



KINETIC AND ISOTHERM STUDY OF METHYLENE BLUE ADSORPTION ON ORANGE PEEL ACTIVATED CARBON

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ABSTRACT

The aim of this work is to use activated carbon derived from orange peel to remove methylene blue from water. The adsorption of this dye was carried out in batch mode and the analysis of the methylene blue solution samples was carried out on a Shimadzu UV-visible spectrometer. The mass of carbon, the initial concentration of the dye solution, as well as kinetic models, isotherm models and thermodynamic studies were studied. Analysis of the adsorption data showed that the optimum dose of activated carbon was 300 mg/L for an 90.84 % adsorption rate. The concentrations used to study the influence of concentration proved to be too low to achieve saturation of the adsorbent. Modelling of the kinetics showed that the methylene blue adsorption kinetics followed the pseudo-first-order kinetic model. Isotherm modelling revealed that methylene blue adsorption follows the Freundlich-Langmuir model. The values of the thermodynamic parameters show a spontaneous and exothermic phenomenon.

Keywords: Methylene blue, Orange peel, Activated carbon, Adsorption, Modelization

INTRODUCTION

The increase in industrial activities, particularly those linked to the textile industry, is putting increasing pressure on the planet's freshwater reserves, as they generate a wide range of chemicals that are discharged into water, threatening the natural balance (Daud et al., 2010). Textile industry wastewater is laden with numerous organic micropollutants, including certain dyes that are often used in excess to improve dyeing (Lucas et al., 2007). Furthermore, in response to socio-economic criteria, the textile industry is attempting to

synthesise increasingly stable dyes with often complex molecular structures (Daud et al., 2010). According to Mansour et al (2009), annual world production of synthetic dyes was estimated at 800,000 tonnes. However, a significant proportion of this around 140,000 tonnes is discharged during the manufacturing and fabric colouring stages. These dyes accumulate in water either because they are resistant to conventional treatment processes due to their synthetic nature and the complexity of their structures, which include aromatic nuclei that considerably reduce their biodegradability, or because of the lack or inadequacy of treatment systems (Daud et al., 2010). The presence of these dyes and their metabolites in water remains a matter of environmental and health concern. These substances could lead to under-oxygenation and changes in the colour and turbidity of aquatic environments (Barka, 2008). In addition, they are known to have mutagenic and carcinogenic effects on humans and animals. Different physical, chemical and biological methods have been developed and tested to treat effluents containing dyes. These include flocculation, precipitation, ion exchange, membrane filtration, irradiation and ozonation. However, these processes are expensive and lead to the generation of large quantities of sludge (Robinson *et al.*, 2001). Among the processes, adsorption remains a relatively widely used technique that is easy to implement (Juang et al., 1997). Several authors, including Oyelude and Appiah-Takyi (2012) have studied the adsorption of dyes on various materials. Activated carbon remains by far the adsorbent of choice in environmental pollution control, given its high adsorption capacity and selectivity (Bouchemal et al., 2011). In order to overcome the cost problems of commercial activated carbons, research is increasingly focusing on the development of more economical activated carbons produced from locally and widely available materials. This is the context of the present study. The aim is to use activated carbon made from orange peel (ACOP) to eliminate methylene blue in aqueous media.

The choice of orange peel as an adsorbent is linked to the fact that orange is a fruit widely available and consumed throughout Algeria. It is an agricultural by-product which can constitute an inexpensive and environmentally friendly adsorbent.

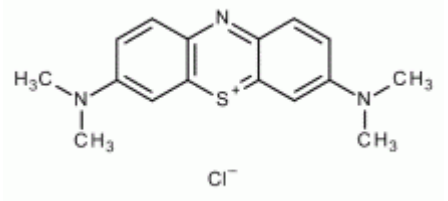
MATERIAL AND METHODS

The adsorbent used in this study is an activated carbon derived from orange peel. It was synthesised using the chemical method described by (Konan et al., 2021)

Reagents and solutions

The chemicals used for this work were orthophosphoric acid (H_3PO_4) and sodium hydroxide (NaOH), all of analytical quality. The Phosphoric acid is used as an activation agent for the adsorbent. Methylene blue, a cationic dye whose characteristics are shown in Table 1, was supplied by were from Sigma-Aldrich, Germany.

