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Elimination of Heavy Metal by the Adsorption Process on Activated Carbon from Olive Pomace

A. Nait Merzoug^{a,b*}, M.I. Bellazi^a, O. Guellati^{b,c}

^a *Laboratoire des Science et Techniques de l'eau et d'environnement, Université Mohamed Cherif Messadia de Souk Ahras, BP1553, 41000-Souk-Ahras, ALGERIA.*

^b *Université Mohamed Cherif Messadia de Souk Ahras, Fac. Sci, BP. 1553, 41000-Souk-Ahras, ALGERIA.*

^c *Laboratoire d'Etude et de Recherche des Etats Condensés (LEREC), Dép. de Physique, Université Badji-Mokhtar de Annaba, BP. 12, 23000 Annaba, ALGERIA.*

*Corresponding author. Tel.: + 05 55 14 01. E-mail:abenlala@yahoo.fr.

Abstract. Waste water pollution by heavy metals remains one of the major problems to be solved throughout the world. Various conventional methods are used to remove heavy metals from existing wastewater. They are based on phenomena of chemical precipitation, ion exchange or adsorption, which is always the simplest and most effective technique. Our work has a dual environmental aspect; On the first hand a valorization of a natural by-product in this case the olive-pomace collected in the region of Souk Ahras (East Algeria) and on the other hand the study of the adsorption of lead on this biomaterial. The activated carbon obtained after calcination and chemical activation has undergone a whole range of physicochemical analyzes such as: pH, moisture content, elementary analysis, surface area and infrared spectrometry. Indeed, the efficiency of our adsorbent is evaluated through the study of the various parameters that affects the adsorption phenomenon, namely: contact time, mass of the adsorbate, temperature, pH and initial concentration metal. The results obtained have shown a good efficiency of our support for the adsorption of metal ions in aqueous solution.

Keywords. Adsorption; Olive pomace; Activated carbon, Biosorption, Heavy metal, Characterization.

INTRODUCTION

The pollution by heavy metals has received wide spread attention in the recent years (Li 2010, Salem 2014), due to the toxicological importance in the ecosystem (Wang 2011, Prado 2010). These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organism causing health problems in animals, plants and human being (Reddy 2010).

Lead is one of the most harmful heavy metals which is present in water and in air. In water, lead is released in effluents from lead treatment and recovery industries, especially from battery manufacturing (Martin-Lara 2011, Drogana-Linda 2011). For drinking water, the maximum permissible limit of lead is 0.1 mg/l (Raji 1997, Tuabamme 2010), where the maximum concentration allowed for discharge into inland water is less than 1 mg/l.

Several methods such solvent extraction, ion exchange, precipitation and adsorption have been reported for the treatment of waste water contaminated with heavy metals (Gupta 2004, Ahmad 2006). Among these several physical and chemical methods, the adsorption onto activated carbon has been found to be superior to the other techniques because of its capability for

adsorbing a broad range of different types of adsorbates efficiently and also its simplicity of design (Charbraborty 2005). However the commercial activated carbon is very expensive, so several works have been carried out to develop alternative non-conventional and low-cost adsorbents. In fact the olive-growing industry generates significant amounts of products which have been misused until today and represent a real source of pollution. These products offer activated carbon recycling opportunities. As a result, we have been interested in the valorization of olive pomace for activated carbon which can be used as an adsorbent material. This which will allow us to achieve three objectives respectively the reduction of pollution, valorization and waste water treatment.

MATERIALS AND METHODS

Activated carbon preparation

The olive pomaces used in this study were taken from olive stones at the region of Souk Ahras during the 2014-2015 year. The sample taken consists of pulp and core fragments. The samples were firstly washed with de-ionized water, dried and then ground into fine particles and sieved to a particle size of 160 μm . Secondly 300 g of samples was impregnated with concentrated potassium hydroxide (KOH) at the ratio 1:1 (wt%). After cooling to the ambient temperature the sample was washed with de-ionized water until pH 6-7, filtered with Whatman filter paper and dried in the oven at 105 $^{\circ}\text{C}$ for 6 hours. The samples were then carbonized in a muffle furnace at 600 $^{\circ}\text{C}$ for 2 hours and stored in a tight bottle ready for use.

Characterization of activated carbon

The physicochemical parameters such as pH, moisture ash content and bulk density were made after the elaboration of the activated carbon. The first analysis was the elementary analysis to determine the composition of our activated carbon. The morphological analysis was characterized using FESEM (JEOL 6700-FEG microscope) in order to control the quality, structure and overall morphology of the adsorbent support. Fourier-Transform Infrared (FTIR) spectra of our activated carbon were recorded using a Bruker Vertex 77v spectrometer in the 400 to 4000 cm^{-1} range with 4 cm^{-1} resolution and with Opus software analysis system.

