TRAITEMENT DES EFFLUENTS AQUEUX PAR ADSORPTION SUR DES FIBRES NATURELLES
WASTE WATER TREATMENT BY ADSORPTION ON NATURAL CORDS

H. CHERIFI[1], S. HANINI[1], F. BENTAHAR[2] , A. KETTAB[3]

[1]*University of Medea, LBMPT, 26000 Medea, Algeria, (email: ha_cherifi@yahoo.fr)*
[2]*University USTHB, LPT, 16000, Algiers, Algeria.*

[3] *ENP, LRSE, 16000, Algiers, Algeria*

Résumé

Ce travail est une étude quantitative du comportement physico-chimique des fibres de loofa, et son utilisation potentielle pour l'adsorption des contaminants. Dans un premier temps, nous avons étudié la cinétique de l'adsorption statique du système phénol / fibre de loofa en utilisant le phénol comme un modèle de pollution. La spectrophotométrie UV / Visible est utilisée comme méthode d'analyse. Dans un deuxième temps, on a étudie l'influence de certains paramètres essentiels sur l'adsorption, à savoir la concentration initiale du phénol, le temps de contact, la température et la granulométrie. Les modèles d'adsorption de Freundlich et Langmuir ont été utilisés pour la description mathématique de l'équilibre d'adsorption. Les résultats ont montré que le procédé d'adsorption du phénol obier parfaitement au modèle de Langmuir. Cette étude confirme l'importance de l'utilisation des fibres de loofa pour le traitement des eaux usées industrielles.

Mots clefs : Fibres de loofa; Phénol; Adsorption statique; Modélisation

Abstract

This work is a quantitative study of the physicochemical behaviour of the cords of loofa, and its potential use for adsorption of contaminants. In a first stage, we examined the static kinetic of adsorption of the phenol/cord of loofa system using phenol as a pollution model. UV/Visible spectrophotometry is used as a method of analysis. In a second stage, the influence of some essential parameters, namely, initial phenol concentration, contact time, temperature and granulometry on the static adsorption of the system phenol/loofa has been investigated. The Freundlich and Langmuir adsorption models have been used for the mathematical description of the adsorption equilibrium. The results show that experimental data fit perfectly to the Langmuir model. This study demonstrates the potential use of the cord of loofa for industrial waste water treatment.

Key words: Cord of loofa; Phenol; Static adsorption; Modelling.

1. Introduction

Removal of hazardous conpounds from industrial effluents is one of the growing needs of the present time. Various techniques like, coagulation, adsorption, chemical oxidation and froth floatation etc., have been used for the removal of organics as well as inorganics from wastewaters. Amongst these, adsorption is considered to be most potential one due to its high efficiency and ability to separate wide range of chemical compounds (Mittal et al., 2005).

Phenols are generally considered to be one of the important organic pollutants discharged into the environment causing unpleasant taste and odour of drinking water. The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, petroleum and petrochemicals industries (Dabrowski et al., 2005). Introducing phenolic compounds into the environment or degradation of these substances means the appearance of phenol and its derivatives in the environment.

Traditionally, biological treatment, activated carbon adsorption, reverse osmosis, ion exchange and solvent extraction are the most widely used techniques for removing phenols and related organic substances (Dursun et al., 2005). Amongst these methods, adsorption on the activated carbon is still one of the most commonly used techniques. Many researchers have shown that activated carbon is an effective adsorbent for organic compounds especially for phenolic compounds. However, its high initial cost and the need for a costly regeneration system makes it less economically viable as an adsorbent. Taking these criteria into consideration, the search for a low cost and easily available adsorbent has led many investigators to search more economic and efficient techniques using natural and vegetal adsorbents (Ho et G. Mckay, 1998; Rahman et al., 2005; Ho Yuh-Shan, 2005; Montanher et al., 2005).

Several attempts were recorded in many laboratories in order to replace the activated carbon by other adsorbents such as cords of loofa. Loofa sponge, a natural material consisting of a fibrous network, obtained from the matured dried fruit of loofa cylindrical.

The objective of this work is the study the static capacity of adsorption of phenol by the cylindrical loofa. Firstly, a physicochemical characterization of the loofa has been carried out with the establishment of the kinetic of adsorption. Secondly, the effects of initial phenol concentration, contact time, temperature and granulometry on the static adsorption of the system phenol/loofa have been examined.

