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# Adsorption of dyes from aqueous solution under batch mode using cellulosic orange peel waste

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**ABSTRACT**

The present work aimed at studying the use of orange peel (OP) biosorption for the removal of methylene blue (MB) and Congo red (CR) from aqueous solution. The influences of initial dye concentration and contact time on the biosorption process were studied. Experimental data were modeled by Langmuir and Freundlich isotherms. The former fitted better the equilibrium data for both dyes. The monolayer biosorption capacity of OP was 256.4 and 102.0 mg/g for MB and CR, respectively. The calculated thermodynamic parameters, namely ΔG, ΔH and ΔS showed that the biosorption of the two dyes was spontaneous and exothermic under the examined conditions. Experimental data were also analyzed using biosorption kinetic models. The results showed that the biosorption processes of dyes on OP obey pseudo-second-order kinetics. Our results prove that an agriculture waste (i.e. OP) can be used to eliminate dyes from aquatic solution efficiently.

*Keywords:* Waste orange peel; Congo red; Methylene blue; Adsorption; Kinetic modeling; Thermodynamic modeling

## 1. Introduction

The primary source of aquatic pollution is toxic effluents from textile, paper, plastics and dyestuffs industries [1] which consume huge amounts of water, inorganic/organic chemicals and dyes to color their products. These industries represent a threat to the environment as they lead to the damage of water sources [2,3]. Treatment of effluent from textile and related industries is considered to be a global environmental issue. Indeed, dyes are organic compounds that cause damage to the environment and harmful effects on the public health [4,5]. Color is the first contaminant to be recognized in wastewater and is undesirable [6]. It is highly visible even when water contains a little amount of dyes (less than 1 ppm for some of them) [7]. Moreover, a number of dyes are known to be toxic for humans and animals and even carcinogenic [8,9]. Methylene blue (MB) and Congo red (CR) which are respectively a cationic and an anionic dye are mostly used as coloring agents. Hence, removal of these two dyes from water is a crucial issue that needs attention. Many techniques have been proposed for the removal and separation of dyes from contaminated water, including adsorption [10], photo-degradation [11], coagulation [12], electro-oxidation [13] and membrane filtration [14]. Because of its simplicity, cost effectiveness and higher performance, adsorption is considered to be the most efficient method. Several organic and inorganic adsorbents like clays [15,16], activated carbon [17,18], cellulose [19,20], carbon nanotubes [21], magnetic composites [22], biocomposite [23,24], bio wastes [25,26], by-products from industries and natural materials like biopolymers have been used for the removal of dyes [27] and [6].

The present investigation aimed at studying the removal of CR and MB from aqueous solutions by means of a cellulosic waste, i.e. orange peel. Food industry in Tunisia gen-

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erates large amounts of these wastes (estimated to be more than 700,000 tons in 2017). Variables which influence the treatment of wastewater, such as dyes concentrations, stirring time, adsorbent quantity and stirring rate were investigated in a closed jacketed reactor (batch-mode) equipped with a paddle stirrer. Adsorption isotherms were established and studied using Langmuir and Freundlich models. Thermodynamic and kinetic parameters of the adsorption process were deduced from experimental data.

## 2. Experimental

### 2.1 Materials

Orange peels used in this study were gathered in the northern part of Tunisia (Cap Bon). They were initially washed several times with pre-heated double distilled water. Then, they were dried under ambient conditions, sliced, crushed and sifted to a geometric mean size of 500 µm. The resulting adsorbent was then characterized with FTIR spectrum analysis, SEM micrographs and point of zero charge measurements.

The chemical structures and other related information of MB and CR are listed in Table 1.

The visible spectra of MB and CR were obtained using a thermo Scientific, Genesys 10 S UV-VIS spectrophotometer. Dyes concentrations were determined at the wavelength corresponding to the highest absorbance, $\lambda_{max}$ = 664 nm for MB and $\lambda_{max}$ = 500 nm for CR. Dilutions were carried out when the absorbance exceeded a value of 0.6. Calibration plots were made in the concentration range of 1–10 mg/L.

