

## **REMOVAL OF ACID DYES FROM AQUEOUS SOLUTIONS USING ORANGE PEEL AS A SORBENT MATERIAL**

**H. Benaïssa**

Laboratory of Sorbent Materials and Water Treatment, Department of Chemistry,  
Faculty of Sciences, University of Tlemcen, P.O. Box. 119, 13 000 Tlemcen, Algeria  
E-mail: ho\_benaïssa @ yahoo.fr

### **ABSTRACT**

An agricultural by-product waste: orange peel was tested for the removal of four acid dyes from aqueous solutions in batch conditions. As results obtained, kinetics of dyes sorption was time of contact, initial dyes concentration and dyes type dependent. The pseudo second-order reaction rate model adequately described the kinetics of dyes sorption with high correlation coefficients. Langmuir model gave a good fit to the experimental data. A high dyes sorption was observed by this sorbent material. For Nylosane Blue, a maximum sorption capacity about 65.88 mg/g was obtained followed by Erionyl Yellow (64.14 mg/g), Nylomine Red (62.07 mg/g) and Erionyl Red (40.72 mg/g), respectively.

**Key Words:** Dyes; Removal; Sorption; Orange peel.

### **INTRODUCTION**

Synthetic dyes are extensively used by industries including dye houses, paper printers, textile dyers, colour photography and as additives in petroleum products (Zollinger [1], Selvam et al. [2]). The effluents of these industries are highly coloured and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm (Zollinger [1]). Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration (O'Mahony et al. [3]). Due to low biodegradability of dyes a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and/or chemical methods (Garg et al. [4]). Although these treatment methods are efficient, they are quite expensive and have operational problems (Garg et al. [4], Kapdan et al. [5]). Adsorption of the molecules onto various adsorbents is an ideal option for decolourization, which is evidenced by the effectiveness of adsorption for various dye types (Kapdan et al. [5], Porter et al. [6]). The main drawbacks which exist at the present time are the high costs involved in the regeneration of the adsorbent. Also, since activated carbon is the most widely used and most effective adsorbent, its high cost tends to increase the cost of adsorption systems (Garg et al. [4], Kapdan et al. [5]). As a result, there is a search for low-cost adsorbents that can serve as viable

alternatives to activated carbon. Orange peel waste can be an alternative and favourable adsorbent for pollutants such dyes, heavy metals,... However, only a limited number of studies on the use of orange peel waste as a sorbent material have been found in the literature (Namasivayam et al. [7])

This work studies the possibility of using a certain biological waste: orange peel, as an inexpensive sorbent for the removal of acid dyes from aqueous solutions. This material is abundantly available through our country and the world. The dyes used in this study were: Nylosane Blue, Erionyl Yellow, Erionyl Red, and Nylomine Red. The present study reports their sorption potential through kinetics tests and sorption isotherms, in batch conditions. The experimental data of dyes adsorption equilibrium were fitted by either the Langmuir and Freundlich equations or those of sorption kinetics by three simplified kinetic models namely: first-order, pseudo second-order and second-order equations in order to identify a suitable kinetic equation. These fundamental data will be useful for further applications in the treatment of practical waste or process effluents.

## MATERIALS AND METHODS

### 1. Sorbent and Dyes

The low-cost material used in the present work is: orange peel. As an agricultural by-product waste, it was collected in spring end from the region of Bensekrane, in Tlemcen, Algeria, in the form of large flakes. It was used as an sorbent material after the following treatment: 10 g of orange peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of 25°C during 4 hours, then continuously washed with distilled water to remove the surface adhered particles and water soluble materials, and oven-dried overnight at 60-80°C for 24 hours after filtration. This material was crushed and sieved to have particles of size 0.125 – 1.60 mm for further batch sorption experiments.

The dyes used in this study, as commercial salts and whose the structures are unknown, are listed in Table 1. They were kindly donated by SOITEX Company, located in the City of Tlemcen-Algeria. All these dyes were used as received without further purification.

**Table 1:** List of dyes chosen for the present study

Commercial Name	Colour	Type of dye	$\lambda_{\max}$ (nm)	Supplier
Nylosane Blue	Blue	Acid	591.3	Sandoz
Erionyl Yellow	Yellow	Acid	407.4	Ciba-Geigy
Erionyl Red	Red	Acid	522	Ciba-Geigy
Nylomine Red	Red	Acid	510.5	ICI

The dye solutions were prepared by dissolving the different dyes in distilled water at desired concentration.

