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## Preliminary study on zinc ion removal from synthetic aqueous solutions using hard almond peel as a low-cost sorbent material

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### Abstract

In the present work, a preliminary study on the potential of hard almond peels for the removal of zinc ions from aqueous synthetic solutions has been investigated. Kinetic data and equilibrium sorption isotherm were measured in batch conditions. For an initial metal concentration of 100 mg/L tested here, the quantity of zinc sorbed was contact time dependent: it increased with an increase of this parameter. The necessary time to reach the sorption equilibrium was about 6 h and an increase of removal time to 24 h did not show notable effects. At equilibrium, about 24 % of initial zinc solution was removed by hard almond peels ( $q_e = 23.86$  mg/g) under these experimental conditions. Two simplified kinetic models including a first-order rate equation and a pseudo second-order rate equation were selected to describe the metal sorption kinetics. The process followed a pseudo second – order rate kinetics. Langmuir and Freundlich models were used to describe sorption equilibrium data at natural pH of solution. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich model. Maximum zinc uptake obtained was  $q_m = 56$  mg/g under the investigated experimental conditions.

**Keywords:** Removal; Zinc ion; Hard almond peel.

### 1. Introduction

The presence of heavy metals in the aquatic environment is a source of great environmental concern. Use of zinc is widespread, with major inputs to the aquatic environment being likely from the manufacture of alloys, from galvanising and paper production [1]. Though zinc is potentially less toxic compared to others heavy metals, special care needs to be taken in order to prevent its accumulation in the environment [2]. The conventional methods of zinc (II) ions removal from wastewaters, become inefficient and expensive especially when the heavy metal concentration is less than 100 ppm [3-5]. This situation has in recent years

led to the search of alternative low cost adsorbents including biosorbents, wastes from agriculture or industry and natural materials for the removal of pollutants such heavy metal ions from aqueous solutions. In this work, the sorption of zinc ions from synthetic aqueous solutions by hard almond peel, in single metal solutions, was investigated. Kinetic data and equilibrium sorption isotherm were measured in batch conditions. Two simplified kinetic models including a pseudo first-order and pseudo second-order equations were selected to follow the sorption process. The sorption equilibrium data were obtained at natural pH of solutions. In order to describe the metal sorption isotherms mathematically and to obtain information about the maximum sorption capacity of this sorbent, the experimental sorption equilibrium data were analysed using Langmuir and Freundlich models.

## 2. Materials and methods

### 2.1. Sorbent material and metal ion

Hard almond peel waste used as sorbent is cheap and highly available lignocellulosic wastes in Algeria. It was collected from the region of Bensekrane (Tlemcen – Algeria), in summer 2006 in the form of large flakes. This waste was sun/air dried at ambient temperature during many days, crushed and sieved to keep only the size range 1.25-2 mm. To be used as a sorbent material, this material was washed thoroughly with distilled water to remove all the adhering dirt particles until constant pH and no colour were observed, filtered and then oven-dried at  $85 \pm 5$  °C for 24 h. Zinc solutions of desired concentration were prepared from ZnSO<sub>4</sub> · 7H<sub>2</sub>O (Fluka, Lot: 280 424, France) by dissolving the exact quantities of zinc salts in distilled water. All chemicals were commercial products used without purification.

### 2.2. Sorption kinetics

For metal sorption kinetics studies, 1 g of hard almond peel was contacted with 1 L of metal solutions of 100 mg/L initial solution metal concentration, in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25 °C. In all cases, the working pH was that of the solution and was not controlled. The residual zinc concentration in the aqueous solution at appropriate time intervals, was obtained by using a Varian Model AA-100 atomic absorption spectrophotometer at  $\lambda_{\text{max}} = 213.9$  nm. The metal uptake  $q_t$  (mg ion metal/g hard almond peel) was determined as follows:

$$q_t = (C_0 - C_t) \times V / m \quad (1)$$

where:  $C_0$  and  $C_t$  are the initial and time metal ion concentration (mg/L), respectively,  $V$  is the volume of solution (mL), and  $m$  is the hard almond peel weight (g). Preliminary experiments had shown that zinc sorption losses to the container walls were negligible.