Finally modelling of the isotherms of adsorption has been undertaken by fitting the parameters of the two traditional models: model of Langmuir and model of Freundlich

2. Materials and methods

a. Preparation of Loofa

The vegetable sponge of loofa cylindrical is a natural product which grows in the north of Algeria. The pre-treatment of the sponges consisted of cooking with boiling water for 30mn followed by washing with distilled water in order to remove the seeds and loose cord fragments. These sponges were then placed in solution of NaOH (12%) for 15 mn and washed again with tap water. Whitening with bleach 12% for 3 hours at ambient temperature after which the sponges are rinsed with distilled water several times. The sponge were oven dried at 105°C for 24 hours, then crushed and sifted on a standard sifting and crushing.

b. Characterization of materials

Infrared spectra were used in order to characterise the principal groups. The spectra are obtained by analysis of a powder sample of the loofa cylindrical dissolved in spectroscopic Nujol on a NaCl sample, the product thus obtained is exposed to the radiation of an infra-red spectrophotometer (SHIMADZU FTIR-8400).

The concentration of initial and residual phenol in the adsorption media was determined using UV/Visible spectrophotometer (SHIMADZU UV Mini-1240).

i. Preparation of adsorbate

A stock solution was prepared by dissolving 0.5 gr of phenol of analytical reagent grade in 500 ml solution of sodium bicarbonate 0.1 N. The test solutions were prepared by diluting of stock solution to the desired concentration. The ranges of concentrations of phenol prepared from stock solution varied between the values of 0 and 50 mg/l. The pH of the each solution was adjusted to the required value pH=8.5 with the 0.1 N sodium bicarbonate.

Process of adsorption

The method retained for the establishment of the isotherm of adsorption consists in putting a series of bottles in a Marie bath provided with an agitator. Each bottle contains a (*V)* volume of phenol solution of different known concentration and a mass *(m)* of adsorbent (Loofa). After a fixed time contact, the filtrate of the solution is recovered to be anylized by UV/Visible spectrophotometer with λ=270nm which is appropriate to the maximum of absorption of the light. The equilibrium concentration of the solution is deduced from a calibration curve: $DO=0.018C(mg/l)$ with $\lambda=270nm$ (1)

The quantity adsorbed of aqueous solution *(q)* per unit mass of the solid support is calculated by the following formula: $q=(C_0-C_e)\frac{V}{m}$

(2)

Where: q is the quantity adsorbed of phenol per gram of adsorbent at time t (mg/g).
qe: is the quantity adsorbed of phenol per gram of adsorbent at equilibrium (mg/g).
Ce : is the concentration of the solution at equilibrium (mg/l).
C_0 : is the initial phenol concentration (mg/l).
V : is the volume of phenol solution (l).
m : mass of loofa (g).

Thus the curve of the isotherms of adsorption is: $q(mg)=f(C_e(mg/l))$

3. Results and discussion

a. Morphological characterization of material (Loofa)

The observation under the optical microscope (figure 1) enabled us to discern the following aspects:

- The fibres have the cylindrical shape with average length of 0.9 mm.
- The circular section of the fibre has an average diameter ranging from 8 to 30 λm.

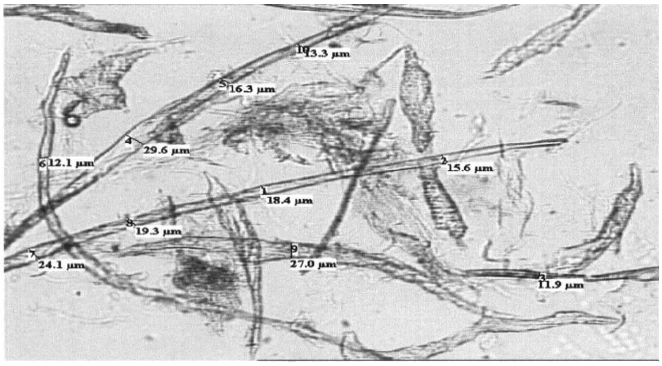

Figure 1: Structure of the cord of loofa (Hanini et al., 2003).

b. Infra-red spectroscopy analysis

The analysis of the spectrum (figure 2) shows that the material (cord of loofa) contains impurities characterized by bands of adsorption, in addition to the following functional groups: · OH group corresponding to the frequency range 2800 and 3500 cm^{-1}

· C=C group corresponding to the frequency range 1450-1600 cm^{-1}.