## **2. Sorption Studies**

### **2.1. Sorption Kinetics**

The initial solution dye concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of dyes. For dyes removal kinetics studies, 0.6 g of adsorbent were contacted with 0.3 L of dye solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of  $25 \pm 1^\circ\text{C}$ . In all cases, the working pH was the natural pH of dyes solutions and was not controlled. Samples from the clear supernatant, at appropriate time intervals, were pipeted from the reactor by the aid of the very thin point pipette, which prevented the transition to solution of sorbent samples. Their dye concentrations were determined with a UV-visible spectrophotometer, model Beckman 52, at the dyes respective  $\lambda_{\text{max}}$  value. The dye uptake  $q_t$  (mg dye/g adsorbent) was determined as follows:

$$q_t = (C_o - C_t) \times V/m$$

where  $C_o$  and  $C_t$  are the initial and time dye concentration (mg/L), respectively,  $V$  is the volume of solution (mL), and  $m$  is the sorbent weight (g) in dry form.

Blanc runs, with only the sorbent in 100 mL of distilled water, were conducted simultaneously at similar conditions to account for any color leached by the sorbent and sorbed by the glass container. Blanks were also run simultaneously, without any sorbent to determine the impact of pH change on the dye solutions.

Each experimental point was an average of two independent sorption tests. Duplicate tests showed that the standard deviation of the results was  $\pm 5\%$ .

### **2.2. Sorption Isotherms**

The equilibrium isotherms were determined by contacting a constant mass 0.2 g of sorbent material with a range of different concentrations of dye solutions: 5-800 mg/L. The mixture obtained was agitated in a series of 250 ml conical flasks with equal volumes of solution 100 ml for a period of 24 hours at room temperature. The contact time was previously determined by kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24 h, the final pH was measured. The equilibrium concentration of unbound dye was determined spectrophotometrically. The amount of dye adsorbed by the material was determined as the difference between the concentrations before and after adsorption.

All studies were carried out in duplicate. Preliminary experiments had shown that dyes adsorption losses to the container walls were negligible.

## RESULTS AND DISCUSSION

### 1. Sorption Kinetics

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye. As shown in Fig. 1, the kinetics of dyes sorption was contact time dependent. Sorption increases with time and it remains constant after a contact time i.e. the equilibrium time. The response of the sorbent material used is not similar with all dyes used. The results given in Table 2 indicate that orange peel adsorb the largest quantity of Nylosane blue followed by Nylomine red, Erionyl yellow and Erionyl red, respectively. The necessary time to reach equilibrium is in the range of 3-8 h depending on the type of dye, and, an increase of sorption time to 24 hours did not show notable effects. A possible explanation for the difference in sorption of the dyes can be given on the basis of their molecular weight and structural complexity (Özacar and Sengil [8]). According Desai et al. [9], the sorption kinetics and equilibrium are dependent upon the molecular dimensions of dyes.

