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Low cost bio-sorbent for the removal of phenolic compounds from olive mill wastewater

Laila Mandi[1], Mounia Achak[1], Abdellatif Hafidi[2], Naaila Ouazzani[1]

[1] Laboratoire d'Hydrobiologie, d'Ecotoxicologie et d'Assainissment, Université Cadi Ayyad, Faculté des Sciences Semlalia, Marrakech, Morocco.
[2] Laboratoire Sciences des Aliments, Université Cadi Ayyad, Faculté des Sciences Semlalia, Marrakech, Morocco.

Abstract. The adsorption of phenolic compounds from olive mill wastewater (OMW) has been investigated as a function of adsorbent dose, pH and contact time. The results showed that the increase in the banana peel dosage from 10 to 30 g/L significantly increased the phenolic compound adsorption rates from 60 to 88%. Increase in the pH above neutrality resulted in the increase in the phenolic compound adsorption capacity. The adsorption process was fast, and it reached equilibrium in 3h contact time. The equilibrium process was described well by the Langmuir and Freundlich isotherm models with maximum sorption capacity of 688.9 mg/g of phenolic compounds on banana peel at 30°C. Banana peel, an inexpensive and easily available material, can be an alternative to more costly adsorbents used for the removal of phenolic compounds from olive mill wastewater (OMW).

Keywords. Banana peel – Adsorption – Phenolic compounds – Olive mill wastewaters.

Les biosorbants à faible coût pour l'élimination des composés phénoliques des eaux usées d'huile d'olive

Résumé. *L'adsorption des composés phénoliques des eaux usées d'huile d'olive (OMW) a fait l'objet d'une étude visant à évaluer la dose adsorbante, le pH et la durée du contact. Les résultats ont montré que si on accroît le dosage des pelures de banane de 10 à 30 g/L, le taux d'adsorption des composés phénoliques augmente significativement, en passant de 60 à 88%. L'élévation du pH jusqu'à atteindre la neutralité a eu comme résultat l'augmentation de la capacité d'adsorption des composés phénoliques. Le processus d'adsorption s'est avéré rapide et il a atteint l'équilibre après un temps de contact de 3 heures. Le processus d'équilibre a été décrit d'une manière appropriée par les isothermes de Langmuir et Freundlich avec une capacité d'adsorption maximale de 688.9 mg/g de composés phénoliques sur les pelures de banane à 30°C. Les pelures de banane, un matériel économique et facilement disponible, peuvent représenter une alternative aux adsorbants plus coûteux utilisés pour l'élimination des composés phénoliques des eaux usées d'huile d'olive (OMW).*

Mots-clés. *Pelures de banane – Adsorption – Composés phénoliques – Eaux usées d'huile d'olive.*

I – Introduction

Olive mill wastewaters (OMW) are a significant source of environmental pollution related to olive oil production industries. Olive oil extraction processes generate three phases: olive oil, solid residue and aqueous liquor (OMW) which averagely represent 20, 30 and 50% respectively of the total weight of the processed olives. OMWs cause serious environmental deteriorations such as colouring of natural waters, alteration of soil quality, phytotoxicity and odour nuisance.

Conventional methods for the removal of phenolic compounds from OMW can be divided into three main categories: biological(Dias *et al.*, 2004, Mantzavinos and Kalogerakis, 2005, Balice *et al.*, 1990), chemical (Jaouani *et al.,* 2005, Achak *et al.*, 2008, Khoufi *et al.,* 2008) and physical treatment (Aktas *et al.,* 2001, Canepa *et al.,* 1988, Dhaouadi and Marrot, 2008).

Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Aksu and Yener, 2001). Adsorption also does not result in the formation of harmful substances and the organic sorbents can be used as fuel for power generation or as ferment substrate.

Many sorbents based on low cost agricultural by-products had been used for dye sorption from wastewater, which included banana pith (Namasivayam and Kanchana, 1992), orange peel (Namasivayam *et al.,* 1996), wheat straw (Robinson *et al.,* 2002), sawdust (Garg *et al.,* 2004), powdered waste sludge (Serpil and Fikret, 2006), wheat shells (Bulut *et al.,* 2007), wheat bran (Sulak *et al.,* 2006) and hen feathers (Mittal *et al.,* 2007). However, at the best of our knowledge, the adsorption and removal of specific organics from OMW by banana peel has not been reported.

The aim of this work is to investigate the efficiency of banana peel as a biosorbent for the removal of phenolic compounds from OMW. The effects of various operating parameters on biosorption such as sorbent dosage, initial pH and contact time were monitored and optimal experimental conditions were determined. Different adsorption isotherms (Langmuir and Freundlich isotherms) were used to find out the most suitable models describing our experimental findings.

