

Optimization of phenol sorption in aqueous solution by date stone through response surface methodology

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Abstract

The adsorption performance of date stones was evaluated by varying experimental conditions such as, contact time, pH, adsorbent dosage, temperature and phenol initial concentration. The response of carbonized date stone "efficiency" was analyzed as a function of the experimental parameters (contact time, pH, adsorbent dosage, pollutant initial concentration and temperature), using the complete factorial design of 32 experiments. The response has been described by a first order model that was adequate to predict responses in all experimental regions. The experimental values obtained were in good agreement with the values predicted from the model, with relatively small errors between the predicted and the actual values. Through this study, we have confirmed that the activated carbon derived from date stones has a large capacity for adsorption, making it an effective and inexpensive adsorbent in the removal of phenolic compounds in aqueous solutions.

Keywords: Activated carbon, Adsorption, Dates stones, Experimental design, Phenol.

I. Introduction

In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement. Contamination of aqueous environments by heavy metals and phenolic compounds is a worldwide environmental problem due to their toxic effects and accumulation through the food chain [1, 2].

The presence of phenolic compounds has been documented in different mediums such as sewage sludge, influent and effluent of wastewater, river water and soil [3]. Pocurull et al. showed concentrations of nitro phenols (2-nitrophenol, 4-nitro -phenol and 2,4-dinitrophenol) in Ebro river (Spain) ranging from 0.1 to 5.0 µg/l [4]. The other results indicated concentration of phenol over 40mg/l in river water, which was receiver of wastewater from petrol industry [5]. Moreover, in the area fertilized by municipal sewage sludge, the concentration of 4-nonylphenol was 2.7 mg/kg of soil [6]. Phenols are also included in The List of Priority Pollutants by the US Environmental Protection Agency (EPA) [7]. They are also highly toxic which is very important due to ecological aspects [8,9]. Beside the toxic effects, phenolic compounds create an oxygen demand in receiving waters, and impart taste and odor to water with

minute concentrations of their chlorinated compounds. Chronic toxicity of phenols in humans results in: headache, vomiting, difficulty in swallowing, liver injury, fainting and etc. [10]. Therefore, due to the environmental and ecological safety the waste waters containing phenolic compounds must be treated before their discharging into the water streams [1- 3]

With regard to increasing effluent discharge standards to the environment, high considerations should be made when selecting proper treatment processes. Any of chemical, biological and physical treatment processes has its own advantages and disadvantages. Application of some waste products that could help in this regard, in addition to reuse of these waste materials, can be an advantage (Mahvi, 2008). Among the different organic pollutants in wastewater, phenolic compounds are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations. The objective of this study is to remove phenol present from waste water by an activated carbon prepared from date stones which are a very abandoned agricultural waste in Algeria.

II. Material and methods

A. Phenol properties

Properties of Phenols: Molecular weight 94.11g/mol; Boiling point 182.0°C; Melting point 43.0°C; Vapour pressure 0.3513mm Hg at 25°C; Solubility in water 8.3g/100ml; Viscosity 3.437mPa; pH 6; pKa 9.99. Phenol removal is a pre-requisite, as it has many harmful effects on plants, animals and humans.



Figure 1. Absorbance spectrum of phenol

B. Material

The biomaterial used in this study is date stones which are very abundant in Algeria due to high production of dates in Sahara. Date stones were:

- 1) Washed with distilled water.
- 2) calcined in oven at (600 ° C) for 15 min.
- 3) Crushed with porcelain mortars and pestles.
- 4) Sieved at 125µm.
- 5) Heated in oven at 50 ° C for 15 minutes before each use.



Figure 2. Date stone, raw, calcined and crushed

C. Batch adsorption experiments

Mixture of 2g of the solid material with 100ml of phenol solution at 50mg/L, under agitation at room temperature 20°C and with stirring speed of 300tr/min during 120min. We centrifuge the solutions for 10 min, then we analyze the supernatant by UV-Visible (UV-Visible Spectrophotometer UV 1601.Shimadzu) directly after filtration at $\lambda_{\max}=270$ nm. Finally we calculate the adsorption capacity q (mg/g) according to the following equation [3]:

$$qt = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

q_t : sorption capacity at time t (mg/g), C_t : concentration of phenol at time t (mg/L), C_0 : initial concentration (mg/g), V : solution volume (L) and m : sorbent mass (g).