### 2.2. Adsorption procedure

To compare the adsorption capacity of OP towards the two dyes, 0.1 g of cellulosic waste orange peel (OP) was added into 100 mL of dye (MB and CR) solutions with initial concentrations ranging between 50 and 500 mg/L, respectively. The resulting suspensions were shaken at a constant stirring rate (600 rpm) for 1 h to reach equilibrium. The experiments were carried out at 298, 303, 313 and 323 K with a pH value adjusted to 5.

The effect of pH on dyes adsorption was investigated by stirring 1 g/L of OP in several conical flasks containing 100 mL of dyes solution having an initial dye concentration of 100 mg/L with a solution pH between 2.0 and 7.0.

The amount of dyes adsorbed onto the OP at equilibrium, $q_e$ (mg/g), was obtained as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where $C_0$ and $C_e$ are respectively the initial and equilibrium dye concentrations in solution and $m$ is the mass of dry OP (g).

Kinetic study was carried in a thermostated reactor of 2-L volume equipped with a paddle stirrer. Experiments were conducted at 298 K and pH 5 with one liter of dye solutions at concentrations varying between 10 and 40 mg/L for various amounts of OP, ranging from 0.4 to 1.2 g and for various stirring rates, varying between 200 and 600 rev/min. Aliquots of 5 mL were withdrawn from the reactor at regular time intervals, and their concentrations were determined as shown above.

The amount of dyes adsorbed $q_t$ (mg/g) onto OP, at various time intervals, was obtained as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

where $C_t$ is the concentration of dye solution at any time $t$ (mg/L).

## 3. Results and discussion

### 3.1. Characterization

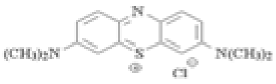
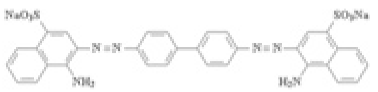
The FTIR, SEM photograph, $pH_{PZC}$ and XRD of OP were described in a previous work [28]. The FTIR spectroscopy depicts the presence of hydroxyl groups, an aliphatic skeleton in addition to carbonyl, carboxyl and amine groups in the OP. The SEM images show an irregular image and a porous surface which indicate that OP has an adequate morphology for dyes adsorption. The $pH_{PZC}$ value was 3.85. Therefore, the surface of the adsorbent is negatively charged for pH values higher than 3.85, whereas it is positively charged for pH values less than 3.85. The baseline of the X-ray diffractogram is not flat. It has two large diffraction peaks at 20 and 40° indicating that orange peel is completely amorphous. Nevertheless, there are many narrow diffraction peaks on the whole 2q range.

### 3.2. Adsorption studies

#### 3.2.1. Effect of the pH of the solution

Fig. 1 shows the effect of pH on the adsorption process for MB and CR. In particular, it is observed that the adsorption of MB is positive at basic pH while that of CR is higher

Table1
Chemical structures and other related information about tested dyes

| Dye | Color index number | Molecular weight (g/mol) | Chemical structure | Dye class |
|---|---|---|---|---|
| Methylene blue | 5201 | 355.89 |  | Quinone-imine |
| Congo red | 22120 | 640 |  | Diazo |

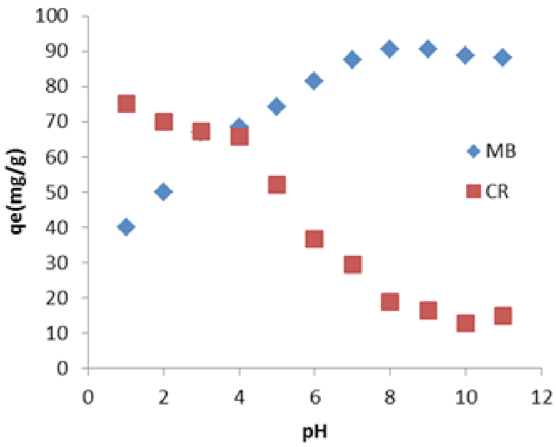


Fig. 1. Effect of pH on the adsorption of MB and CR onto OP. Concentration of dye, C = 20 mg/L, amount of CWOP, m = 1 g/L.

under acidic conditions. Such results comply with expectations, given that the value of the $pH_{PZC}$ is 3.85 and that MB and CR are respectively cationic and anionic dyes.