Table 1: Physico-chemical characteristics of methylene blue

| Organic compound | Methylene blue |
|--------------------------|---|
| Chemical structure |  |
| CAS Number | 7220-79-3 |
| pKa | 3.8 |
| Water solubility | 40g/l at 20°C |
| Molar weight | 319.85 g/mol |
| Chemical formula | C ₁₆ H ₁₈ ClN ₃ S |
| Physical characteristics | Breaks down when heated above 190°C |

Preparation and activation of adsorbent

The orange peels were collected from the city of Sétif, Algeria. The orange peel was washed several times with tap water, then with distilled water to remove impurities, and then spread on a clean surface in the open air. It was then dried in an oven at 110° C for 24 hours then finally stored away from air in hermetically sealed bottles. Orange peel was activated with H₃PO₄ as activating agent. So, the dried peels were then ground into powder with an homogeny size ranging. Equal amounts of orange peels and phosphoric acid were mixed for several hours. The carbonization of samples is carried out in a calcination furnace at 450°C. Finally, our adsorbent used was the activated carbon orange peel (ACOP).

CHARACTERIZATION

Zero-charge pH

An adsorbent's zero charge (pHpzc) is ascertained. This involves adding a certain quantity of the adsorbent to a reactor containing 20 mL of distilled water, the initial pH of which is measured beforehand and adjusted from 2 to 12 using sodium hydroxide (NaOH) or hydrochloric acid (HCl) solutions. After agitating the suspension for a full day, the final pH (pH_f) of the mixture is determined. Plotting the difference (ΔpH) between the starting and end pHs in relation to the initial pH. The intersection of the curve obtained using the x-axis is known as the pHpzc.

Adsorption tests

The stock solution of methylene blue (MB) is prepared by dissolving a quantity of MB powder from the commercial product. Solutions with concentrations ranging from 1 mg/L to 10 mg/L were then prepared by diluting the stock solution in distilled water. In order to conduct adsorption tests, a number of factors were examined, including temperature, initial concentration, and adsorbent mass. These adsorption tests were carried out in batch mode at room temperature in beakers stirred at 250 rpm. The initial or residual dye of MB were determined using a UV/visible spectrophotometer (Shimadzu UV/Vis 1700, Japan) at $\lambda_{max} = 664 \text{ nm}$.

Adsorption kinetics and isotherm

Kinetic and isothermal studies are essential for assessing the adsorption efficiency of the adsorbent. The models that are most frequently encountered are pseudo-order 1 and pseudo-order 2 kinetic models, as well as Freundlich and Langmuir isotherm models. Three kinetic and isotherm models were used in this study to explain the adsorption kinetics mechanism. The Freundlich, Langmuir, and Langmuir-Freundlich isotherm models, as well as the pseudo-first-order, pseudo-second-order, and Elovich kinetic models, are listed in (Table 2). Non-linear models were used for the graphical representation of the kinetic and isotherm models. The linearisation of the model equations gives greater weight to points with low concentrations and less weight to points with high concentrations (Chang et al., 2010). It is possible to generate biases from non-linear equation transformations of isotherm equations into linear forms, for instance, by using high linear regression coefficients to produce poor linearity or by favoring the Freundlich model for data fitting at low experimental concentrations and the Langmuir model for data fitting at higher concentrations. As a result, performing a non-linear optimisation appears mathematically more rigorous for assessing the fit of an adsorption process to a model. To do this, it is necessary to determine one or more error functions (Table 2).