II – Experiment

1. OMW origin

OMW were obtained from a three-phase continuous extraction unit from Marrakech, southern Morocco. The OMW were first stored in a plastic can (120L-capacity) at ambient temperature.

2. Preparation of the adsorbent

Banana peel was from a local market. The collected biomaterial was extensively washed under tap water to remove soil and dust, sprayed with distilled water. This biosorbent was cut into small pieces, dried in sunlight, crushed and sieved through a 1mm size before its use in adsorption experiments without any further treatment.

A. Physical-chemical analysis of OMW

pH was determined with a pH meter (716 DMS Titrino). Electrical conductivity (EC) was measured with a conductivimeter (Tacussel) (Rodier, 1984). Total suspended solids (TSS) were determined after filtering a sample through a GF/C filter (0.45 μm) and drying the retained residue at 105°C for 60 min (Rodier, 1984). Total and dissolved chemical oxygen demand (COD) was determined by a colorimetric method (APHA, 1992). The biochemical oxygen demand (BOD_5) was assessed by measuring the oxygen uptake in a sample over a period of 5 days at 20°C, in the dark using the BOD Track apparatus (AFNOR, 1983). Kjeldhal N (Kj-N), ammoniacal nitrogen (NH_4) and nitrite (NO_2) were determined by AFNOR method (AFNOR, 1983). Nitrate (NO_3) was determined like nitrite after its reduction by passage in a cadmium-copper column (Rodier, 1984). The phosphorus content (expressed as phosphate equivalents) was determined colorimetrically using the AFNOR method (AFNOR, 1983). Phenolic compounds were quantified by means of the Folin-Ciocalteu colorimetric method (Box, 1983) using caffeic acid as a standard.

B. Adsorption experiments

Batch adsorption experiments were carried out using a rotary shaker (rotatest 74581) at 200 rpm.min^{-1} at 30°C ± 2°C in a 250 mL shaking flasks containing 100 mL of OMW with a known concentration of phenol (13.45 g/L). Different doses (1-5 g) were tested at various pHs (2-11). The pH of the suspension was adjusted by 0.1 N HCl or NaOH. The changes in the adsorption rates of phenols were monitored at different time intervals (1; 1.5; 2; 2.5; 3; 4; 18; 24h). Samples were taken out from flasks and the solutions were separated from the adsorbent by filtration with a 0.6 mesh stainless steel sieve and centrifuged for 20 min at 5100 rpm min^{-1}. Phenolic compounds concentration in the supernatant solutions was determined.

The amount of adsorption at equilibrium, q_e (mg/g), and the percent adsorption (%) were computed as follows:

$$q_e = [(C_0 - Ceq)\ V]/\ X \quad (1)$$

$$\text{Percent adsorption (\%)} = (C_0 - C) * 100 / C_0 \quad (2)$$

Where C_0 and Ceq are the initial and equilibrium concentration of phenolic compounds (g/L), V volume of solution (L), X the weight of banana peel (g) and C the phenolic concentration at the end of adsorption.

III – Results and discussion

1. OMW characterization

Table 1 shows the main properties of OMW after one week decantation to remove the total suspended solids. As depicted in table 1, the sample shows an acidic pH value (5.06), the electrical conductivity was very low (6.9 mS/cm) compared to that reported by Zenjari *et al.* which varies between 25.3 and 36.6 mS/cm (Zenjari *et al.,* 1999). OMWs contain also a high level of organic matter (70.2 g O_2/L of total COD, 48.7 g O_2/L of dissolved COD) and high amounts of total phenolic compounds (13.4 g/L) which are toxic. The OMWs contain some valuable nutrients such as nitrogen and potassium, which would be useful in agriculture after effluent treatment.

Table 1. Physical-chemical determination of the raw OMWs (mean values of 3 separate analyses ± standard deviation).

Parameters	Data
pH (25°C)	5.06
Electrical conductivity (mS/cm) à 20°C	6.85
Total suspended solids (TSS) (g/L)	2.07±0.02
TKN (g/L)	1.96 ± 0.01
NH_4^+ (mg/L)	0.64 ± 0.04
NO_3^- (mg/L)	0.4 0 ± 0.07
NO_2^- (mg/L)	4.00 ± 0.03
Total phenols (g/L)	13.45 ± 0.01
Total COD (gO_2/L)	70.22 ± 1.22
Dissolved COD (g O_2/L)	48.69 ± 3.18
BOD_5 (g O_2/L)	16.74 ± 0.19
PO_4^- (g/L)	0.36 ± 1.43
Total P (g/L)	0.42 ± 0.003

2. Effect of adsorbent rates

The equilibrium uptake for the adsorption of phenolic compounds on banana peel was determined with 100 mL of OMW containing 13.45 g/L total phenolic compounds. The system was agitated for 24h (200 rpm) at a constant temperature (30°C ± 2°C) at the origin pH 5.