### 3.2.2. Effect of contact time and initial dye concentration

The removal of dyes through adsorption onto OP was fast in the beginning, then slow until equilibrium after 100 and 35 min for CR (pH = 8) and MB (pH = 7.5), respectively. Higher initial dye concentrations result in an increase in the uptake percentage but slow the kinetics. Indeed, the boundary layer resistance to mass transfer increased by increasing the initial dye concentration. The optimal concentration was 30 and 50 mg/L for MB and CR, respectively Fig. 2.

## 3.3. Adsorption isotherms

Adsorption isotherms (weight of MB and CR) adsorbed per weight unit of OP as function of equilibrium dye concentration in bulk solution were studied at different temperatures (Fig. 3). In the initial stages (low $C_e$ and $q_e$ values), isotherms rise with high slopes. This signifies that there exist several readily accessible sites. At higher $C_e$ values, a plateau takes place. This corroborates the monolayer coverage of dye onto OP.

From Fig. 3, the results indicate that when the temperature increased from 298 to 338K, the equilibrium biosorption experimental maximum capacity of OP decreased from 150 to 80 mg/g and from 45 to 15 mg/g respectively for MB and CR. A decrease in dye removal capacity of the biomass with temperature indicates that the biosorption of MB and CR dyes on OP is thermodynamically controlled by an exothermic process.

### 3.3.1. Equilibrium isotherm modeling

The isotherm equations explain give the relationship between the quantity of adsorbed dyes at equilibrium and their remaining concentration in the liquid phase, which gives essential data about the most main mechanisms for the elimination of dyes. The Langmuir and Freundlich models were selected.

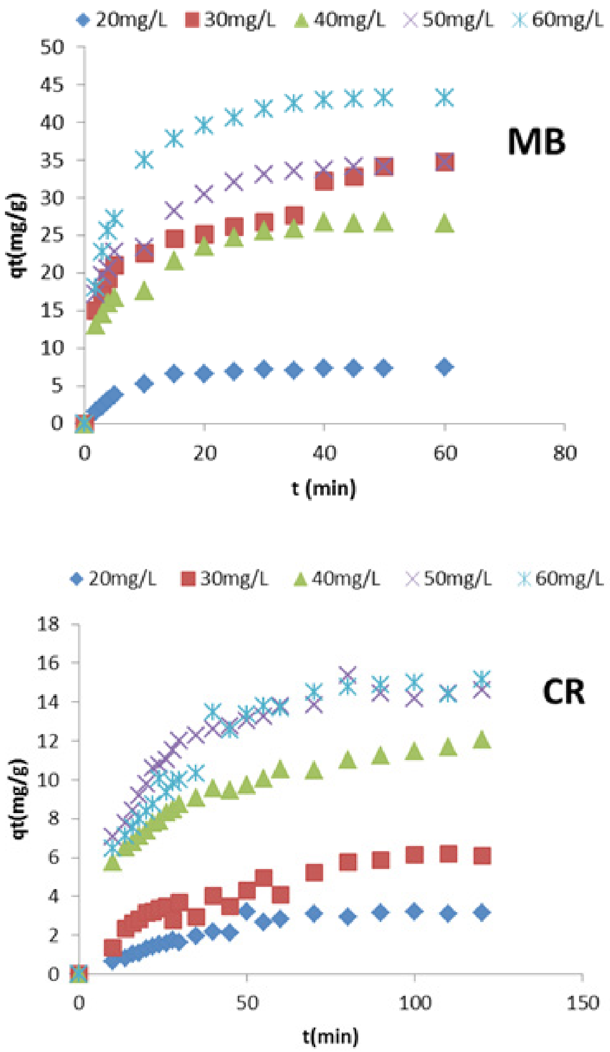


Fig. 2. Effects of initial dye concentration upon its adsorption onto OP (MB and CR). Amount of OP: 1 g/L for CR and 0.5 g/L for MB.