Table 2: Kinetic and isotherm models and error functions

| Kinetic models | | |
|---|--|--|
| Pseudo order 1 | Pseudo order 2 | Elovich |
| $q_t = q_e (1 - \exp^{-k_1 t})$ | $q_t = \frac{k_2 \times q_e^2 \times t}{1 + k_2 q_e \times t}$ | $q_t = \frac{1}{\beta} \times \ln(1 + \alpha \times \beta \times t)$ |
| Isotherm models | | |
| Langmuir | Freundlich | Langmuir-Freundlich |
| $\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e}$ | $q_e = k_F \times C_e^n$ | $\frac{q_e}{q_m} = \frac{(bC_e)^n}{1 + (bC_e)^n}$ |

| Model validation | |
|--|---|
| Relative error (RE) | $RE = \frac{1}{n} \sum_{i=1}^n \frac{q_{e,i \text{ model}} - q_{e,i \text{ experience}}}{q_{e,i \text{ experience}}}$ |
| Coefficient of determination (R^2) | $R^2 = 1 - \frac{\sum_{i=1}^n (q_{e,model} - q_{e,experience})_i^2}{\sum_{i=1}^n [q_{e,model} - \text{moyenne}(q_{e,experience})]_i^2}$ |

RESULTS AND DISCUSSION

pH at zero charge point (pH_{PZC})

The surface of the adsorbent becomes negatively charged at pH levels above pH_{PZC} and positively charged when the pH of the solution is lower than pH_{PZC}. According to Fig. 1, the pH_{PZC} of our activated carbon is 7.9 and the adsorbent in question is a cationic dye. Thus, at a pH above 7.9, adsorption of the dye under study (methylene blue) should be favourable compared with a lower pH (Mishra et al., 2021). However, in this investigation, we opted to operate at pH 4 to evaluate our activated carbon's ability to adsorb acidic water.

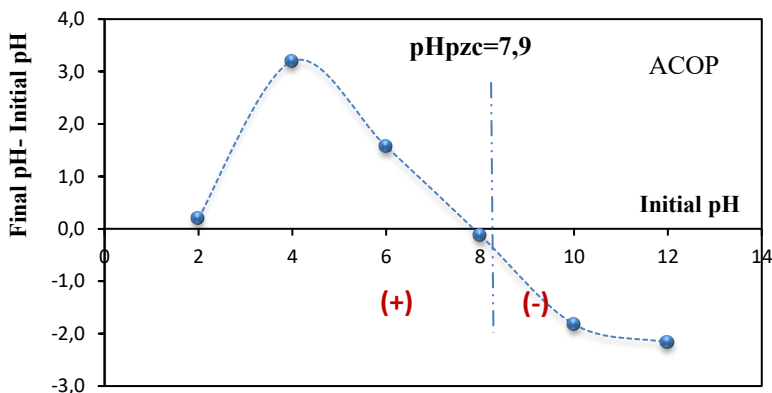


Figure 1: pH at zero charge point (pH_{PZC}) of adsorbent used the activated carbon orange peel (ACOP).

Kinetics of adsorption

Impact of mass

Effect of activated carbon mass on adsorption was studied at 25°C with a 5 mg/L dye solution (pH 4.0). The activated carbon dose was between 30 mg/L to 800 mg/L. The results of the adsorption tests as part of the study of the influence of adsorbent mass are shown in Fig .2.

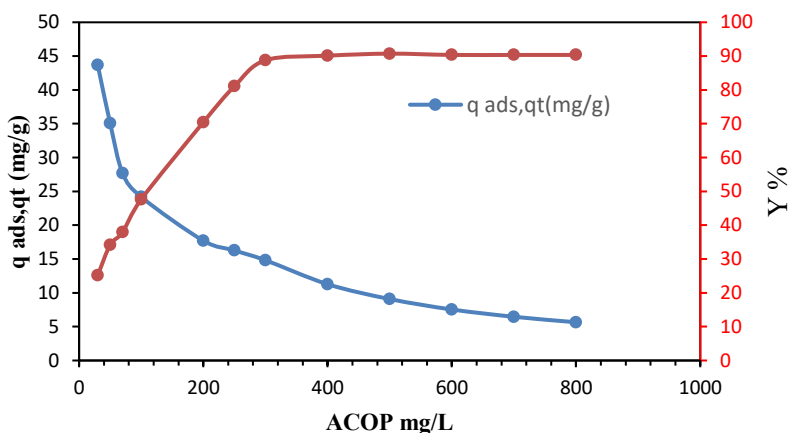


Figure 2: Effect of activated carbon mass on the quantity adsorbed and the percentage of MB elimination