Adsorbate preparation and adsorption study

The reagents used were lead nitrate salt ($\text{Pb}(\text{NO}_3)_2$) and de-ionized water in order to prepare a stock solution of 1000 g/l. The reagents were of high grade. A known weight of our activated carbon was added to 100 ml of adsorbate in a flask and stirred at 500 rpm in a controlled temperature shaker at 298 $^{\circ}\text{K}$. At predetermined time intervals, the samples were removed from the solution by filtration. The effect of pH on the lead ions adsorption onto the adsorbent was studied over a pH range of 2.0 to 12.0. The pH was adjusted by adding aqueous solutions of 0.1M HCl or 0.1M NaOH. The residual Pb^{2+} concentrations were determined spectrophotometrically using atomic absorption at 210 nm. The adsorption rate was calculated by the following equation:

$$R (\%) = \frac{(C_0V_0 - C_eV_e).100}{C_0V_0} \quad (1)$$

Where C_0 and C_e are the initial and the equilibrium concentrations of sorbent and V is the solution volume.

RESULTS AND DISCUSSIONS

Characteristics of activated carbon derived from olive pomace

The physico-chemical characteristics of activated carbon are shown in table 1.

TABLE 1. The physico-chemical characteristics of activated carbon derived from olive pomace.

Activated carbon proprieties	pH	Moisture content (%)	Ash content (%)	Bulk density (g/cm ³)
Values	6.02	10.4	2.17	0.59

According to the obtained results we noted that the ash content is very low, which is an interesting characteristic for its use for the preparation of an activated carbon.

The composition of the main elements of the activated carbon from the olive pomaces is shown in the Table 2. As shown, we can see that our adsorbent contains two major elements, namely carbon with 62.76 % and oxygen with 33.25 %, followed by aluminum and then silica.

TABLE 2. Chemical composition of activated carbon.

Element	C	O	Al	Si	P	Cl	Ca	Bi
Percentage (%)	62.766	33.251	2.516	0.584	/	0.274	0.207	0.403

The representative high magnification FESEM micrograph (Fig. 1) of the obtained activated carbon shows a homogeneous phase with cavities. These are the result from the treatment of the olive pomaces. We also noted the presence of macro and micro pores.

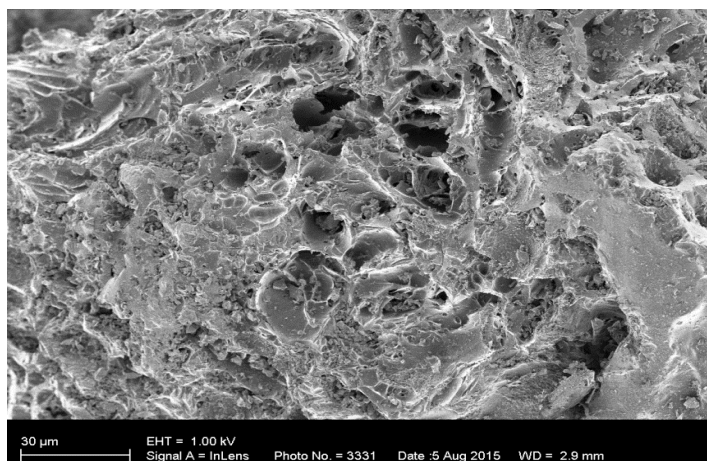


Fig. 1. High magnification FESEM micrograph of activated carbon.

FTIR spectrum for the activated carbon from olive pomaces is shown in figure 2. It can be seen that there is a strong peak at 3400 cm⁻¹ represents the O-H stretching, and a peak at 3031cm⁻¹ and another at 2930 cm⁻¹ which corresponding to =C-H stretching of aldehyde group and C-H stretching of aliphatic (CH₂ and CH₃). The peaks at 1700 cm⁻¹, 1630 cm⁻¹ and 15450 cm⁻¹ were attributed respectively to the carbonyl (C=O) stretching of aldehyde group, C=C for alkene group and C=C for aromatic one. The peak at 1000 cm⁻¹ can be assigned to the C-O stretching. Also the peaks between 900 and 600 cm⁻¹ can be related to the deformation δ C-H of aromatic groups.