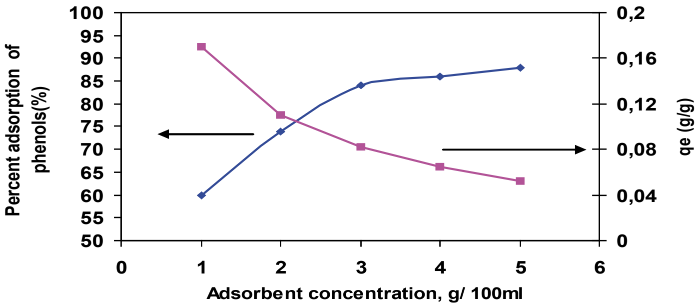

Figure 1. Influence of adsorbent concentration on adsorption rates of phenolic compounds and the equilibrium uptake (Conditions: 100 mL of OMW, temperature: 30°C, contact time: 24h and initial pH 5).

Figure 1 shows that the increase in adsorbent dosage from 10 to 50 g/L resulted in a decrease from 60 to 88% in phenolic compounds of the OMW. It is readily understood that the number of available adsorption sites increases with the increase in the adsorbent dosage and it, therefore, results in the increase in the amount of adsorbed phenolic compound.

A. Effect of pH on phenolic compounds biosorption

The most important parameter influencing the adsorption capacity is the pH of adsorption medium (Goyal *et al.,* 2003). The final pH of an adsorption medium affects the adsorption mechanisms on the adsorbent surface and influences the nature of the physico-chemical interactions of the species in solution and the adsorptive sites of adsorbents (Aksu *et al.,* 2002).

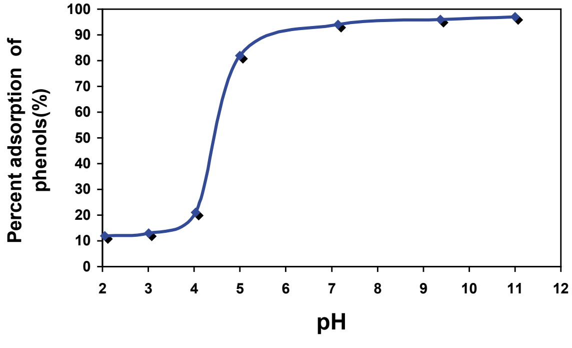

Figure 2. Effect of pH on adsorption of phenolic compounds by banana peel (Conditions: 100mL of OMW, Temperature: 30°C, contact time: 24h and sorbent dose: 30 g/L).

The effect of pH on the adsorption of phenolic compounds by banana peel at pH ranging between 2 and 11 is shown in figure 2. The adsorption efficiency increased from 12 to 97% when the solution pH varied from 2 to 11.

As shown in figure 2, at low pH values, the rate of the sorbed phenolic compounds was very low. At higher pH, the adsorption increased and stabilized from pH 7 to pH 11. Thus, the high elimination (97%) of natural phenolic compounds in OMW is achieved in a large pH zone above neutrality. From a practical point of view, this will be of great interest, since it will not necessitate very accurate adjustment of the medium pH.

The mechanisms of action of pH cannot be reduced to a surface charge modification and the adsorption of phenolic compounds and other compounds must not be seen only as the result of electric interactions. Many other interactions can lead to the adsorption of molecules on adsorbent surfaces especially in the case of bioadsorbants. Adsorption can result from weak forces interactions, ionic strength and chemical reactions leading to irreversible bindings.

B. Effect of contact time

The effect of contact time on adsorption of phenolic compounds by banana peel is presented in figure 3. The adsorption equilibrium of phenolic compounds was obtained after 3 h and no remarkable changes were observed for longer contact time.

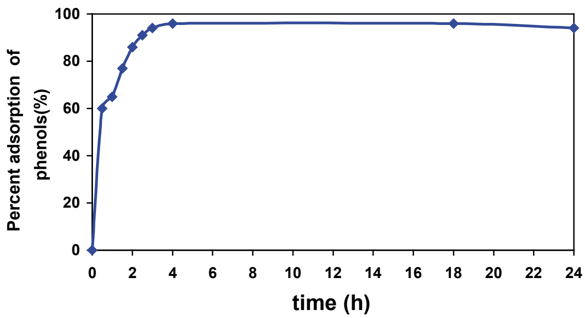

Figure 3. Effect of contact time on the adsorption of phenols by banana peel (Conditions: 100 ml of OMW, temperature: 30°C, sorbent dose: 30g/l and pH 7).

Adsorption rate of phenolic compounds on banana peel was found to be relatively much faster than those reported for some other normal adsorbents (Xiaolo and Youcai, 2006, Thawornchaisit and Pakulanon, 2007, Bhatnagar, 2007). Initially, a large number of vacant surface sites is available for adsorption; the adsorption rate is very fast, thus it rapidly increases the amount of adsorbates accumulated on the banana peel surface mainly within the first hour of adsorption. As a result, the remaining vacant surface sites are difficult to be occupied due to the formation of repulsive forces between the phenolic compounds on the solid surface and the bulk phase (**Srivastava *et al.,* 2006**).

