

## **An Experimental Parametric and Kinetics Study of Cu (II) Retention by Orange Peels as Adsorbent**

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The present study concerns the elimination of toxic metallic cations such as Copper, from waste waters by means of orange peels as an adsorbent.

A priori, the solid support was thermally pre-treated and the copper II adsorption was carried out batchwise. The influence of various parameters such as the contacting time, the initial copper concentration, the temperature, the solid to liquid ratio, etc. on the copper retention onto the orange peel, was investigated.

The parametric study showed that the adsorption on the thermally pretreated orange peels was optimal in the first ten minutes before saturation. Also an increase of the initial Copper concentration enhanced the adsorption capacity. The study showed that the liquid to solid ratio and the temperature did not have a great influence on the adsorption capacity. Finally, the kinetic study showed that the adsorption process is of a second order.

### **1. Introduction**

It is now well established that the presence of heavy metals in soil and industrial wastewater, can be an important source of pollution, and may be a severe health hazard. The main reasons for that are their non-degradability and their toxicity (Ayhan, 2008). For instance, copper which is the heavy metal considered in the present study, may lead to severe mucosal and a central nervous irritations, necrotic changes in the liver and kidney, etc., if an intake of excessively large doses, takes place.

Through, the above example, one can measure the up most importance of developing techniques capable of eliminating and recovering these metallic species and keeping their concentrations within safe and tolerable limits.

Various techniques including chemical precipitation, extraction, adsorption, electroflotation, flotation, ion exchange, reverse osmosis, electrodialysis, electrolysis, etc. can be used for removing the heavy metals contained in wastewaters. However, the technique of adsorption which is the main scope of this work has shown great capabilities, particularly when an adequate, performing and efficient adsorbent is selected and used (Kurniawan and Babel, 2003a).

Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Kurniawan and Babel, 2003b). It is with no doubt the simplest and cheapest operation for the elimination of metallic pollutants. It uses granulated or

powdered solid materials, such as activated carbon which has been extensively tested and proven to be very efficient in removing heavy metals from industrial aqueous effluents such as Ni(II) (Shim et al., 1996), Cr(VI) (Ouki et al., 1997), etc. However its relative cost can be in certain cases a major drawback, a fact which has motivated and encouraged the search for new materials which can be used as good adsorbents, which are abundant enough, with no cost and with no evident use. In the literature, many examples of these are reported and one can cite coconut coir pith (Kadirvelu et al., 2003), sawdust (Sreejalekshmia et al., 2009), citrus peels (Silke and Ankit, 2009), etc. Still in valorization perspective of natural material for heavy metals retention, the present study concerns the experimental test of orange peels for the removal of Cu (II). This was mainly encouraged by the great capability shown by this solid support to eliminate different types of pollutants as reported in the literature such as (Azza et al., 2009), hence granting a good credibility to the investigated waste water treatment method, i.e. adsorption onto orange peels.

## 2. Method and materials

### 2.1 The adsorbent

The adsorbent used in this study is the orange peels. It was cut into small pieces, naturally dried in sunlight and then thermally pre-treated at 873.15 K in a furnace (HERAEUSd-6450 HANAU) during 2 hours. This is followed by a crushing and sieving to recover the particles of about 0.315mm in diameter.

### 2.2 The copper retention

The experimental study is carried out in a batch reactor, consisting on preparing copper (II) aqueous solutions of different concentrations ranging from 5 to 30 mg/L, in a 50 ml beaker. The pH of the solution is maintained constant at 5.58, and the quantity of the solid support (calcinated orange peel) varied between 250 and 1000 mg. The resulting suspension from the mixture is agitated with at 600 rpm during 2 hours at ambient temperature of 296.15 K. Filtration is carried out through millipores 0.2µm of diameter. The analysis of the filtrate is carried out by atomic absorption and the adsorbed amount of copper at equilibrium,  $q$  (mg/g), was calculated by the relation (1) as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where  $C_0$  and  $C_e$  (mg/L) are the initial and the equilibrium liquid-phase concentrations of the metal cation, respectively,  $V$  (L) is the volume of the solution and  $m$  (g) is the mass of the adsorbent used.

## 3. Results and discussion

The obtained results for Copper cations are shown and discussed in the following section by first presenting the effects of the different parameters on the retention capacity of the solid support i.e. the orange peels.