Analysis of Fig .2 shows that the adsorption efficiency increases as the dose of activated carbon in solution increases, reaching a plateau in the efficiency curve. A rapid adsorption phase is observed from 30 mg/L to 300 mg/L. The rate of adsorption then slows from 300 mg/L to 800 mg/L, with a maximum rate of 90.84 %. The rapid adsorption phase is probably due to the abundance and availability of active sites within the adsorbent material. According to Tcheka et al. (2015), Addition of adsorbents increases the number of MB adsorption sites. The second phase corresponds to a decrease in the adsorption rate despite the increase in the dose of activated carbon. It reflects a desorption of the MB molecules. Similar results were observed by Tcheka et al (2015) who studied the elimination of BM on activated carbon based on Vitexdoniana shells activated with phosphoric acid (H₃PO₄). Furthermore, the addition of adsorbent certainly increases the number of adsorption sites but, the dye cations have more difficulty approaching these sites due to crowding. In addition, a large quantity of adsorbent creates particle agglomerations, resulting in a reduction in the total adsorption surface area and, consequently, a decrease in the quantity of adsorbate per unit mass of adsorbent (Karim et al., 2010).

Effect of initial concentration

Fig. 3 shows the results of the effect of starting concentration on the kinetics of methylene blue adsorption.

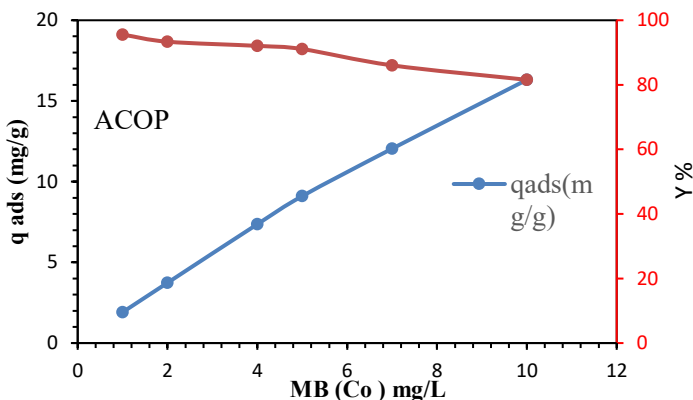


Figure 3: Influence of starting focus on the quantity adsorbed and the percentage of MB elimination, pH 4

Analysis of Fig. 3 shows that the quantity adsorbed increases from 1.91 to 16.31 mg/g (i.e. an adsorption efficiency of 95.57 to 81.55%) as the methylene blue concentration increases. This can be explained by the diffusion of methylene blue molecules, which increase in number towards the adsorption sites that are still free. Similar findings are presented by numerous studies, such as those conducted by Asmaa et al. (2010). These authors explain this by saying that an increase in dye concentration speeds up the diffusion of dye molecules from the solution to the adsorbent's surface. According to Khalfaoui et al (2012), the increase in initial ion concentrations is synonymous with an increase in the number of collisions between the ions in solution and those on the surface of the adsorbent, hence the intensification of the adsorption process. Unlike the quantity adsorbed, the adsorption rate decreases as the methylene blue concentration increases. This behaviour could be explained by the increase in the number of pollutant molecules in the solution compared with the active sites available. In addition, the ascending linear aspect of the adsorbed quantity curve indicates that the adsorbent has not reached saturation despite the increasing concentrations of methylene blue. To gain a better understanding of this phenomenon, the concentrations associated with the eliminated fraction were calculated (Table 3).

Table 3: Methylene blue concentration and elimination efficiency of both eliminated and residual

| [MB] Initial (mg/L) | [MB] Eliminated (mg/L) | [MB] Residual (mg/L) | Yield (%) |
|---------------------|------------------------|----------------------|-----------|
| 1 | 0.9557 | 0.0443 | 95.57 |
| 2 | 1.867 | 0.133 | 93.35 |
| 4 | 3.6824 | 0.3176 | 92.06 |
| 5 | 4.5535 | 0.4465 | 91.07 |
| 7 | 6.0221 | 0.9779 | 86.03 |
| 10 | 8.155 | 1.845 | 81.55 |

Modelling adsorption kinetics

Fig.4 demonstrates the outcomes of non-linear kinetic models used to study MB's adsorption onto activated carbon.