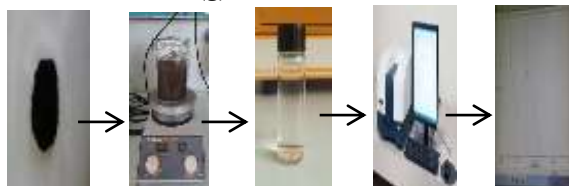


Figure 3. Experimental method

III. Design of experiment

The preliminary study previously presented shows that the rate of phenol elimination by date stones depends on several parameters which do not act in the same way. It is therefore useful to perform an experimental design to identify the most influential parameters during phenol removal.

A. Full factorial design

In order to obtain the optimal conditions for phenol adsorption, a complete design factor of the n_k type was used, where n =number of levels and k =number of factors being tested (here $n=2$ and $k=5$). Thus, the total number of experiments needed for this study is 2^5 (32). If Y is the response variable, then the five-parameter regression equation and their interaction is given by Akhnazarova and Katarov (1982) [11-13]:

$$Y_{\text{est}} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 + b_{45}X_4X_5 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{125}X_1X_2X_5 + b_{134}X_1X_3X_4 + b_{135}X_1X_3X_5 + b_{145}X_1X_4X_5 + b_{234}X_2X_3X_4 + b_{235}X_2X_3X_5 + b_{245}X_2X_4X_5 + b_{345}X_3X_4X_5 + b_{1234}X_1X_2X_3X_4 + b_{1235}X_1X_2X_3X_5 + b_{1245}X_1X_2X_4X_5 + b_{1345}X_1X_3X_4X_5 + b_{2345}X_2X_3X_4X_5 + b_{12345}X_1X_2X_3X_4X_5 \quad (2)$$

Where b_0 , b_1 , b_2 , b_3 , b_4 and b_5 are the linear coefficients, b_{12} , b_{13} , b_{14} , b_{15} , b_{23} , b_{24} , b_{25} , b_{34} , b_{35} and b_{45} are the second order interaction terms. X_1 , X_2 , X_3 , X_4 and X_5 are, respectively, the factors of coded dimensions of the parameters studied: carbon dose, pH, initial phenol concentration and temperature. In Table 1, low and high levels are listed for the studied parameters:

Table 1. The Factor Plan 2^5

Level	X_1 [t (min)]	X_2 [pH]	X_3 [C_0 (mg/l)]	X_4 [m (g)]	X_5 [T (°C)]
-1	5	2	10	1	20
+1	60	7.57	50	2	40

According to the factorial design for phenol removal by carbon of date stones, thirty-two experiments (2^5) are required to remove the matrix according to Table 2. The last column corresponds to the results obtained..

Table 2. Matrix of experiments with coded and uncoded factors and the response.