Figure 2 : IR-spectrum of the cord of loofa

c. Characterization of adsorption

The effects of some essential parameters on the rate of adsorption are examined.

- ***Effect of contact time***

In order to determine the time of contact necessary for the establishment of adsorption equilibrium, the quantity absorbed of aqueous solution on cords is measured as function of time of contact corresponding to adsorption equilibrium. This time will be used for temporary planning of the experiments of adsorption on fibrous loofa. The variation of the quantity adsorbed according to the time of contact is shown in figure 3.

Adsorption studies were carried out for 2 h and it was observed that, the amount of adsorbed phenol increased linearly with time at the beginning of adsorption. Then attained saturation called the equilibrium time. A larger amount of phenol was removed in the first 20 min of contact time and the equilibrium was established in 50 min for all temperatures studied.

- ***Effect of the initial concentration of phenol***

To determine the impact of the concentration on the adsorption of phenol in aqueous solution in contact with fibrous loofa, the variation of the quantity of phenol adsorbed with respect to time of contact has been examined for two initial concentrations: C_0=25ppm and 50ppm. The results of these experiments are shown in figure 4 which shows that the initial concentration has a clear influence on the amount of phenol absorbed on fibrous loofa. This is high for high initial concentrations therefore it is recommended for highly charged waste waters and less interesting for less charged solutions.

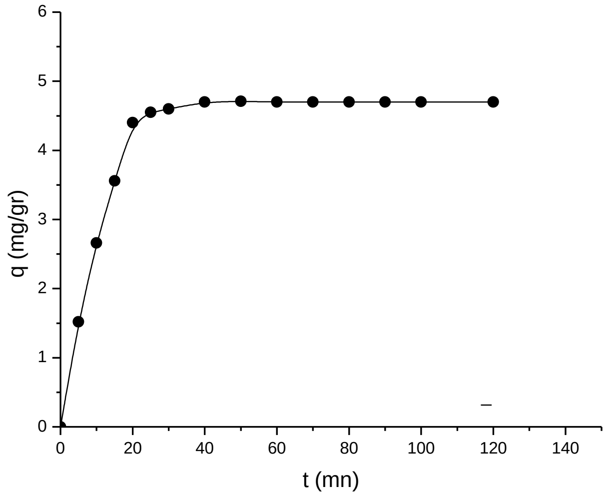

Figure 3: Phenol adsorption curves (phenol/loofa) at given conditions: pH=8.5, C_0=50mg/l, m=0.1g, V=50ml, T=23°C and stirring velocity=150 rpm.

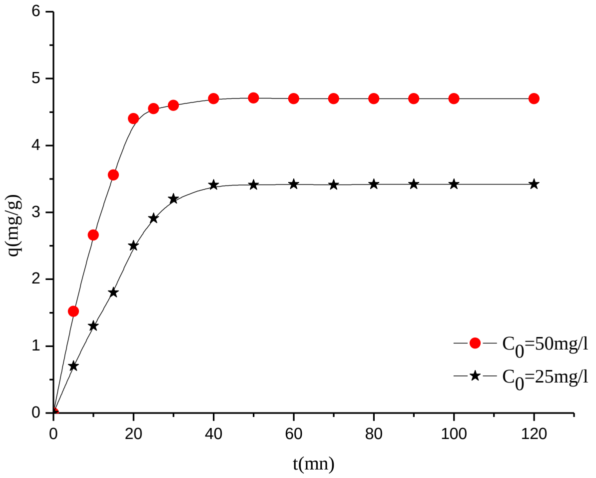

Figure 4: Effect of initial concentration on adsorption (phenol/loofa) at given conditions: pH=8.5, m=0.1g, V=50ml, T=23°C and stirring velocity =150rpm.

- ***Effect of the granulometry of the loofa***

The tests are carried out for two kinds of loofa, one crushed and the other in a raw state. All the experiments were conducted under the same initial conditions of temperature, quantity of dry mass, time of contact, pH of the solution, volume and initial concentration of the solution of phenol. The results obtained which are consigned in figure 5. This shows clearly that the amount of phenol absorbed in the case of crushed loofa is well above of that of raw loofa. This can be explained by the fact that the mechanical crushing of the cord loofa induces a geometrical modifications as well as physicochemical modifications which will cause the delaminating of the walls and an increased flexibility of the cords, which involves an increase a closed fibrous structure (formation of small pores) and a reduction in external porosity and thus more the granulometry of the loofa decreases, more the adsorbed quantity will be large.