Langmuir model: It is used to characterize the monolayer adsorption, supposing that each site contains only one adsorbate molecule and that the site surfaces are uniform. It also supposes that intermolecular forces diminish fast with the increase in the distance between the adsorption surface and the molecule. Langmuir isotherm equation is given as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L Ce} \qquad (3)$$

Its linearized form is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (4)$$

where $q_e$ is the sorption capacity at equilibrium (mg/g), $C_e$ is the solute concentration at equilibrium (mg/L) and $q_m$ (mg/g) and $K_L$ (L/mg g) are the Langmuir's constants.

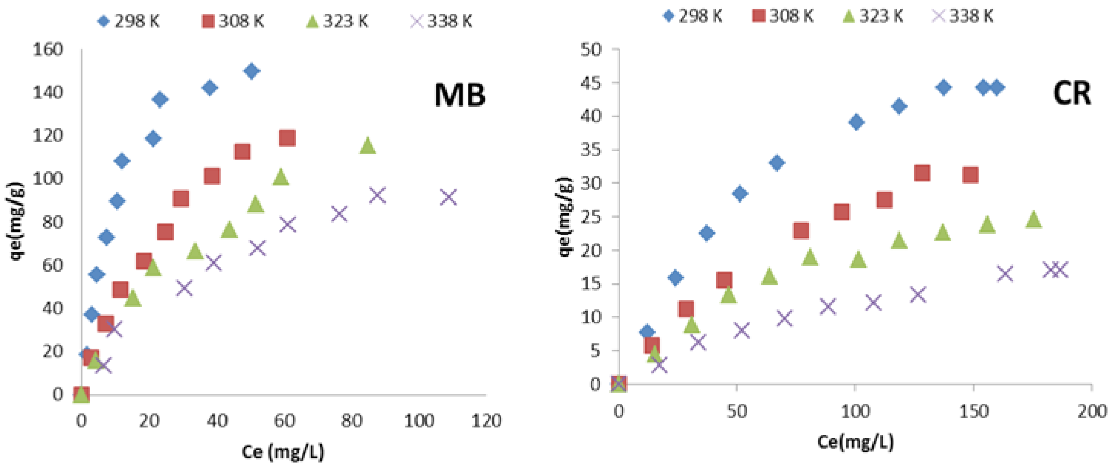


Fig. 3. Effects of temperature onto OP adsorption of dyes MB and CR.

Table 2
Langmuir and Freundlich model parameters for dyes adsorption onto OP at different temperatures

| T(K) | Dyes | Langmuir isotherm | | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|---|
| | | $q_m$ (mg/g) | $K_L$ $10^{-3}$ (L/g) | $R^2$ | $R_L$ | $1/n$ | $K_f$ (L/mg) | $R^2$ |
| 298 | MB | 256.41 | 0.0509 | 0.992 | 0.246 | 0.586 | 19.519 | 0.920 |
| | CR | 102.04 | 0.0068 | 0.99 | 0.4231 | 0.673 | 1.736 | 0.957 |
| 308 | MB | 185.185 | 0.0298 | 0.994 | 0.358 | 0.653 | 9.161 | 0.991 |
| | CR | 67.114 | 0.0066 | 0.998 | 0.428 | 0.724 | 0.927 | 0.986 |
| 323 | MB | 156.25 | 0.0265 | 0.999 | 0.999 | 0.649 | 6.971 | 0.978 |
| | CR | 55.248 | 0.0057 | 0.989 | 0.989 | 0.677 | 0.841 | 0.951 |
| 338 | MB | 129.87 | 0.0223 | 0.993 | 0.993 | 0.681 | 4.448 | 0.965 |
| | CR | 39.525 | 0.0046 | 0.986 | 0.986 | 0.723 | 0.424 | 0.971 |

Table 2 illustrates the Langmuir's constants with the regression coefficients.