Experiments	X_1 [t (min)]		X_2 [pH]		X_3 [C_0 (mg/l)]		X_4 [m (mg)]		X_5 [T (°C)]		$Y_{réel}$	Y_{estim}
1	-1	5	-1	2	-1	10	-1	1	-1	20	85.67	85.9039
2	1	60	-1	2	-1	10	-1	1	-1	20	91.476	91.2417
3	-1	5	1	7.57	-1	10	-1	1	-1	20	57.134	56.9002
4	1	60	1	7.57	-1	10	-1	1	-1	20	79.741	79.975
5	-1	5	-1	2	1	50	-1	1	-1	20	25.756	25.5228
6	1	60	-1	2	1	50	-1	1	-1	20	53.269	53.035
7	-1	5	1	7.57	1	50	-1	1	-1	20	20.182	19.948
8	1	60	1	7.57	1	50	-1	1	-1	20	48.72	48.954
9	-1	5	-1	2	-1	10	1	2	-1	20	77.641	77.875
10	1	60	-1	2	-1	10	1	2	-1	20	78.999	78.765
11	-1	5	1	7.57	-1	10	1	2	-1	20	61.592	61.352
12	1	60	1	7.57	-1	10	1	2	-1	20	80.573	80.807
13	-1	5	-1	2	1	50	1	2	-1	20	57.707	57.473
14	1	60	-1	2	1	50	1	2	-1	20	79.939	80.173
15	-1	5	1	7.57	1	50	1	2	-1	20	26.646	26.88
16	1	60	1	7.57	1	50	1	2	-1	20	64.429	64.195
17	-1	5	-1	2	-1	10	-1	1	1	40	86.411	86.645
18	1	60	-1	2	-1	10	-1	1	1	40	93.391	93.157
19	-1	5	1	7.57	-1	10	-1	1	1	40	62.261	62.027
20	1	60	1	7.57	-1	10	-1	1	1	40	77.888	78.122
21	-1	5	-1	2	1	50	-1	1	1	40	68.421	68.187
22	1	60	-1	2	1	50	-1	1	1	40	94.862	95.096
23	-1	5	1	7.57	1	50	-1	1	1	40	56.707	56.941
24	1	60	1	7.57	1	50	-1	1	1	40	82.123	81.889
25	-1	5	-1	2	-1	10	1	2	1	40	87.214	86.98
26	1	60	-1	2	-1	10	1	2	1	40	82.088	82.322
27	-1	5	1	7.57	-1	10	1	2	1	40	51.266	51.5
28	1	60	1	7.57	-1	10	1	2	1	40	52.255	52.021
29	-1	5	-1	2	1	50	1	2	1	40	87.848	88.082
30	1	60	-1	2	1	50	1	2	1	40	95.587	95.353
31	-1	5	1	7.57	1	50	1	2	1	40	36.254	36.02
32	1	60	1	7.57	1	50	1	2	1	40	61.627	61.861

The results of the previous matrix are analysed using the Minitab V16 program for Windows 7. The graphical representation of parameters and

interaction effects are shown in the following figures:

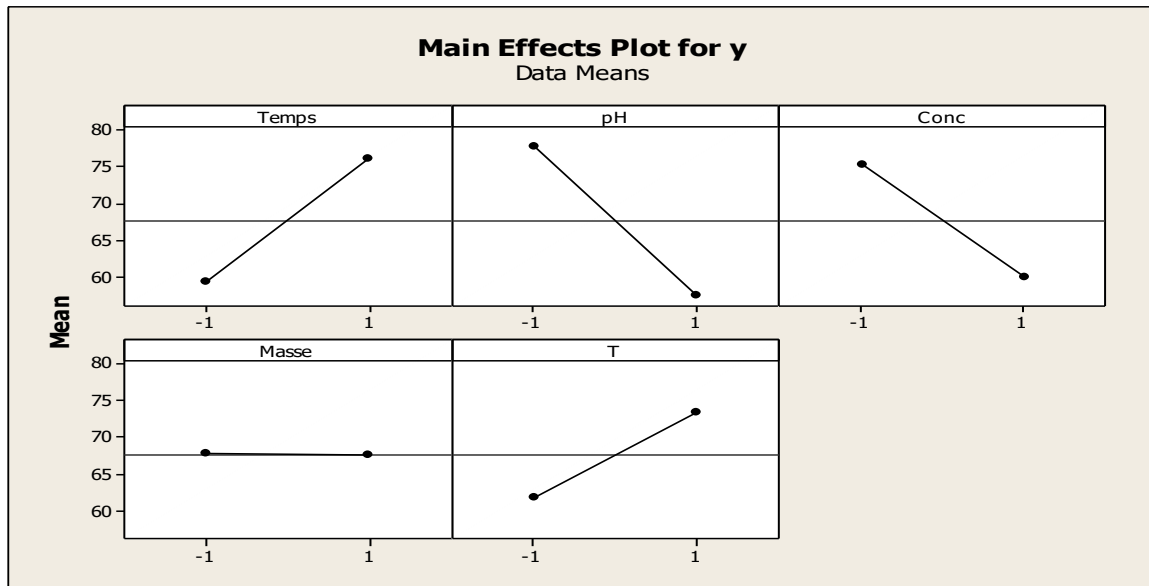


Figure 4. The graphical representation of effects

According to the plots the effect of the mass can be eliminated because their graph is horizontal and parallel to the X axis. pH and initial concentration

have a negative effect while contact time and temperature have a positive effect.

