Kinetic Sorption of Methyl orange from aqueous solution onto activated Date Pits Waste

FELLA-NAOUEL ALLOUCHE[1]*, SONIA AIT SAADI[2], SARAH ROUMANE[2], ANISSA GHEZLOUN[1]
[1]Centre de Développement des Energies Renouvelables (CDER), Bp. 62
Route de l'Observatoire, Bouzaréah, 16340
Algiers,
ALGERIA

[2] Université des Sciences et de la Technologie Houari Boumedienne (USTHB).
Algiers,
ALGERIA

*Corresponding Author

Abstract: - In this study date pits with potential applications as effective local waste were selected as biosorbents to remove Methyl orange. For the first time, the date pits waste was chemically treated with phosphoric acid (H3PO4, 85%) and carbonized in a muffle furnace at 600 °C for 3 hours. Batch adsorption experiments for methyl orange were performed, and the experimental parameters such as contact time, initial dye concentration, and adsorbent dose have been varied in order to evaluate their effect on the sorption. It was found that the optimal value of the pH was 7.0, and the adsorption capacity for Methyl orange (MO) is 3 mgg-1. Adsorption at equilibrium was best described by the empirical Freundlich model. The kinetic data were well described by the pseudo-first-order model. This study demonstrated that date pit waste has a high sorption capacity to remove methyl orange in aqueous solution.

Key-Words: - date pits, sorption, methyl orange, activated carbon, isotherm data, modeling.

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1 Introduction

Today, water pollution has become a major issue and a worldwide environmental challenge. Wastewater frequently contains various toxic dyes that originate from industries such as chemical production, printing, and battery manufacturing. A global regulatory effort is necessary to prevent dyes from reaching wastewater or other water systems. At present, the literature shows that it is best to reduce the footprint of dyes in the production process. Most of these dyes are difficult to biodegrade and are known to be toxic and harmful to humans through the food chain and animals. Despite the fact that dyes are resistant to the treatment processes applied and exhibit a high resistance to degradation, various technologies are being developed and applied simultaneously, including adsorption, ion exchange, osmosis, and membrane etc., [1].

Adsorption is currently considered the most widely used treatment method for removing dyes from aqueous solution due to its simplicity, high effectiveness, ease of adsorbent recovery, and reusability [2].

There are several solid materials found in the literature, such as clays, activated carbon, zeolites, agricultural wastes, and industrial by products can be used in water decolorization processes. Activated carbon is the most significant carbonaceous material used in water treatment, [3].

According to published literature, a significant quantity of waste materials is considered as promising carbonaceous adsorbents for treating colored water, [4], [5], [6], [7], [8], [9].

To demonstrate the performance of date pits carbon to remove methyl orange, the present study aims to develop a biosorption system as an alternative and economical treatment.

The present study aims to develop a biosorption system as an economical and effective alternative for methyl orange removal by demonstrating the performance of activated carbon derived from date pits. This approach uses date pits as a low-cost, eco-friendly adsorbent with high adsorption capacity, making it a promising substitute for conventional treatment methods.

The objective of this study is to produce activated carbon from date pits waste using chemical and physical activation methods. The sorbent produced was evaluated for its effectiveness in removing methyl orange, and the results are compared with commercial activated carbon. The prepared activated carbon material was characterized with Fourier transform infrared spectroscopy (FTIR).

2 Experimental

2.1 Materials and reagents

The date pits waste was collected from Daglet Nour of the Ouled Djallal region (Southwest of Algeria). The harvested material was initially washed with tap water to remove any particles and then dried in sunlight for one week. After drying, the material was ground into a granular form. The date pits (DP) were sieved in different particle size ranges: G1(<125μm), G2(125-250 μm), G3(250-500 μm), G4(500-710 μm), and G5 (750-1000 μm).

For comparison, a commercial activated carbon (CAC) was used in this study in the form of granules (12-20 mesh) purchased from Sigma Aldrich with a surface area of 650 $m^2.g^{-1}$.

All chemicals and reagents used in this study were of analytical grade purity. The following reagents were used as received, without further purification: phosphoric acid (H_3PO_4, 85%), (Sigma-Aldrich). The solution pH was adjusted using appropriate amounts of molecular solution 0.1M (HCl/NaOH) purchased from Fluka.

2.1.1Standard solutions

Methyl orange (MO) $C_{14}H_{14}N_3NaO_3S$ molecular weight 327.33 $g.mol^{-1}$ from Merck. A stock solution of methyl orange (MO) at a desired concentration was prepared by dissolving the dye in demineralized water (Mill-Q) in an appropriate dilution. The dye concentration was then determined using a UV-visible spectrophotometer (Thermo Electron Corporation) at a wavelength of 460 nm. Figure 1 shows the chemical structure of Methyl orange (MO).