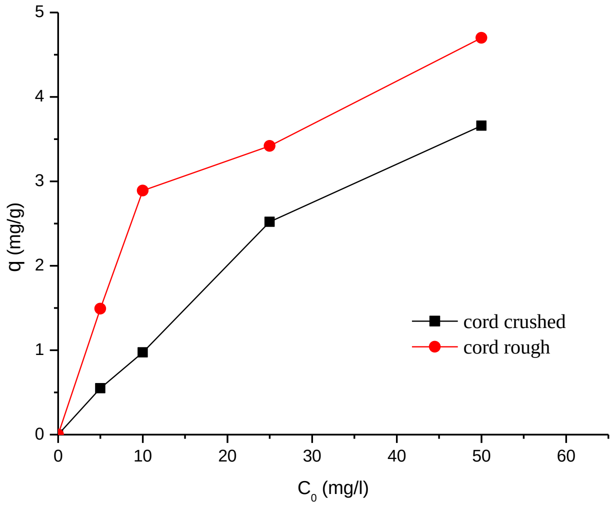

Figure 5: Effect of the granulometry of the loofa on adsorption (phenol/loofa) at given conditions: pH=8.5, m=0.1g, V=50ml, T=23°C and stirring velocity =150rpm.

d. Effect of initial phenol concentration on temperature-dependent adsorption

The initial phenol concentration provides an important driving force to overcome all mass transfer limitations of phenol between the aqueous and solid phases. Thus a higher initial phenol concentration will enhance the adsorption process (Dursun et al., 2005; Ozer et al., 2005). The effect of initial phenol concentration was investigated in the range of 25–50 mg/l at 4, 17, 23 and 30 °C. The results obtained are illustrated on figure 6.

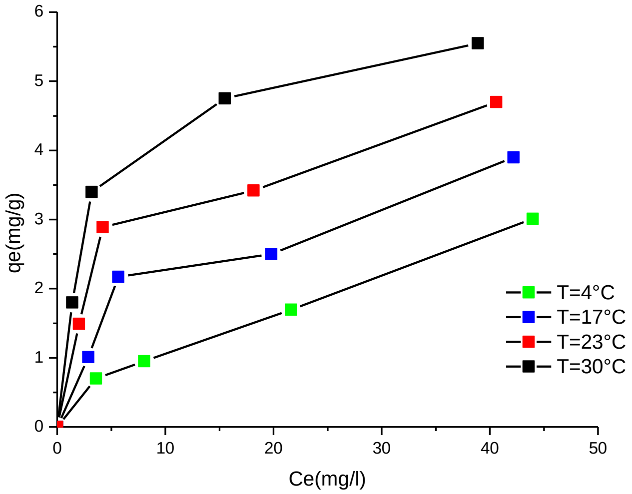

Figure 6: Effect of initial phenol concentration on temperature- dependent adsorption at given conditions: pH=8.5, m=0.1g, V=50ml, T=23°C and stirring velocity =150rpm.

Table 1 shows the change of the equilibrium adsorption capacity of the loofa with initial phenol concentration and temperature. It was indicated that q_e values increased with both increasing initial phenol concentrations and increasing temperature. The maximum equilibrium adsorption capacity values were determined as 3.01, 3.9, 4.7, and 5.55 mg g^{-1} for 50 mg/l initial phenol concentration at 4, 17, 23 and 30 ◦C respectively. The adsorbent showed saturation at high phenol concentration as the adsorbent offers a limited number of surface binding sites. The increase of the adsorption capacity at increased temperature indicated that the adsorption of phenol onto the loofa is endothermic in nature and may involve physical adsorption as well as somewhat chemical adsorption.

Table 1: The equilibrium uptake capacities and adsorption yields obtained at different initial concentrations and temperatures

T°C	4°C	17°C	23°C	30°C
C_0(mg/l)	q_e(mg/g)	q_e(mg/g)	q_e(mg/g)	q_e(mg/g)
5	0.7	1.01	1.49	1.8
10	0.95	2.17	2.89	3.4
25	1.695	2.5	3 .42	4.75
50	3.01	3.9	4.7	5.55

e. Adsorption equilibrium depending on temperature

In this study, the adsorption equilibrium of phenol on Loofa was modelled using Langmuir and Freundlich isotherms. Their isotherm plots obtained at four different temperatures are presented in figues. 7- 8.