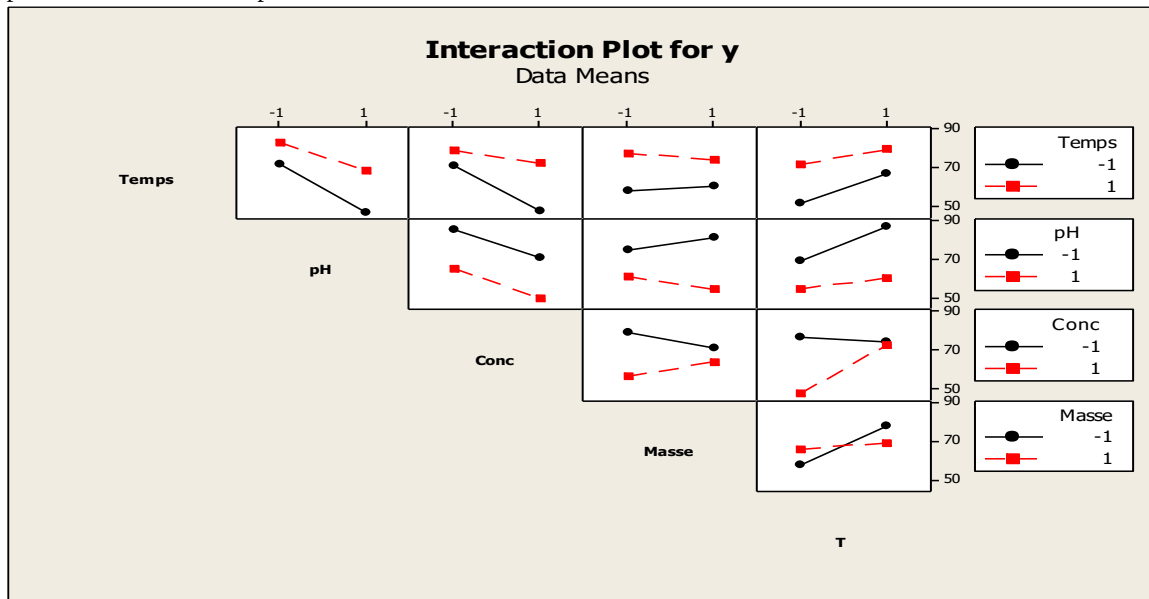


Figure 5. The graphical representation of interactions

In this figure we notice that the effects time*Conc, Conc*mass pH*T, pH*mass and Conc*T have an important effect because of the crossing between the curves. On the other hand for the effect of pH*Conc there is no interaction because the curves are parallel.

$$Y_{est} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 + b_{45}X_4X_5 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{125}X_1X_2X_5 + b_{134}X_1X_3X_4 + b_{135}X_1X_3X_5 + b_{145}X_1X_4X_5 + b_{234}X_2X_3X_4 + b_{235}X_2X_3X_5 + b_{245}X_2X_4X_5 +$$

$$b_{345}X_3X_4X_5 + b_{1234}X_1X_2X_3X_4 + b_{1235}X_1X_2X_3X_5 + b_{1245}X_1X_2X_4X_5 + b_{1345}X_1X_3X_4X_5 + b_{2345}X_2X_3X_4X_5 \quad (3)$$

The error is calculated as the difference between the experimental and the estimated values and the results are shown in the following table:

Table 3. Error Between Experimental Values and Estimated Values Using the Linear Model