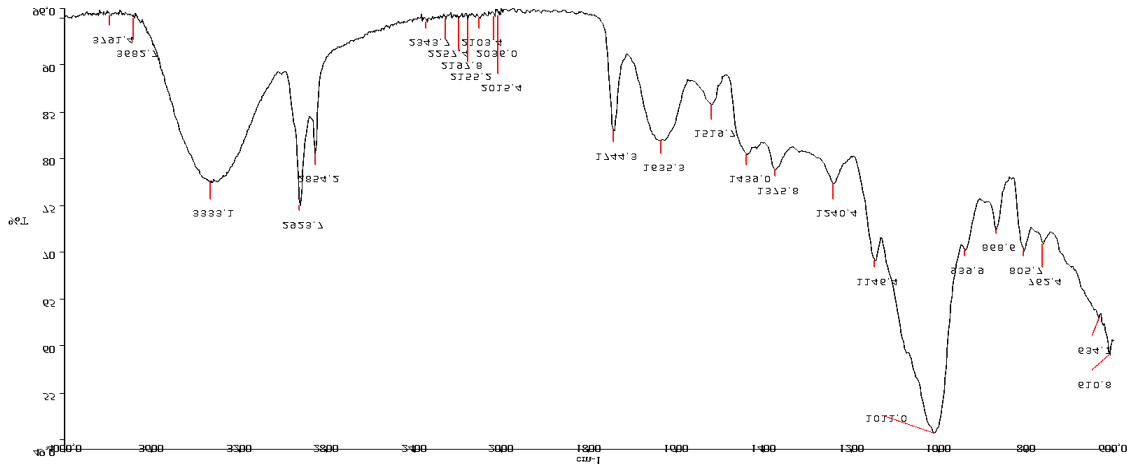


Fig. 2. IR spectrum of activated carbon from Olive pomace.

Influence of operation conditions in the adsorption process

Effect of contact time on adsorption equilibrium

The effect of contact time on lead ions sorption by activated carbon from olive pomaces is shown in figure 3. The results showed that a contact time of 200 mn assured attainment of equilibrium.

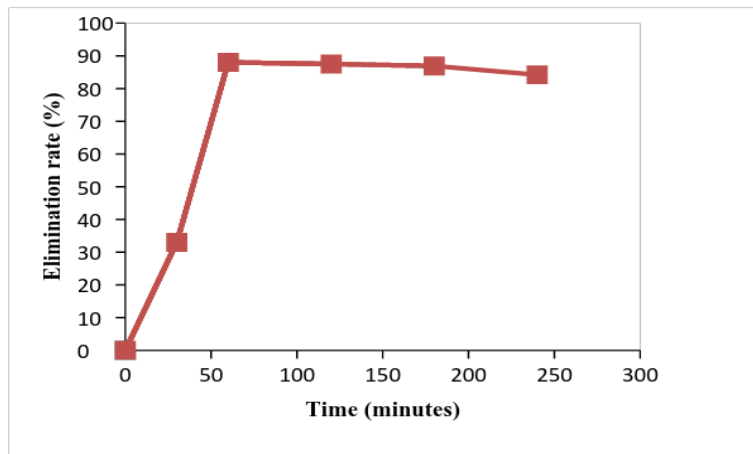


Fig. 3. Effect of contact time on the removal of ions lead on activated carbon.

Metal uptake, us function of contact time, was noticed to occur in two phases. The first one was extremely rapid and this is probably due to the ions diffusion into the available sites of adsorption. However, the second phase was slow and the metal remove over a longer period until equilibrium was reached.

Effect of initial pH

Solution pH is a significant control parameter affecting the sorption processes; Batch experiments were conducted at different initial pH values ranging from 2 to 12. The results obtained are shown in figure 4.

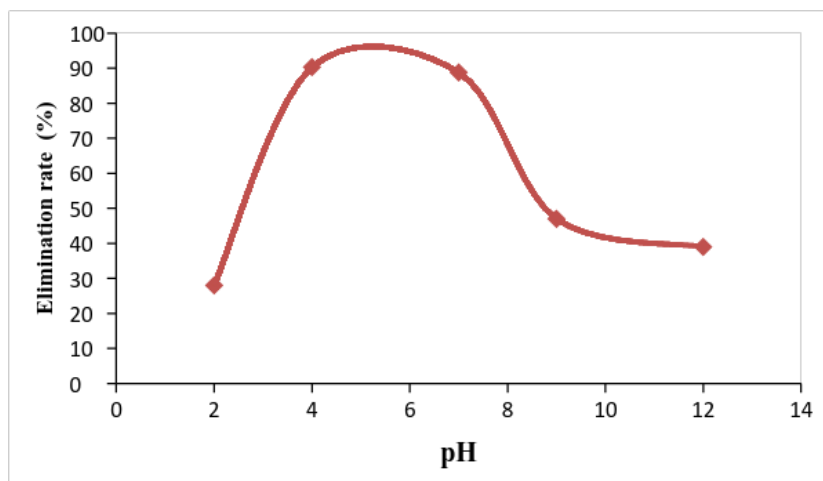


Fig. 4. Effect of pH on the removal of lead ions.