The results show that OP has a high adsorption capacity, i.e. 256 and 100 mg/g for the MB and CR at 298 K, respectively. Low values of $K_L$ mean weak interactions between the absorbate and adsorbent. However, there are some differences between MB and CR. Indeed, the MB/adsorbent interactions at pH = 7.5 are more significant than those of CR/adsorbent at pH = 8 demonstrating that orange peels have better MB affinity (cationic dye). The last result is consistent with data from studies on the adsorption of methylene blue onto activated carbon prepared from rattan sawdust [29] and adsorption of Congo red from coir pith onto activated carbon [30].

A dimensionless constant called the equilibrium parameter can be used to express the important characteristics of the isotherm as follows:

$$R_L = \frac{1}{1+K_L C_0} \tag{5}$$

where $K_L$ is the Langmuir constant and $C_0$ is the initial dye concentration [31,32]. The value of $R_L$ shows if the adsorption process is favorable or not as follows:

- $R_L > 1$ : Unfavorable adsorption
- $R_L = 1$ : Linear
- $0 < R_L < 1$ : Favorable
- $R_L = 0$ irreversible.

Table 2 shows that $R_L$ values range from 0.2 to 0.4 between 298 and 308 K indicating that OP particles adsorb MB and CR satisfactorily.

Freundlich model: It is suitable for systems where the energies of the surfaces are mixed and vary according to $q_e$ with respect to the variation of the temperature of adsorption. The equation used here is as follows:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where $K_f$ and $1/n$ are the Freundlich's constants.

A logarithmic plot linearizing Eq. (7) enables the constant $K_f$ and the exponent $1/n$ to be determined.

$$Lnq_e = LnK_f + \frac{1}{n} LnC_e \tag{7}$$

Table 2 depicts $K_f$ and $1/n$ values computed from the intercepts and slopes of the plots at different temperatures.

The estimated 1/*n* values in the present work (comprised between 0 and 1) corroborate the favorable adsorption of CR and MB on orange peel. As can be seen from this Table 2, the Langmuir model is relatively appropriate for designing industrial adsorption processes. This finding is in agreement with observations from previous studies concerning the adsorption of Acid Red 44 dye onto macro-fungus [33].

Table 3 illustrates the values of maximum adsorption capacities of various adsorbents towards MB and CR in the literature, demonstrating that OP is characterized by acceptable performances.

### 3.3.2. Comparison of dye removal costs

To evaluate the economic feasibility of the new adsorbent, we compared the cost of activated carbon and OP. Isotherm studies were performed under similar conditions at 298 K by means of a uniform particle size of 500 μm leading to determining the maximum values of the adsorption capacity $q_m$. Activated carbon was used as a reference, which has a comparative cost of one currency unit per kg; whereas that of OP is one hundred times lower (Table 4). The results of this cost comparison revealed that the relative cost to remove 1 kg of MB and CR by OP is respectively 1.4% and 2% of that using activated carbon as an adsorbent.

Table 3
Comparison of the maximum adsorption capacity of various adsorbents towards MB and CR

| Dyes | Adsorbent | Adsorption capacity (mg/g) | References |
|---|---|---|---|
| Congo Red (CR) | Coir pith | 6.72 | [30] |
| | Banana peel | 11.2 | [38] |
| | Orange peel | 7.9 | [38] |
| | Chitosan | 450.4 | [39] |
| | Activated Clay | 96.246 | [40] |
| | OP | 102.4 | This work |
| Methylen blue (MB) | Activated Kaolinite | 78.1 | [16] |
| | Grass waste | 457.640 | [41] |
| | Tea waste | 86.16 | [42] |
| | Banana peel | 15.9 | [42] |
| | Garlic peel | 82.64 | [42] |
| | Wood apple shell | 92.2 | [42] |
| | Jack fruit peel | 285.713 | [43] |
| | Coal | 250 | [43 |
| | Rice husk | 312 | [43] |
| | Luffa cylindrical fibers | 47 | [41] |
| | AC Rattan sawdust | 294.14 | [41] |
| | Saw dust-walnult | 59.17 | [43] |
| | OP | 256.41 | This work |