### 3.1 Effect of initial concentration

Figure 1a shows the influence of the initial concentration on the orange peels retention capacity of copper cations. Different initial concentrations of Cu (II) ranging from 5 to 30 mg/L, at 296.15 K, were considered. It is clear from Figure 1 that the adsorbed amount increased with the initial concentration of Cu (II) in the aqueous phase for a constant solid support (orange peels) to liquid (water) ratio  $r_{SL}$  of 10 g/L. When the initial copper concentration was increased from 5 to 30 mg/L, the sorption uptake of orange peels increased also. A higher initial concentration provides an important driving force to overcome all resistances of metal ions between aqueous and solid phases, thus increasing the uptake. In addition, increasing the initial ions concentrations of Cu (II) increases the number of collisions between the metal ions and the adsorbent, hence enhancing the adsorption process.

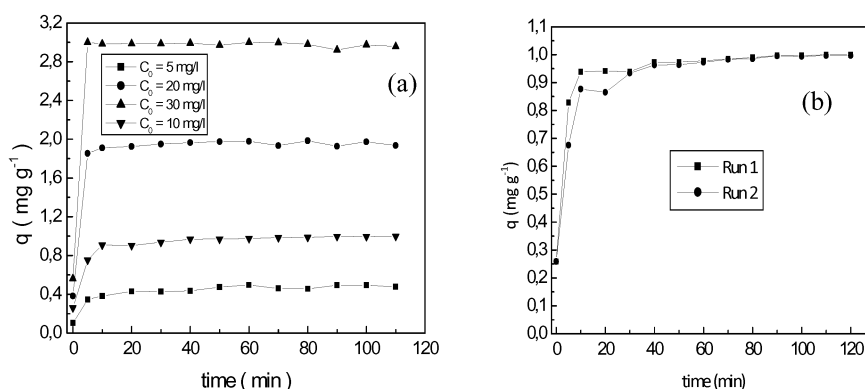


Figure 1: The effect on the retention of Cu (II) of a) the initial Cu (II) concentrations; b) the contact time, at  $T=296.15 \text{ K}$ ; speed = 600 rpm,  $r_{SL}=10 \text{ g/L}$ ,  $\text{pH}=5.58$ ,  $d=0.315 \text{ mm}$

### 3.2 The effect of contact time

Figure 1b shows that an elimination percentage of the metal ions of 82.82 is achieved in only 5 minutes, indicating a great affinity of the orange peels for the copper cations. The retention capacity increases with time reaching the equilibrium in about 40 minutes with a percentage removal of about 98.

### 3.3 The effect of solid– liquid ratio

The three curves shown on Figure 2a are close, with is a slight increase in the amount of copper adsorbed corresponding to the lowest solid /liquid ratio  $r_{SL}=5 \text{ g L}^{-1}$ . It can also be seen that the saturation times vary similarly to the solid / liquid ratio.

### 3.4 The effect of temperature

Three different temperatures of 293.15, 303.15 and 333.15 K, with an initial concentration of  $C_0=10 \text{ mg L}^{-1}$  at  $\text{pH}=5.58$ , were considered. From Figure 2b, the percentage Copper removal decreases from 99.80% ( $q = 0.9980 \text{ mg g}^{-1}$ ) to 90.35 % ( $q = 0.9033 \text{ mg g}^{-1}$ ), when the temperature varies from 20 to 60°C, respectively. These results

indicate that adsorption may be exothermic and can be explained by the fact that the temperature rise may not be in favour of any metallic cation agglomeration at the solid support surface. Also the temperature rise does not seem to induce any thermal activation of the adsorbent surface by acting on its pore sizes.

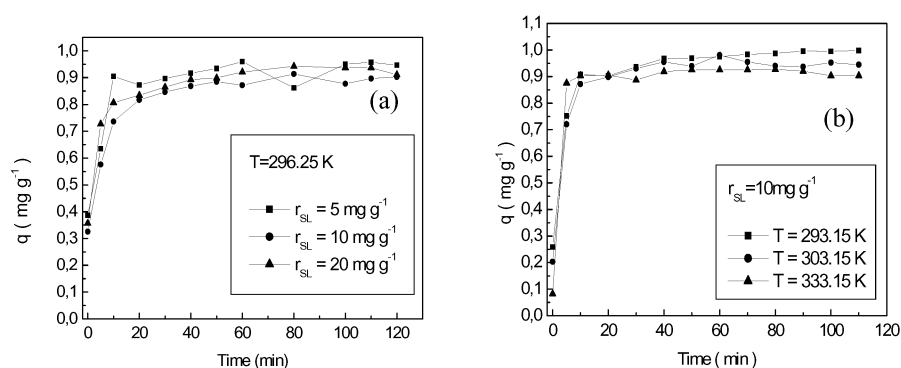


Figure 2: The effect on the retention of Cu (II) of a) solid/liquid ratio effect  $r$ ; b) temperature effect, both with an agitation speed=600 rpm, pH=5.58,  $d = 0.315 \text{ mm}$

The curves of the figures 1b & 2a do not start from zero, due to the fixing of a very small amount of copper on the walls of the glass beaker, causing a reduction in the initial concentration.