$Y_{réel}$	Y_{estim}	e_i	e_i^2	$Y_{réel}$	Y_{estim}	e_i	e_i^2
85.67	85.9039	-0.234	0.054756	77.888	78.122	-0.234	0.054756
91.476	91.2417	0.234	0.054756	68.421	68.187	0.234	0.054756
57.134	56.9002	0.234	0.054756	94.862	95.096	-0.234	0.054756
79.741	79.975	-0.234	0.054756	56.707	56.941	-0.234	0.054756
25.756	25.5228	0.234	0.054756	82.123	81.889	0.234	0.054756
53.269	53.035	0.234	0.054756	87.214	86.98	0.234	0.054756
20.182	19.948	0.234	0.054756	82.088	82.322	-0.234	0.054756
48.72	48.954	-0.234	0.054756	51.266	51.5	-0.234	0.054756
77.641	77.875	-0.234	0.054756	52.255	52.021	0.234	0.054756
78.999	78.765	0.234	0.054756	87.848	88.082	-0.234	0.054756
61.592	61.352	0.234	0.054756	95.587	95.353	0.234	0.054756
80.573	80.807	-0.234	0.054756	36.254	36.02	0.234	0.054756
57.707	57.473	0.234	0.054756	61.627	61.861	-0.234	0.054756
79.939	80.173	-0.234	0.054756	77.888	78.122	-0.234	0.054756
26.646	26.88	-0.234	0.054756	68.421	68.187	0.234	0.054756
64.429	64.195	0.234	0.054756	94.862	95.096	-0.234	0.054756
86.411	86.645	-0.234	0.054756	56.707	56.941	-0.234	0.054756
93.391	93.157	0.234	0.054756	82.123	81.889	0.234	0.054756
62.261	62.027	0.234	0.054756	87.214	86.98	0.234	0.054756
77.888	78.122	-0.234	0.054756	56.707	56.941	-0.234	0.054756
68.421	68.187	0.234	0.054756	82.123	81.889	0.234	0.054756
94.862	95.096	-0.234	0.054756				

The common variance of the residues is therefore [32, 33]:

$$S^2 = \frac{1}{n-p} \sum_{i=1}^4 e_i^2 \quad (4)$$

With $S=1.3237$.

The common variance of all effects is then:

$$S_i^2 = \frac{s^2}{n} \quad (5)$$

Numerically $S_i^2 = 0.054756$

The Student's "t" for each effect is calculated as:

$$t_i = \frac{|b_i|}{S_i} \quad (6)$$

Table 4. Significance test

Factor	Effect	t	Result	Factor	Effect	t	Result
Constant b ₀	67.6774063	1235.98	S*	X ₁ X ₂ X ₃ time*pH*Conc	-0.50003125	9.13	NS
X ₁ time	8.38303125	153.09	S	X ₁ X ₂ X ₄ time*pH*mass	0.98359375	17.96	S
X ₂ pH	-10.2150313	186.55	S	X ₁ X ₂ X ₅ time*pH*T	-0.61340625	11.2	NS
X ₃ Conc	-7.67259375	140.12	S	X ₁ X ₃ X ₄ time*Conc*masse	0.62615625	11.43	NS
X ₄ mass	-0.07334375	1.33	NS	X ₁ X ₃ X ₅ time*Conc*T	-0.02546875	0.46	N S
X ₅ T	5.83528125	106.56	S	X ₁ X ₄ X ₅ time*mass*T	-1.29309375	23.61	S
X ₁ X ₂ Time*pH	2.57409375	47.01	S	X ₂ X ₃ X ₄ pH*Conc*mass	-3.03803125	55.48	S
X ₁ X ₃ Time*Conc	4.18165625	76.36	S	X ₂ X ₃ X ₅ pH*Conc*T	-0.08203125	1.49	NS
X ₁ X ₄ Time*mass	-1.54996875	28.3	S	X ₂ X ₄ X ₅ pH*masse*T	-2.39303125	43.7	S
X ₁ X ₅ time*T	-1.91809375	35.02	S	X ₃ X ₄ X ₅ Conc*mass*T	-2.17746875	39.76	S
X ₂ X ₃ pH*Conc	-0.20378125	3.72	NS	X ₁ X ₂ X ₃ X ₄ time*pH*Conc*mass	1.09046875	19.91	S
X ₂ X ₄ pH*mass	-3.05878125	55.86	S	X ₁ X ₂ X ₃ X ₅ time*pH*Conc*T	0.61546875	11.24	NS
X ₂ X ₅ pH*T	-3.25003125	59.35	S	X ₁ X ₂ X ₄ X ₅ time*pH*mass*T	0.02434375	0.44	NS
X ₃ X ₄ Conc*mass	3.82315625	69.82	S	X ₁ X ₃ X ₄ X ₅ time*Conc*mass*T	-0.12621875	2.3	NS
X ₃ X ₅ Conc*T	7.08853125	129.45	S	X ₂ X ₃ X ₄ X ₅ pH*Conc*mass*T	0.85221875	15.56	S
X ₄ X ₅ mass*T	-4.17196875	76.19	S				