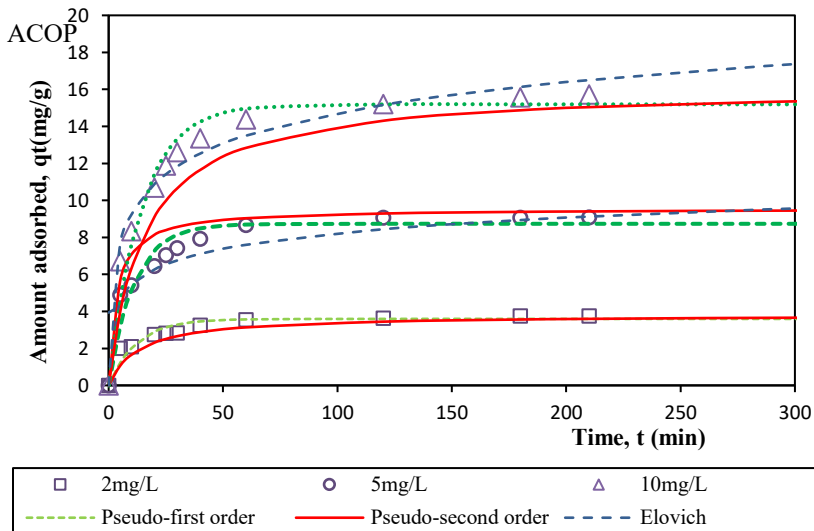


Figure 4: Kinetic models of adsorption

Analysis of Fig. 4 shows that the equilibrium time increases with the initial concentration. However, it stabilised at a concentration of 5 mg/L. An equilibrium time of 20 minutes was obtained for the 2 mg/L concentration, compared with 60 minutes for the 5 and 10 mg/L concentrations. Analysis of Fig .4 also shows that all the kinetic models appear to fit the curves derived from the experimental data. To better differentiate these models, the characteristic parameters of these models were calculated and summarised in Table 4.

Table 4: Elovich, pseudo-order 1 and 2 kinetic parameters for the adsorption of methylene blue on activated carbon

| C_0 (mg/L) | 2 | 5 | 10 |
|----------------------------------|-------|-------|-------|
| $q_{e,exp}$ (mg/g) | 3,75 | 9.09 | 15.73 |
| Pseudo-first-order model | | | |
| q_e (mg/g) | 3.59 | 8.73 | 15,19 |
| k_1 (min ⁻¹) | 0.081 | 0.08 | 0.069 |
| R^2 | 0.93 | 0.93 | 0.97 |
| Pseudo-second-order model | | | |
| q_e (mg/g) | 3.82 | 9.56 | 16.14 |
| k_1 (min ⁻¹) | 0.02 | 0.03 | 0.004 |
| R^2 | 0.89 | 0.69 | 0.90 |
| Elovich | | | |
| α (mg/g.min) | 3.09 | 10.29 | 11.01 |
| β (mg/g) | 1.953 | 0.82 | 0.4 |
| R^2 | 0.94 | 0.93 | 0.92 |

Table 4 shows that the theoretical MB adsorbed quantity values of all the kinetic models except the Elovich model are closer to the experimental data. In contrast to the pseudo second-order model, the pseudo first-order model's coefficients of determination for all concentrations are nearer unity. Consequently, the physisorption-based pseudo first-order kinetic model appears to be a good fit for explaining the methylene blue adsorption process as reported by Çalışkan et al. (2010).

Furthermore, a comparative study of the experimental adsorbed amount of methylene blue obtained in this study with those of other authors who have worked on the adsorption of methylene blue on different adsorbents (Table 5).