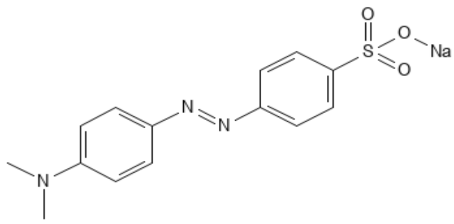

Fig. 1: Chemical structure of Methyl orange (MO)
Source: created by the authors

2.2.2 Preparation of Activated Carbon

Activated carbon is produced by a chemical and physical activation process of date pits waste. Waste materials are treated by activating the chemical agents using (H_3PO_4 20%) for 90 min. The obtained material is chemically treated with HCl solution (0.1 N) and kept at room temperature for 90 min, and then the sample was filtered after washing several times with distilled water until a neutral is reached and dried. The material was carbonized under airflow for 180 min at 600°C. The resulting material is repeatedly washed with tap water. Following washing, the samples were dewatered and dried in an oven at 105°C for about 24 hours. The dried, prepared material is considered activated date pits (ADP). On the other hand, a control commercial activated carbon was used as a comparison in granular form to remove Methyl orange (MO) from water was examined with regard to their sorption kinetics and isotherms were examined.

2.2.3 Batch Sorption experiments

Batch sorbent experiments of the activated date pits were investigated to study pH and contact time. The effect of pH to remove (MO) on activated carbon was studied in the pH range from 2 to 7 with an initial dye concentration of 10 mg/L. Adsorption kinetics were investigated for initial concentrations of 5, 10, and 25 mg/L in 250 mL glass vessels. The mixture was shaken at a constant temperature of 25 °C at 200 rpm for 24 h and then filtered through filter paper, and the absorbance was analyzed using a UV-visible spectrophotometer of the THERMO ELECTRON CORPORATION to measure the absorbance at the analytical wavelength corresponding to the maximum absorption, and all experiments were performed in duplicate.

Equilibrium adsorption was studied with the initial concentrations varying from 5 to 100 mg/L. The amount of Methyl orange (MO) on the activated carbon was calculated from the following equation:

$$q_e = (C_0 - C_e) \times V/m. \quad (1)$$

C_0: Initial (MO) concentration in mg/L; C_e: (MO) concentration at equilibrium. m: Mass of biomass in g; V: Volume of dye solution in L; q_e: sorption capacity at equilibrium (mg g^{-1}).

3 Results and discussions

3.1 Characterization of adsorbents

FTIR Spectra

The adsorption bands indicate the presence of the most important functional groups: alkane, aldehyde, aliphatic, ketone, aromatic, nitro groups, and ester. Figure 2 shows the FTIR spectra of the (ADP) and (CAC) before and after methyl orange (MO) sorption for a 400-4000 cm^{-1} wavenumber range. The peaks observed before (MO) sorption at 2964 cm^{-1} and 2970 cm^{-1} correspond to the symmetric and asymmetric C-H stretching vibrations with strong intensity, belonging to alkane groups (CH_3). Around 2880 cm^{-1}, a weak intensity is noted attributed to aliphatic –C-H groups. An absorption of variable intensity at 1696 cm^{-1} confirms the presence of the C=O bond associated with aromatic ketone groups, [9]. Four medium intensity at 1575 cm^{-1} correspond to C=C bonds, confirming the presence of aromatic groups. A strong intensity C-O bond appears at 1212 cm^{-1}, suggesting the existence of acid groups. The peak at 1073 cm^{-1} indicates the presence of a primary alcohol group with variable intensity.

The most significant changes after adsorption of methyl orange (MO) on activated date pits (ADP), as shown in Figure 2. Strong intensity bands are observed at 2884 and 2971 cm^{-1} with a more pronounced profile compared to the profile of (ADP) without (MO) dye.

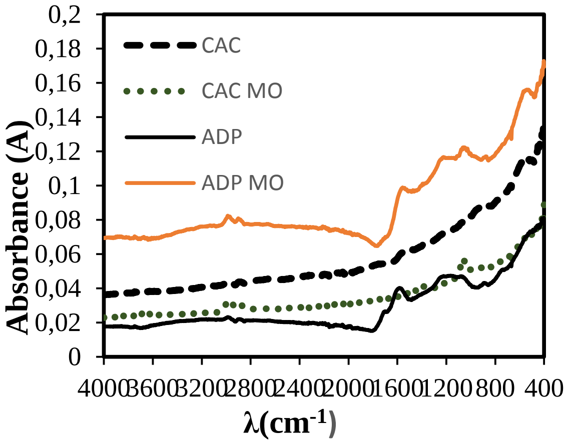

Fig. 2: Comparative FT-IR Spectra of the (ADP) / (CAC) before and after Methyl orange (MO) sorption
Source: created by the authors