The results indicate a relatively little sorption at initial pH of 2 with only 21.5 % of lead ions removed. However, the increase of pH from 2 to 6 increases the percentage removal from 21.5 to 92.9 %. The fact that the amount of Pb^{2+} removal at low pH is considerably lower may be accounted by the competition between lead ions and H^+ ions onto the active sites on sorbent surface. Also, the amount decreases when the $pH > 6$ due to the formation of soluble hydroxyls complexes. Our results are in agreement with similar studies (Goyal 2008, Iqbal 2009, Panda 2008).

Many studies have shown also, that the pH of aqueous solutions affects both of the solubility of metal ions and the functional groups of adsorbent. As a result, the affinity of the adsorbent varies considerably for the metal ions.

Effect of initial concentration of metal

Dependency of the process of lead ions removal from different concentrations ($0.5-2.5 \cdot 10^{-4}$ M) by the activated carbon is illustrated in figure 5. The examination of the data reveals that the adsorption capacity increases as the value of the initial concentration increases to a maximum adsorption rate (92.1 %).

An increase in the concentration leads to an increase in the ionic strength which leads to a reduction in the adsorption capacity of the activated carbon and this may entail a shielding of the negative charge of the adsorbent and consequently repulsion is produced between the adsorbent surface and these metallic cations.

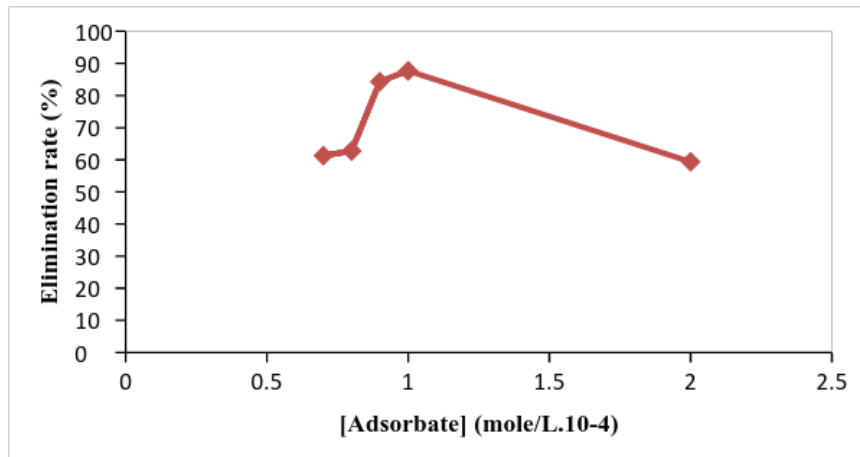


Fig. 5. Effect of initial dye concentration on the removal of lead ions.

Effect of adsorbent dose

The effect of sorbent dose on the lead ions sorption kinetics by the activated carbon is illustrated in figure 6. As we can see, the percentage of removal increases with an increase in sorbent dose from 45.9 to 93.4 %. This can be attributed to increased surface area and the availability of more sorption sites.

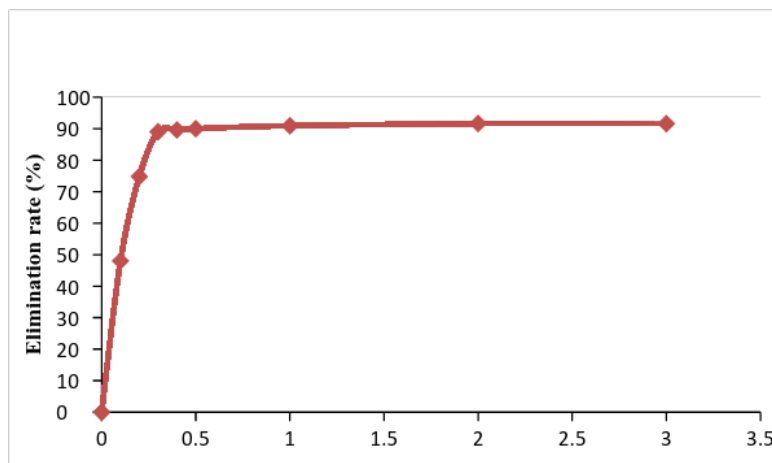


Fig. 6. Effect of adsorbent amount on the removal of lead ions.

CONCLUSION

All the conclusion that can be drawn are:

- The activation of olive pomace was successful and has favored the adsorption process of metallic ions;
- The presence of functionalizes groups improve the efficiency of metal ions removal;
- The output of metal removal by adsorption on our activated carbon is important;
- The adsorption processes of ions metal is clearly influenced by the initial pH of the solutions.
- The adsorption is also influenced by the adsorbent dose and the initial concentration of the concentration of the synthetic solution;

Indeed, it is possible to use this agricultural waste as less expensive and very effective adsorbent for the removal of heavy metals after its activation.

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