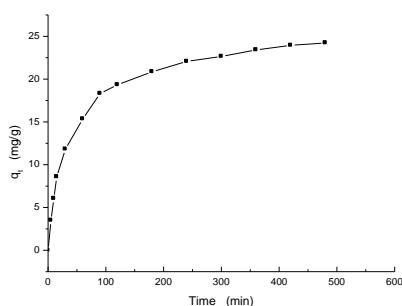
### 2.3. Sorption Isotherm

The sorption equilibrium isotherm was determined by contacting a constant mass 0.2 g of hard almond peel with a range of different concentrations of zinc solutions: 50-500 mg/L. Mixtures sorbent-solution were agitated in a series of 250 ml conical flasks with equal volumes of solution 200 ml for a period of 24 h at room temperature  $25 \pm 1$  °C. The mixture pH was not controlled after the initiation of experiments. After shaking the flasks, the equilibrium pH was measured. The concentration of unbound zinc ions at equilibrium was obtained using the same procedure described above, and, the copper loading by hard almond peel was determined.

### 3. Results and Discussions

#### 3.1 Sorption kinetics

A preliminary experiment was performed to determine the equilibrium time. According to Fig. 1 obtained for an initial zinc concentration of 100 mg/L, the kinetics of zinc sorption by hard almond peels presents a shape characterized by a strong increase of the amount of zinc ions sorbed during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium. The necessary time to reach this equilibrium is about less 6 h and an increase of removal time to 24 h did not show notable effects. At equilibrium, about 24 % of initial zinc solution was removed by hard almond peels ( $q_e = 23.86$  mg/g) under these experimental conditions. During the course of zinc sorption by hard almond peel, a decrease in the initial pH value of the solution was observed (Fig. not shown here).

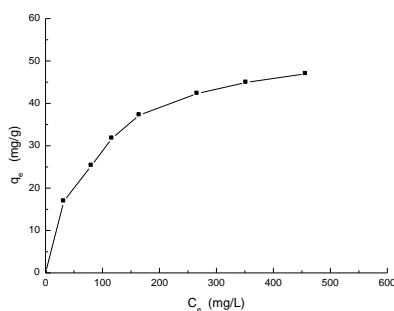


**Figure 1.** Kinetics of zinc ions sorption by hard almond peels. (Initial metal concentration: 100 mg/L, dose= 1g/L,  $d_p = 1.25$ -2 mm,  $N = 400$  tr/min, natural solution initial pH,  $T = 25$  °C)

To analyze the kinetic data of zinc sorption by hard almond peel under these experimental conditions tested, two common equations from the literature, namely, the first-order rate model of Lagergren [6] and the pseudo second-order rate model [7] were chosen and tested in their linear forms. As results obtained (Fig. and results not shown here), compared to the first-order rate equation ( $R^2 = 0.9789$ ), the pseudo second-order rate model adequately described the kinetics of zinc ions sorption with acceptable correlation coefficient ( $R^2 = 0.9993$ ).

#### 3.2. Sorption equilibrium

Fig. 2 shows the zinc sorption ions isotherm ( $q_e$  vs.  $C_e$ ) by hard almond peel at natural pH of solutions which is of L type according to the classification of Giles et al. [8] for liquid-solid adsorption..



**Figure 2.** Isotherm of zinc ions sorption by hard almond peel at 25 °C

From the plot of this isotherm, a maximum capacity of zinc ion sorbed by hard almond peel is about 46 mg/g under these experimental conditions. During the experiments of zinc ions sorption equilibrium, it was also observed that the initial pH value of solutions decreased. To find an appropriate correlation for the equilibrium curve, two simple isotherm equations have been tested in the present study, namely, Langmuir [9] and Freundlich [10] models. This modelling permits us to determine the maximal capacity of sorption. From results obtained (Figs. not shown here) and the model parameters determined by least squares fit of the experimental sorption data (values not presented), Langmuir model acceptably fitted the experimental results over the experimental range with a good coefficient of regression ( $R^2= 0.9980$ ) compared to the low one obtained with the model of Freundlich ( $R^2= 0.9715$ ).

#### 4. Conclusion

The results obtained confirm that hard almond peel can remove zinc ions from synthetic aqueous solution under the experimental conditions tested here. The zinc sorption kinetics is strongly affected by contact time: the amount of zinc removed by hard almond peel increased with the increase of contact time. The kinetics of zinc sorption followed a pseudo-second-order rate kinetics. An acceptable fitting of the equilibrium isotherm was obtained with Langmuir model in all the range of zinc ion concentrations studied. This experimental study is quite useful in developing an appropriate technology for designing a waste water treatment plant. However, further work should be performed in order to better understand zinc ions sorption binding mechanism by hard almond peel.

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