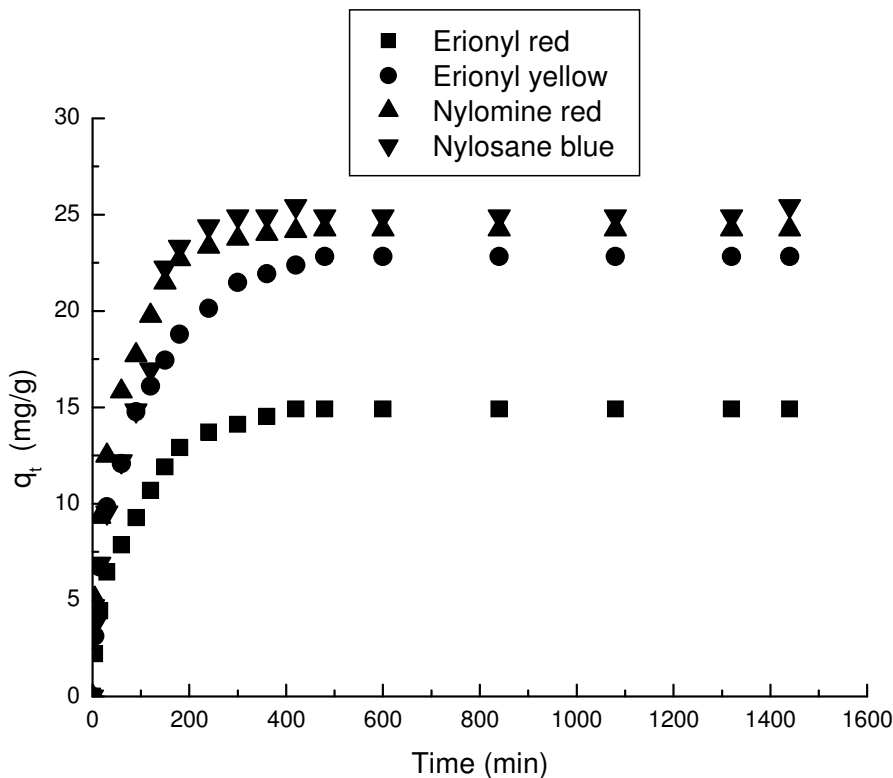


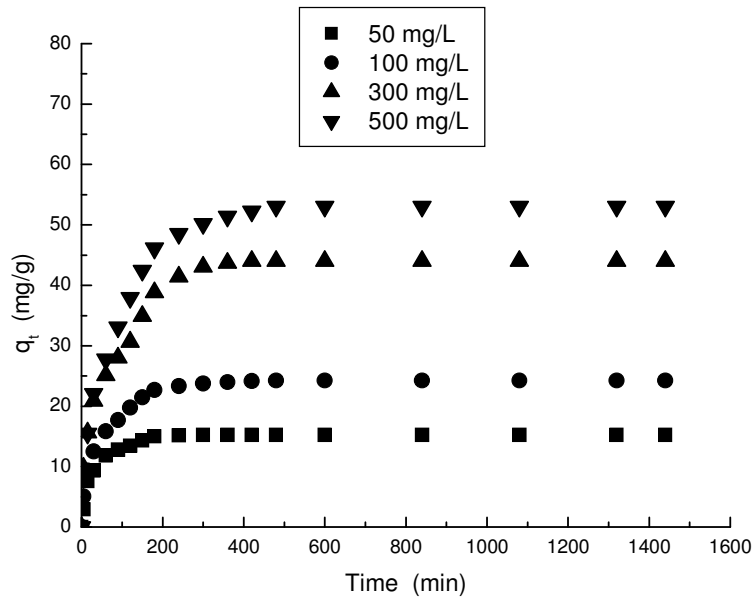
Figure 1: Kinetics of dyes sorption by Orange peel at  $C_o = 100$  mg/L

**Table 2 : Equilibrium parameters obtained from the kinetics of dyes sorption by Orange peel for initial dye concentration  $C_0 = 100$  mg/L.**

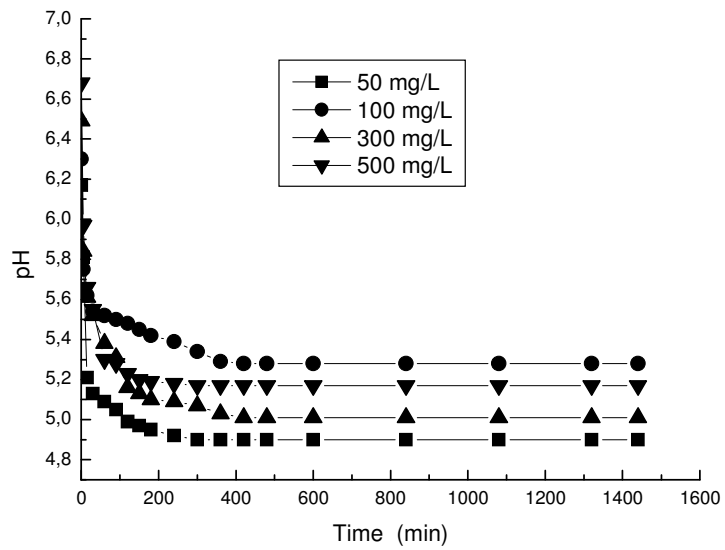
	Nylosane Blue	Erionyl Yellow	Erionyl Red	Nylomine Red
pH <sub>e</sub>	6.03	5.09	5.40	5.28
t <sub>e</sub> (h)	300	480	420	360
q <sub>e</sub> (mg/g)	24.92	22.83	14.92	24.24
Loss in sorbent weight (%)	07.62	09.23	14.11	8.45