*S : significant ; NS : Non significant

So the simplified model is written :

$$Y_{est} = 67.6774 + 8.3830 X_1 - 10.215 X_2 - 7.6726 X_3 + 5.8353 X_5 + 2.5741 X_1X_2 + 4.1817 X_1X_3 - 1.55 X_1X_4 - 1.9181 X_1X_5 - 3.0588 X_2X_4 - 3.25 X_2X_5 + 3.8232 X_3X_4 + 7.0885 X_3X_5 - 4.172 X_4X_5 + 0.9836 X_1X_2X_4 - 1.2931 X_1X_4X_5 - 3.0380 X_2X_3X_4 - 2.3930 X_2X_4X_5 - 2.1775 X_3 X_4X_5 + 1.0905 X_1X_2X_3X_4 + 0.8522 X_2X_3X_4X_5 \quad (7)$$

B. Analysis of variance :validation of the first model

-The variation due to the linear link (regression or model):

$$SCEL = \sum (Y_i^{est} - Y_{moy})^2 \quad (8)$$

Residual variance:

$$SCER = \sum (Y_i^{exp} - Y_i^{est})^2 \quad (9)$$

The total variation:

$$STCE = SCEL + SCER \quad (10)$$

Where : SCEL : Sum of the squares of the deviations due to the liaison

SCER: Sum of squares of the deviations of the residuals

CETS: Sum total of squares of the deviations

Y_i^{est} : The response estimated using the linear model

Y_{moy} : The average of the experimental responses

Y_i^{exp} : The response observed during the experiments.

Table 5. Analysis of Variance ANOVA [13-15].

Variation in	Sum of squares	DDL	Average squares	R ²	F
Liaison	$SCEL = 13682,54$	30	$\frac{SCEL}{p-1} = CML = 456,084$	$R^2 = \frac{SCEL}{STCE} = 0.999$	$F_{obs} = \frac{CML}{CMR} = 260.32$
Residues	$SCER = 1,752$	1	$\frac{SCER}{n-p} = CMR = 1,752$	$R_{adj}^2 = 1 - \frac{CMR}{CMT} = 0.996$	
Total	$STCE = 13684,29$	31	$\frac{STCE}{n-1} = CMT = 441.42$		

$F_{obs} > F_{crit}$, then we accept the hypothesis of linearity of the model with the confidence $1-\alpha$. Although this model contains several significant factors, it is validated by the coefficient of determination R^2 .

IV. CONCLUSION.

The objective of this present study is the recovery of an organic waste in order to have an activated carbon from the stone date, which will be useful for the adsorption of a toxic and eco toxic chemical, in this study we considered phenol as a pollutant. The results shows:

- A balance time equal to 120 min; Kinetic study indicate that the kinetic adsorptions of phenol by calcinated date stone is well represented by pseudo-second-order model with $R^2=0.99$ and $q_{e,the}=2.18$ mg/g which is comparable with the experimental value $q_{e,exp}=2.03$ mg/g.
- Diffusional model reveal that the process is governed by diffusion in pores, but it is not the only limiting step of adsorption phenomenon.
- Upgrading and the circular economy are very important ecological steps as well as economic ones. dates represent a national product, of wide consumption and enormous production, their stones once transformed into activated carbon are effective for the depollution of water contaminated by chemical product. the industry is therefore invited to adopt this depollution approach with a free raw material and a yield very close to 100%. from an ecological point of view, this

approach prevents the loss of biomass, conserves a resource, cleans up water and promotes the production of dates.

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