Table 5: Evaluation of different adsorbents' adsorption capacities in relation to MB Adsorbents

| | q_{exp} (mg/g) | References |
|---|------------------|--------------------------------|
| Banana pith | 04.6 | Kadirvelu <i>et al.</i> , 2003 |
| Sepiolite | 57.3 | Alkan <i>et al.</i> , 2008 |
| Rattan sawdust | 294.1 | Hameed <i>et al.</i> , 2007 |
| Coir pith | 05.8 | Kavitha and Namasivayam, 2006 |
| Pistachio shells | 129.0 | Hashemian and Shayegan (2013) |
| Attapulgate/bentonite | 168.6 | Liu <i>et al.</i> , 2014 |
| Mango seed kernel | 142.8 | Vasanth <i>et al.</i> , 2005 |
| Titanate nanotubes | 133.3 | Xiong <i>et al.</i> , 2010 |
| Coconut coir dust | 15.2 | Macedo <i>et al.</i> , 2010 |
| Coconut leaves | 149.3 | Jawad <i>et al.</i> , 2015 |
| Orange peel activated carbon ([MB]=10 mg/L) | 16,5 | This work |

The difference between the experimental adsorbed quantity values could be linked to the experimental conditions such as pH, MB concentration, quantity and type of adsorbent used.

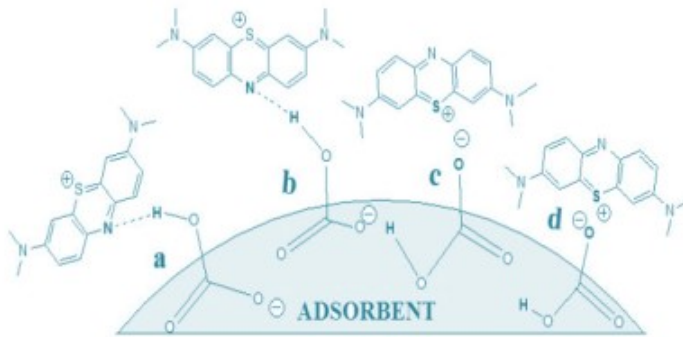


Figure 5: Mechanism of adsorption of Methylene blue

Various mechanisms of adsorption of methylene blue onto these adsorbents can occur. They are schematized in Fig.5 The interactions that can occur are of an electrostatic nature, based on ion exchange, hydrogen bond, complexation or precipitation.

Adsorption isotherm modelling

To explain the adsorption mechanism, non-linear Langmuir, Freundlich, and Langmuir-Freundlich models were used. The adsorption isotherm for MB on activated carbon is displayed in Fig. 6.

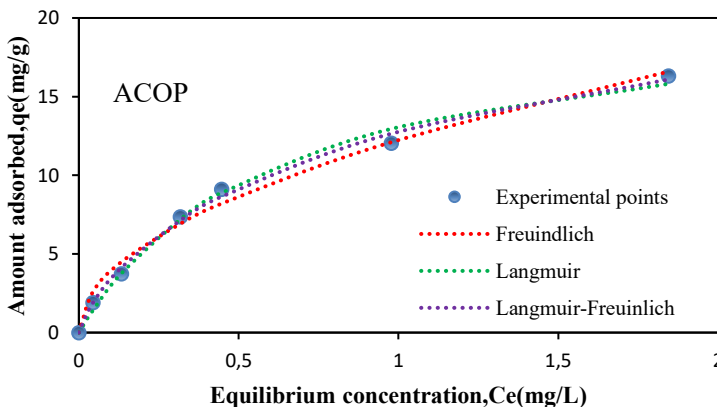


Figure 6: Models of methylene blue adsorption isotherms on activated carbon

Analysis of the curves in Fig.6 shows that the isotherm curves are of the L type. This suggests that adsorption of methylene blue becomes more difficult as the degree of surface coverage increases, but also that BM has a strong affinity for the activated carbon surface, particularly at low concentrations (Limousin et al., 2007). In order to identify the isotherm model best suited to the MB adsorption process, the characteristic parameters of the isotherm models were determined and are shown in Table 6.