C. Adsorption isotherms

Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ration between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium.

In order to optimize the design of a sorption system to remove phenolic compounds from OMW, it is important to establish the most appropriate correlation for the equilibrium curve. Many theories which described adsorption equilibrium were applied. Several isotherm equations are available, and two important isotherms are selected for this study: the Langmuir and Freundlich isotherms (Chan *et al.*, 2008, Lata *et al.*, 2008). The linearised Langmuir equation is represented as follows:

$Ce/qe = 1/bQm + Ce/Qm$ (3)

Where qe (mg/g) and Ce (g/L) are the amount of adsorbed phenolic compounds per unit weight of adsorbent and the unadsorbed phenolic compounds concentration in solution at equilibrium. *b* is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L/g) and *Q*m represents a particle limiting adsorption capacity when the surface is fully covered with phenolic compounds and assists in the comparison of adsorption performance.

The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, R_L, defined as:

$R_L = 1 / (1 + b\ C_0)$ (4)

Where b is the Langmuir constant, C_0 is the initial phenolic compounds concentration (g/L) and R_L values indicate the type of isotherm to be irreversible (R_L =0), favourable (0< R_L <1), linear (R_L =1), or unfavourable (R_L >1) (HO *et al.*, 2002). Our results show that the adsorption for phenolic compounds on the banana peel is favourable and has an R_L value between 0 and 1 (table 2).

Also, data were studied with the Freundlich isotherm, which can be expressed by logarithmic form as:

$\ln qe = \ln K_F + 1/n \ln Ce$ (5)

Where K_F is a Freundlich constant that shows adsorption capacity of adsorbent, n is a constant which shows greatness of relationship between adsorbate and adsorbent.

The Freundlich describes reversible adsorption and is not restricted to the formation of monolayer. It has been found that the adsorption for phenolic compounds on the banana peel is favourable and has an n value between 1 and 10 (table 2). The Qm, b, R_L, R_1^2 (correlation coefficient for Langmuir isotherm), K_F, n, and R_2^2 (correlation coefficient for Freundlich isotherm) are given in table 2.

Table 2. Isotherm constants and the correlation coefficients of Langmuir and Freundlich isotherms.

	Langmuir isotherm				Freundlich isotherm		
Effluent	Qm (mg/g)	b (L/g)	R_1^2	R_L	K_F	n	R_2^2
OMW	688.9	0.24	0.94	0.57	0.13	1.13	0.99

The R_1^2 and R_2^2 values shown in table 2 are evidence that the phenolic compounds adsorption in this study is well fitted to both Langmuir and Freundlich models; a possibility of mono and heterolayer phenolic compounds formation on the adsorbent surface. This observation is not rare as similar findings have been reported before (Mohd Din *et al.*, 2008, Vazquez *et al.*, 2007, Annadurai *et al.*, 2002). This phenomenon can be further explained by understanding the surface chemistry of banana peel used in this study. The presence of active functional groups with different intensity and non-uniform distribution may cause differences in the energy level of the active sites available on the banana peel surface thus affecting its adsorption power. Active sites with higher energy level tend to form heterolayer phenolic compounds coverage with robust support from strong chemical bonding whilst active sites with lower energy level will induce monolayer coverage due to electrostatic forces.

IV – Conclusion

Banana peel has proven to be a promising material for the removal of contaminants from olive mill wastewaters. Not only banana peel is an abundant cheap adsorbent, but it is also highly efficient for removing phenolic compounds from OMW. All those add more credits to banana peel for removing pollutants from wastewaters. The main characteristics of the adsorption process of the natural phenolics from OMW on banana peel can be summarized as follows:

- The banana peel showed a high adsorption capacity of phenolic compounds (688.9 mg/g), revealing that banana peel could be employed as a promising adsorbent for phenolic compounds adsorption.
- The adsorption process was very fast, and it reached equilibrium in 3h of contact. The equilibrium of the solid-phase concentration of phenols (qe, w/w) decreased with increasing adsorbent (banana peel) concentration. This is mainly attributed to the unsaturation of the adsorption sites through the adsorption process. The equilibrium was reached at 82.33 (mg/g) (3 g/100mL) of banana peel.
- The pH played an obvious effect on the phenolic compounds adsorption capacity onto banana peel. An increase in the solution pH leads to a significant increase in the adsorption capacities of phenolic compounds on the banana peel, maximum adsorption capacity occurred at alkaline pH.
- Both Langmuir and Freundlich isotherms provide good correlations for the adsorption of phenolic compounds onto banana peel.

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