Several experiments were also undertaken to study the effect of varying the initial dye concentration on the dye sorption kinetics from solution. As a typical example, the results obtained are shown in Figure 2a and indicate that the obtained curves have the same shape. The necessary average time to reach equilibrium was in the range of 4-8 h for all dyes concentrations tested with this material. This time was dependent on the type of dye used. The capacity of dyes removal by this material at the equilibrium increased with the initial concentration in dyes. During the phenomenon of dyes removal, we noticed a diminution in the initial pH values of solutions for all studied concentrations (see Figure 2b as a typical example).

The stirring rate in the aqueous phase, structural properties for sorbents (e.g. porosity, surface area), amount of sorbent, adsorbate properties (e.g. molecular dimensions and solubility), initial concentration of dyes determine the sorption rate. Existence of other species which may compete with dyes of interest for the active sorption sites is also important parameter for the sorption rate. The extent of sorption is also influenced by the surface chemistry of the sorbent (Denizli et al. [10]).



(a)



(b)

Figure 2 : Sorption kinetics of Nylomine red dye by Orange peel : Effect of initial dye concentration.  $q_t = f(\text{time})$  ; (b)  $\text{pH} = f(\text{time})$

**Table 3: Experimental results obtained at equilibrium from the kinetics of dyes sorption by Orange peel: effect of initial dye concentration****Nylosane Blue**

$C_0$ (mg/L)	50	100	300	500
pH <sub>e</sub>	6.11	6.03	5.98	5.86
$t_e$ (min)	360	300	300	360
$q_e$ (mg/g)	15.22	24.92	46.12	55.20
Loss in sorbent weight (%)	4.67	7.62	2.74	1.43

**Erionyl Yellow**

pH <sub>e</sub>	4.68	5.09	4.50	4.85
$t_e$ (min)	420	480	480	420
$q_e$ (mg/g)	12.63	22.83	41.67	49.81
Loss in sorbent weight (%)	1.63	9.23	3.09	1.53

**Erionyl Red**

pH <sub>e</sub>	5.71	5.40	5.78	5.79
$t_e$ (min)	360	420	360	420
$q_e$ (mg/g)	9.61	14.92	23.69	32.70
Loss in sorbent weight (%)	5.29	14.11	4.14	0.93

**Nylomine Red**

pH <sub>e</sub>	4.90	5.28	5.01	5.17
$t_e$ (min)	240	360	360	480
$q_e$ (mg/g)	15.25	24.24	44.03	53.06
Loss in sorbent weight (%)	1.53	8.45	3.42	2.13

The kinetics of dyes sorption by orange peel can be modelled using by the first-order rate equation of Lagergren [11], the pseudo-order rate equation (Ho [12]) and the second order rate equation shown below as Eqs. (1)-(3), respectively:

$$\log(q_e - q_t)/q_e = -K_L t / 2.3 \quad (1)$$

$$t/q_t = 1/2K'q_e^2 + t/q_e \quad (2)$$

$$1/(q_e - q_t) = 1/q_e + kt \quad (3)$$

where  $K_L$  is the Lagergren rate constant of sorption ( $\text{min}^{-1}$ );  $K'$  the pseudo second-order rate constant of sorption ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) and  $k$  the rate constant ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ );  $q_e$  and  $q_t$  are the amounts of dye sorbed ( $\text{mg} \cdot \text{g}^{-1}$ ) at equilibrium and at time  $t$ , respectively. For an initial dyes concentration of 100 mg/L, the different values of constant from the slopes and intercepts of linear plots of  $\log(q_e - q_t)/q_e$  versus  $t$ ,  $t/q_t$  versus  $t$  and  $1/(q_e - q_t)$  versus  $t$  (Figures non shown presented here) are summarized in the Table 4. Only, the pseudo second-order reaction rate model adequately described the kinetics of dyes

sorption with high correlation coefficients ( $R^2 > 0.998$ ): consequently, it was further used to describe all the kinetics of dyes sorption by orange peel.