### 3.5 The kinetic study of the retention

A kinetic study is important in evaluating adsorption dynamics. For instance, the kinetic constants of metal ions adsorption can be used to optimize the residence time of a treated industrial wastewater in the system.

Two kinetic models have been tested for the obtained experimental data: pseudo first order and second order and are expressed, respectively, as follows:

$$\frac{dq_t}{dt} = K_1 \cdot (q_e - q_t) \quad (2)$$

The integration of the equation (2) leads to the following expression:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

The model of the 2<sup>nd</sup> order is given by the following equation:

$$\frac{dq_t}{dt} = K_2 \cdot (q_e - q_t)^2 \quad (4)$$

An integration of this equation gives:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e2}^2} + \frac{1}{q_{e2}} t \quad (5)$$

Were  $K_1$  ( $\text{min}^{-1}$ ) and  $K_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) are the velocity constants for two kinetic models respectively,  $q_e$  ( $\text{mg.g}^{-1}$ ) and  $q_{e2}$  ( $\text{mg.g}^{-1}$ ) are the adsorbed amount of copper at equilibrium for two kinetic models respectively,  $q_t$  ( $\text{mg.g}^{-1}$ ) is the adsorbed amount of copper at any time,  $t$  (min) is the contact time.

Figures 3a & b show that the adsorption process follows best the pseudo-second order kinetic model, as indicated by the correlation factor values of Table 1, suggesting a chemical sorption of Cu (II) on the orange peels. The obtained kinetic rate constant for both models are also presented in Table 1.

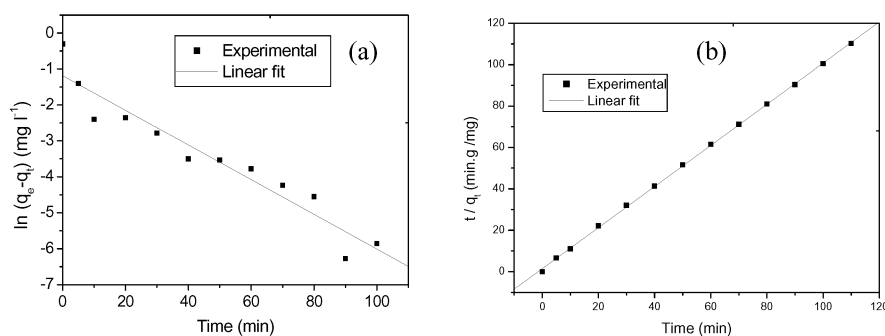


Figure 3: Kinetics of the ions Cu (II) retention onto orange peel a) test of first order; (b) test of second order

Table 1: The kinetics constants of the 1<sup>er</sup> and 2<sup>nd</sup> order

| Kinetics 1 <sup>st</sup> order |                             | Kinetics 2 <sup>nd</sup> order |  |
|--------------------------------|-----------------------------|--------------------------------|--|
| $r^2$                          | $K_1$ ( $\text{min}^{-1}$ ) | $r^2$                          | $K_2$ ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) |
| 0.9212                         | 0.04831                     | 0.9997                         | 1.5414248                                    |

#### 4. Conclusion

Through this experimental study, it is demonstrated that orange peels can be used as a greatly available, a no cost and a performing adsorbent for removal of copper cations from aqueous solution.

As a perspective, the application of orange peels can be extended to heavy metals industrial wastewaters treatment, particularly when the reverse process i.e. desorption, is also envisaged, solving the storage problem of huge amounts of charged solid supports.

## 5. Notations

|          |   |
|----------|---|
| $C_0$    | Initial Concentration ( $\text{mg g}^{-1}$ )                                |
| $C_e$    | Equilibrium Equation ( $\text{mg g}^{-1}$ )                                 |
| $d$      | particle diameter (mm)  |
| $K_1$    | Pseudo first-order adsorption rate constant ( $\text{min}^{-1}$ )           |
| $K_2$    | Second order adsorption rate constant ( $\text{g mg}^{-1}\text{min}^{-1}$ ) |
| $m$      | the mass of the adsorbent (g)   |
| $q_e$    | Equilibrium adsorption capacity ( $\text{mg mg}^{-1}$ )                     |
| $q_b$    | Instantaneous adsorption capacity ( $\text{mg g}^{-1}$ )                    |
| $r_{SL}$ | solid to liquid ratio ( $\text{g L}^{-1}$ )                                 |
| $r$      | Correlation factor  |
| $R$      | Universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )                |
| $T$      | Temperature (K)   |
| $t$      | Contact time (min.)   |

## 6. References

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