### 3.3.3. Thermodynamic analysis

To approximate the thermodynamic parameters, *i.e.* Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS), we used Langmuir isotherm constant, $K_L$. The free energy of adsorption ΔG can be associated to Langmuir adsorption constant using the following expression [34]:

$$\Delta G = -RT\ln K_L \tag{8}$$

Also, enthalpy and entropy changes are related to Langmuir equilibrium constant by the following expression:

$$\ln(K_L) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

Therefore, the plot of ln ($K_L$) vs. 1/T should be a straight line, the slope and intercept values of which allow the extrapolation of ΔH and ΔS. See Fig. 4. Values of ΔG were calculated using Eq. (9). All the parameters are summarized in Table 5. The negative G values for CR and MB indicate that the adsorption process is practicable and spontaneous. The negative values of ΔH indicate that the dyes adsorption process is exothermic. The change in entropy reflects the randomness of OP interface and the solution during the adsorption of dyes. Our experimental findings mirror observations on the adsorption of methylene blue dyes onto agro-based waste material [35]. The difference between the energies is due to the difference in the size and the state of charge of the CR and MB molecules. The former is a bulky molecule and is charged negatively whereas the latter is a small molecule and is charged positively.

### 3.4. Adsorption kinetics

To investigate the bio-sorption kinetics of dyes, we used a pseudo-second order model.

Table 4
Relative costs of dyes (MB and CR) removal by OP and activated carbon

| Dye | Adsorben | $q_{max}$ (mg/g) | Adsorbent mass required to remove 1 kg of dye | Relative cost per kilogram of adsorbent | Relative cost to remove 1 kg of dye |
|---|---|---|---|---|---|
| MB | Carbonnorit | 223 | 4.48 | 1.00 | 1.00 |
| | OP | 256.41 | 6.40 | 0.01 | 0.0014 |
| CR | Carbonnorit | 170 | 5.88 | 1.00 | 1.00 |
| | OP | 102.04 | 12.59 | 0.01 | 0.020 |

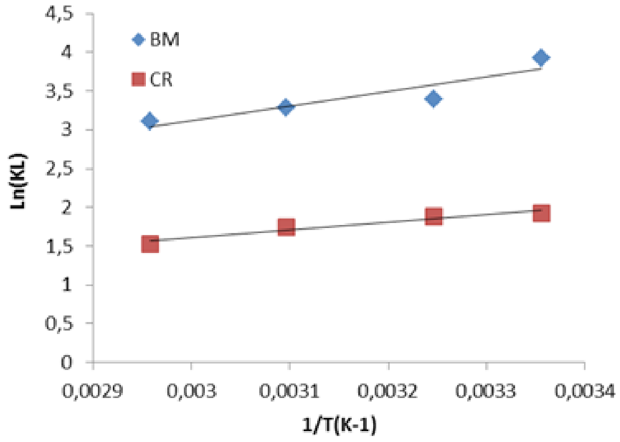


Fig. 4. Van't Hoff plot for MB and RC dyes onto OP.

Table 5
Thermodynamic parameters for the adsorption of dyes (MB and RC) onto OP

| Dyes | T (K) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol·K) |
|---|---|---|---|---|
| MB | 298.15 | –9.39 | –15.64 | –20.98 |
| | 308.15 | –9.18 | | |
| | 323.15 | –8.86 | | |
| | 338.15 | –8.55 | | |
| CR | 298.15 | –4.87 | –8.05 | –10.68 |
| | 308.15 | –4.76 | | |
| | 323.15 | –4.60 | | |
| | 338.15 | –4.44 | | |

This model is described by chemisorption phenomenon. The adsorbate and adsorbent surface establish a covalent chemical bond [36]. The equation of this model is expressed as follows:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{10}$$

where $q_e$ is the adsorbed amount of dyes at equilibrium, $q_t$ is the adsorbed amount of dyes at time $t$ (mg/g) and $k_2$ is the pseudo-secondorder model constant (g/mg·min). Its linearized form is given by:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{11}$$

Table 6 shows the results of the correlation studies for different initial dye concentrations by the pseudo-second order model. For MB, the correlation coefficient ($R^2$) for the pseudo-second-order adsorption model has a high value (> 97%). As a result, the global rate of the dyes adsorption process appears to be controlled by their chemisorption [29]. Our findings provide a confirmation of previous observations with regard to the adsorption of cationic dyes onto activated carbon prepared from sawdust [37] and adsorption of Congo red onto activated carbon from coir pith [30].