**Table 4: Models rate constants for dyes adsorption kinetics by Orange peel at  $C_0=100$  mg/g**

Dyes	$K_L \cdot 10^3$ ( $\text{min}^{-1}$ )	$R^2$	$K' \cdot 10^4$ ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ )	$R^2$	$k \cdot 10^3$ ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ )	$R^2$
Nylosane Blue	15.16	0.9525	5.34	0.9982	5.81	0.6841
Erionyl Yellow	8.74	0.9947	5.21	0.9992	3.90	0.7665
Erionyl Red	9.61	0.9947	8.80	0.9991	5.37	0.8097
Nylomine Red	12.72	0.9944	9.49	0.9996	19.32	0.6153

Table 5 shows the constants obtained from Eq. (2) for all dyes used. All the fits show high correlation coefficients ( $R^2 > 0.999$ ). The equilibrium sorption capacity,  $q_e$ , increases with an increase in the initial dye concentration. The values of  $q_e$  obtained from the fitting to the pseudo second-order reaction rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium. This fact constitutes an additional confirmation of the pseudo-second-order model. The results also indicated that rate constant decreased with increasing initial dye concentration.

## 2. Sorption Equilibrium

Figure 3 shows the dyes sorption isotherms by orange peel waste. For all dyes used, the amount of dye sorbed increases initially with the dye concentration at equilibrium but then reaches saturation. These isotherms obtained are of Langmuir's type according to the classification of Brunauer et al. [13] and of L type according to the classification of Giles et al. [14].

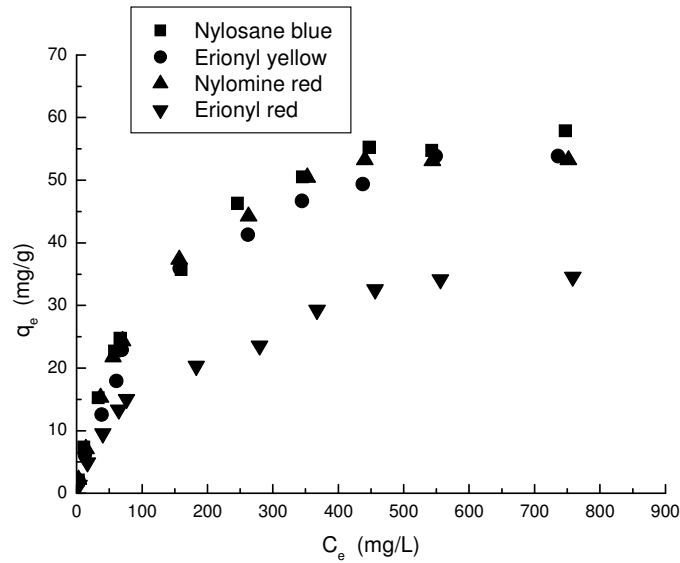
During experiments of dyes sorption equilibrium, it was observed that the initial pH of the solution decreased, and, the equilibrium pH varied with the initial concentration of dyes.

In order to optimise the design of a sorption system to remove pollutants from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations, commonly used to fit experimental data when solute uptake occurs by a monolayer sorption, have been tested in the present study, namely, Langmuir [15] and Freundlich [16].



**Table 5: Pseudo second-order rate constants for dyes adsorption kinetics by orange peel**

<b>Nylosane Blue</b>			
Initial Dye Concentration $C_o$ (mg/L)	$q_e$ (mg/g)	$K' \cdot 10^{+4}$ ( $\text{min}^{-1} \cdot \text{g} / \text{mg}$ )	$R^2$
50	15.80	8.06	0.9987
100	26.02	5.34	0.9982
300	47.35	3.99	0.9993
500	56.66	3.22	0.9994
<b>Erionyl Yellow</b>			
Initial Dye Concentration $C_o$ (mg/L)	$q_e$ (mg/g)	$K' \cdot 10^{+4}$ ( $\text{min}^{-1} \cdot \text{g} / \text{mg}$ )	$R^2$
50	13.04	11.10	0.9992
100	23.70	5.21	0.9992
300	43.37	2.48	0.9988
500	51.41	2.78	0.9992
<b>Erionyl Red</b>			
Initial Dye Concentration $C_o$ (mg/L)	$q_e$ (mg/g)	$K' \cdot 10^{+4}$ ( $\text{min}^{-1} \cdot \text{g} / \text{mg}$ )	$R^2$
50	9.81	24.29	0.9996
100	15.45	8.80	0.9991
300	24.51	5.80	0.9989
500	34.01	3.48	0.9987
<b>Nylomine Red</b>			
Initial Dye Concentration $C_o$ (mg/L)	$q_e$ (mg/g)	$K' \cdot 10^{+4}$ ( $\text{min}^{-1} \cdot \text{g} / \text{mg}$ )	$R^2$
50	15.44	26.63	0.9998
100	24.75	9.49	0.9996
300	45.37	3.54	0.9990
500	54.98	2.42	0.9992