As seen from the table 2, although correlation coefficients of both equations are considerably well obtained at all temperatures, the Freundlich model exhibited better fit to the adsorption data than the Langmuir model. The magnitude of k_f and n_f of the Freundlich isotherm constants showed the tendency of phenol uptake from the adsorption medium with high capacity of the loofa especially at 30 ◦C. The highest k_f value was determined as 1.9180 at this temperature. All n values were greater than unity, indicating that phenol was favourably adsorbed by cord of loofa at all temperatures studied. Both the Q_0 and k values determined from Langmuir equation increased from 2.69 to 6.21 and from 0.09 to 0.3 with increasing temperature from 4 to 30 ◦C respectively. The maximum capacity, Q_0 defines the total capacity of the adsorbent for phenol. The other Langmuir constant, k indicates the affinity for the binding of phenol. The higher value of k found at 30 ◦C showed strong bonding of phenol to the loofa at this temperature.

Table 2: Isotherms constants for phenol adsorbed on loofa

T(°C)	*Langmuir* model			*Freundlich* model		
	Q_0	k	r	k_f	n_f	r
4	2.6857	0.0916	0.9609	0.3073	1.7207	0.9895
17	4.6525	0.10284	0.9597	0.7684	2.3138	0.9288
23	5.0715	0.21817	0.9704	1.4000	3.0251	0.9298
30	6.2112	0.30155	0.9909	1.9180	3.1883	0.9441

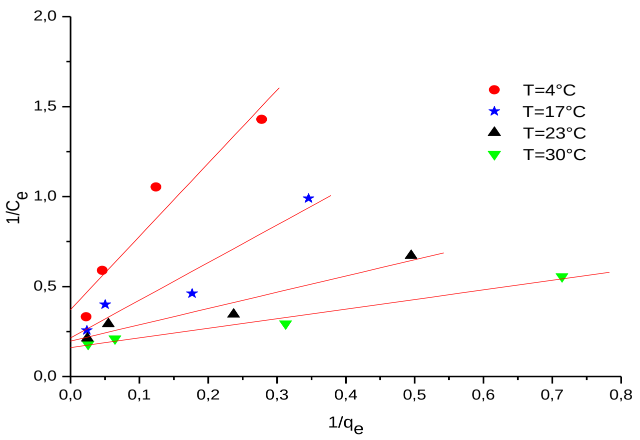

Figure 7 : The linearised Langmuir adsorption isotherm of phenol

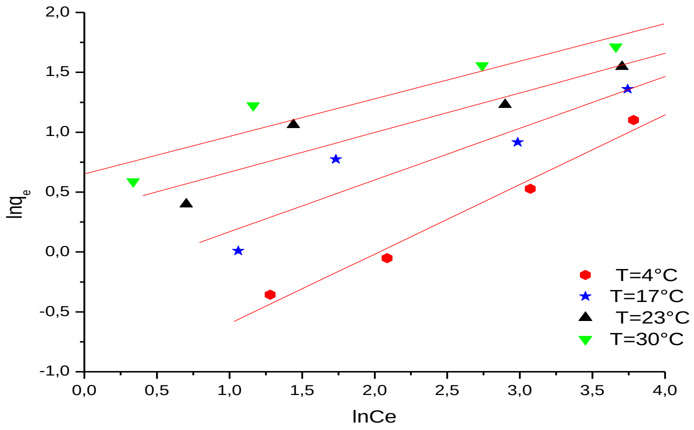

Figure 8: The linearised Freundlich adsorption isotherm of phenol

4. Conclusion

Based on the findings of the current study, it can be concluded that, the increase in the rate of adsorption of phenol in solutions in contact with the cord of loofa is favoured by:

- The increasing in the initial concentration of the solutions.
- The increasing in the temperature and approaches the ambient temperature.
- The whitening of the cords of loofa.
- The narrowed granulometry of cords.

The Langmuir and Freundlich adsorption equations were used to describe the adsorption phenomenon of phenol. The equilibrium data were well represented by the Langmuir model. Therefore, the possibilities of optimisation of the adsorption of industrial waste water by the loofa are in fact real, and let consider on the industrial level of interesting prospects, in particular for the organic species perforating itself in weak concentration. However some fundamentals points remain obscure, particularly the hydrodynamic behaviour of the loofa, dynamic adsorption and the interaction of these cords with other chemical solution other than phenol.

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