصناعية وجد أنها تعطى نسبة إزالة عالية. كما تم دراسة العوامل المختلفة لزيادة نسبة إزالة المنظفات، ومن هذه العوامل درجة الحرارة والزمن والأس الهيدروجينى وعند دراسة التحليل الديناميكى الحرارى لعملية ادمصاص المنظفات، وجد أن عملية الادمصاص عملية ماصة للحرارة .