**Figure 3: Adsorption isotherms of dyes by Orange peel at 25°C**

The Langmuir model has the form:

$$q_e = q_m b C_e / (1 + b C_e) \quad (4)$$

and the Freundlich model has the form:

$$q_e = K C_e^n \quad (5)$$

where:  $q_e$  is the amount of dye adsorbed at equilibrium per g of sorbent (mg/g);  $C_e$  the equilibrium concentration of dye in the solution (mg/L);  $q_m$  and  $b$  are the Langmuir model constants;  $K$  and  $n$  the Freundlich model constants. If the equation of Langmuir is valid to describe the experimental results, it must verify the linearized shape of the basis equation, in system of coordinates  $C_e/q_e$  versus  $C_e$ , that will permit us to obtain the constants  $q_m$  and  $b$  from the intercept and slope. If the equation of Freundlich is also verified, we must obtain a straight line in the system of coordinates  $\ln q_e$  versus  $\ln C_e$ , the slope and the intercept to the origin give  $n$  and  $k$  respectively. Results of the modelling of isotherms of dyes adsorption by the sorbent used, according to these models, are presented in Table 6.

**Table 6: Parameters of Langmuir and Freundlich obtained from the linearization of adsorption isotherms of dyes by Orange peel**

Dyes	Langmuir			Freundlich		
	$q_{\max}$ (mg/g)	b (L/mg)	$R^2$	K	n	$R^2$
Nylosane Blue	65.88	0.010	0.9967	1.72	0.578	0.9595
Erionyl Yellow	64.14	0.008	0.9932	1.34	0.603	0.9718
Nylomine Red	62.07	0.010	0.9960	1.61	0.582	0.9554
Erionyl Red	40.72	0.007	0.9855	0.89	0.591	0.9628

It appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation ( $R^2 > 0.99$ ). A high dyes sorption was observed by this sorbent material confirming the previous tendencies observed in the kinetics sorption. According to the coefficients of correlation ( $R^2 < 0.98$ ), we deduct that the model of Freundlich is not adequate for modelling isotherms in all the studied concentrations domain. A high dyes sorption was observed by this sorbent material but a certain difference in dye sorption capacity is easily distinguished between the dyes used in this study. For Nylosane Blue, a maximum sorption capacity about 65.88 mg/g was obtained followed by Erionyl Yellow (64.14 mg/g), Nylomine Red (62.07 mg/g) and Erionyl Red (40.72 mg/g), respectively. The applicability of these models should be considered as a mathematical representation of the sorption equilibrium over a given dye concentration range. The mechanistic conclusions from the good fit of the models alone should be avoided. In spite of the above limitations, these models can provide information on dye uptake capacities and differences in dye uptake between various species (Kapoor and Viraraghavan [11]).

## CONCLUSION

In laboratory-scale studies, the data show that Orange peel has a considerable potential for the removal of dyes from aqueous solutions over a wide range of concentrations. The dyes sorption performances are strongly affected by parameters such as: contact time, initial dye concentration and dyes type. The amount of dye sorbed by this material increased with the increase of these parameters at a specific time. The results also showed that the kinetics of dyes sorption were described by a pseudo-second order rate model. A good fitting of dyes sorption equilibrium data is obtained with Langmuir model in all the range of dyes concentrations studied. From these results, high maximum dyes adsorption capacities are observed using this material. It may be concluded that orange peel may be used as a low-cost, natural and abundant source for the removal of dyes and it may be an alternative to more costly materials. It may also be effective in removing as well other harmful or undesirable species present in the waste effluents.

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