Table 6
Kinetics parameters of the pseudo-second-order rate equation for dyes adsorption

| $C_0$ (mg/L) | Dyes | Pseudo-secondorder | | |
|---|---|---|---|---|
| | | $q_e$ (mg/g) | $k_2$ g/(mg·min) | $R^2$ |
| 20 | MB | 7.35 | 0.03 | 0.979 |
| | CR | 3.18 | 0.01 | 0.946 |
| 30 | MB | 26.68 | 0.01 | 0.989 |
| | CR | 6.03 | 0.01 | 0.989 |
| 40 | MB | 34.23 | 0.02 | 0.984 |
| | CR | 12.37 | 0.01 | 0.928 |
| 50 | MB | 35.55 | 0.01 | 0.982 |
| | CR | 14.46 | 0.01 | 0.923 |
| 60 | MB | 43.31 | 0.01 | 0.994 |
| | CR | 15.02 | 0.01 | 0.925 |

## 4. Conclusion

This paper is part of a series of works aiming at valorizing orange peel for the removal of Congo Red and Methylene Blue from aqueous solution by adsorption. This work was initiated by a preliminary study on the influence of pH on the adsorption of the two dyes on orange peel and also the determination of the zero point of charge of the adsorbent. We observed that the adsorption of MB is favorable at basic pH while that of CR is higher under acidic conditions.

The following conclusions can be drawn from the experimental data of the adsorption isotherms:

- The variation in temperature has an important effect on the adsorption of the two dyes on orange peel.
- The adsorption isotherms are well described by both the Langmuir and Freundlich models, but the Langmuir model better fits to the experimental data.
- The adsorption capacities calculated from the Langmuir linear equation were respectively 256 and 102 mg/g for MB and CR at 298K.
- A comparison of the cost, based on the adsorption capacity alone, has shown that the costs of the adsorbent required are respectively 1.4% and 2% for MB and CR compared with commercial activated Norit carbon granules.
- Orange peel has more affinity for cationic dyes than anionic dyes at pH 8.
- The calculation of the adsorption energies shows that it is a spontaneous and exothermic physical adsorption with a reduction of disorder.
- A kinetic study was carried out to determine the influence of certain parameters, namely initial concentration, contact time, adsorbent mass and stirring rate on the adsorption process. We can conclude that:
- The adsorption kinetics is reduced by increasing the initial concentration.
- The kinetics of MB adsorption by orange peel is much faster than that of CR. The equilibrium times are 30 min for MB and 100 min for CR.

- The adsorption of the two dyes by orange peel obeys second order kinetics.

## Symbols

$C_0$ — Initial concentration in aqueous solution (mg/L)
$C_t$ — Concentration of dye solution at any time t (mg/L)
$C_{eq}$ — Concentration of dye at equilibrium (mg/L)
$K_L$ — Langmuir constant (L/mg g)
$K_f$ — Freundlich constant (L/mg)
$k_2$ — Second-order model constant ($g/mg\cdot min^{-1}$)
$m$ — Mass of dry adsorbent (g)
$N$ — Stirring speed (rev/min)
$1/n$ — Freundlich parameter
$q_{eq}$ — Equilibrium concentration in solid phase (mg/g)
$q_m$ — Maximum adsorbed per unit mass of adsorbent (mg/g)
$q_t$ — Adsorbed amount at any time t (mg/g)
$R_L$ — Equilibrium parameter of isotherm
T — Temperature (K)
$t$ — Time (min)
ΔG — Free energy of adsorption (kJ/mol)
ΔH — Change in enthalpy (kJ/mol)
ΔS — Change in entropy (J/mol K)

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