Table 6: Methylene blue adsorption parameters on activated carbon in isotherm models

| Isotherm models with two parameters | | | | Isotherm models with three parameters | |
|-------------------------------------|-------------|----------------|-------------|---------------------------------------|-------------|
| Freundlich | | Langmuir | | Langmuir-Freundlich | |
| K _F | 12.237775 | q _m | 21.052129 | q _m | 27.823367 |
| n | 0.4969354 | n | 1.6349321 | b | 0.8106555 |
| | | KL | 0.0567215 | n | 0.7850119 |
| RE | 0.106381662 | | 0.059498999 | | 0.036451847 |
| R ² | 0.98 | R ² | 0.99 | R ² | 0.99 |

All the coefficients of determination are close to unity, whatever the isotherm model considered. As a result, there is a good correlation between the experimental data and the theoretical data. Nonetheless, the Freundlich and Langmuir models have larger relative error values than the Langmuir-Freundlich isotherm model. Therefore, the best model to simulate the methylene blue adsorption process is the Langmuir-Freundlich model.

Thermodynamic study

The thermodynamic parameters of methylene blue adsorption were determined from experimental results obtained at different temperatures. Fig. 7 shows the variation of $\ln K_d$ as a function of $1/T$.

The values of the thermodynamic parameters (ΔG° , ΔH° and ΔS°) obtained from these curves are presented in Table 7. The ΔG° values calculated are negative, indicating that the adsorption process is favourable. These ΔG° values also indicate the spontaneous nature of dye adsorption (Fayoud et al., 2015). The value of $\Delta S^\circ < 0$ would be at the origin of the decrease in disorder at the adsorbent/solution interface during adsorption, thus favouring, a well-organised distribution of the dye molecules at the adsorption sites.

Furthermore, the negative enthalpy value indicates the exothermic nature of the MB adsorption process on orange peel activated carbons (Zhang et al., 2013).

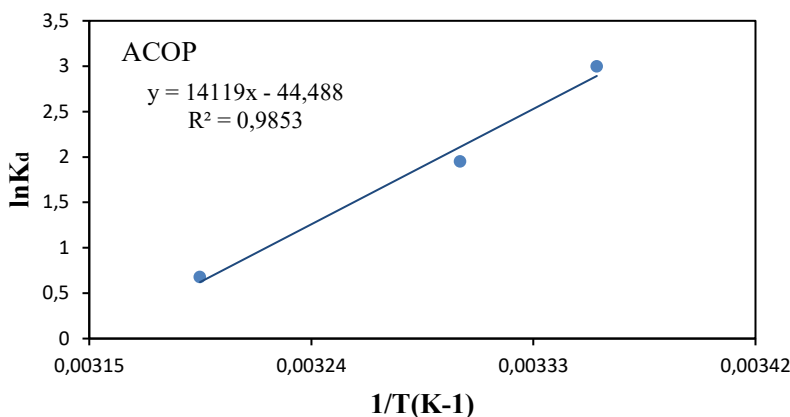


Figure 7: Variation of lnK_d as a function of 1/T

Table 7: Thermodynamic parameters (ΔG° , ΔH° et ΔS°)

| Température (K) | ΔH° (kJ.mol ⁻¹) | ΔS° (J.mol ⁻¹ .K ⁻¹) | ΔG° (KJ.mol ⁻¹) | R ² |
|-----------------|--|--|--|----------------|
| 298 | | | -7.16 | |
| 303 | -117.38 | -369.87 | -5.31 | 0.99 |
| 313 | | | -1.61 | |

CONCLUSION

The main objective of this study was to be part of an approach for the research of natural adsorption supports in the field of water treatment. It was also a matter of valorizing an agricultural waste of fruit widely available in Algeria, namely orange peels. In this view, activated carbon derived from orange peel was used to remove methylene blue (MB) from water.

The obtained results indicate that the activated carbon has interesting BM adsorption capacities, depending on different solution conditions, specifically the mass and concentration of the solution. The pseudo-order 1 kinetic model and the Langmuir-Freundlich isotherm model are what the adsorption process follows, according to modeling of the adsorption kinetics and isotherms. We also observe that the adsorption is an exothermic process.

The adsorption of methylene blue is likely to follow different mechanisms derived from physisorption or chemisorption.

Finally, the results obtained show the practical and economic interest of using an adsorbent such as orange peel to remove an organic dye from water.

Main ratings

G: free energy

H°: enthalpy

MB: methylene blue

pHPZC: pH at zero charge point

RE: relative error

S: entropy

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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