This suggests the involvement of alkane functional groups(CH_3). Additionally, intense peaks at 1221 and 1051 cm^{-1} are attributed respectively to acidic groups and ester groups involving C-O bonds for both groups. When comparing the peak after (MO) sorption, the disappearance of certain bands around 1696 cm^{-1} confirms the loss of the C=O stretching band assigned to aromatic ketone groups. The disappearance of four medium bands at 1575 cm^{-1}, which are associated with C=C bands, was also observed, confirming the presence of aromatic groups. This supports the involvement of these groups in the adsorption of the (MO) dye. It was noted that most bands at 1051, 1221, 2884, and 2971 cm^{-1} became more intense, likely due to the participation of ester, acid, and alkane functional groups, respectively. According to [10], this type of profile indicates that there are no substantial changes on the surface of the adsorbent. For commercial activated carbon, the FT-IR spectrum for Methyl orange (MO) dye adsorption, peaks between 2877 and 2954 cm^{-1} indicate high intensity with symmetrical and asymmetrical C-H stretching vibrations from alkane (CH_3) groups. The peak at 1370 cm^{-1} reveals a high intensity nitro (aliphatic) functional group featuring a C-NO_2 bond. A medium intensity peak near 1208 cm^{-1} confirms the presence of an aliphatic amine group with a C-O bond. The peak at 1037 cm^{-1} corresponds to an ether group with a C-O bond, showing variable intensity. The presence of these functional groups on the surface of the material improves its sorption capacity.

3.1.1 pH effect

Methyl orange (MO) is a pH indicator from the family of azobenzene derivatives. According to the literature, a distinct color change occurs at its pH transition range, approximately between 3.1 and 4.4. This change results from the protonation of the azo group, which forms an azonium ion stabilized by resonance (mesomeric effect). This protonation changes the electronic structure of the molecule, resulting in a visible color change, from red in acidic conditions to yellow in alkaline conditions. Adsorption efficiency of methyl orange on the prepared activated carbon (ADP) and commercial activated carbon (CAC) are presented in Figure 3.

The date pits exhibit acidic characteristics, with a point of zero charge (pHpzc) of 2.57. At different pH values, the surface charge of the adsorbent varies accordingly. Specifically, when the pH is higher than the pHpzc, the surface of the dae pits becomes negatively charged, which promotes the attraction of cations. Conversely, when the pH is lower than the pHpzc, the surface charge is positive, favoring the attraction of anions.

Adsorption capacity for both (ADP) and (CAC) was determined to be 1,65 and 1.80 mg/g, respectively, at an optimal pH of 7. The corresponding elimination yield of 91.55% for (ADP) and 99,6% for(CAC).

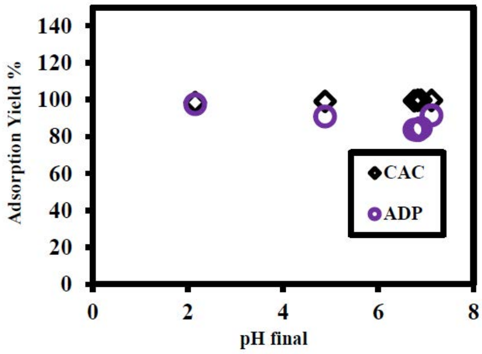

Fig. 3: Influence of pH on Methyl orange (MO) sorption using granular activated carbon date pits (ADP) and commercial activated carbon (CAC) : Sorption capacity (a) and sorption rate (b) (V: 50 mL; C0: 10 mgMOL−1; Sorbent dosage, SD: 1g L−1; PS: G3)

Source: created by the authors

3.1.2 Adsorption Kinetics

Adsorption removal efficiency of Methyl orange on (ADP) and commercial activated carbon (CAC) is presented in Figure 4 in the form of a graph of qt versus time. As can be seen, the adsorption is fast for both adsorbents, and equilibrium was achieved after 60 minutes. The adsorption is rapid in the first and declines over time. The same conclusions are observed by [9]. When contact time is prolonged, the number of active sites available on the surface of the material decreases and eventually reaches equilibrium, [11]. The rate at which dyes are removed from the aqueous solution was determined using two common kinetic rate equations [12], Pseudo-First Order (PFO), [13], and Pseudo-second order (PSO), [11].

Pseudo-First order (PFO) model is given by equation (2)

$$\ln(q_e - q_t) = ln(q_e) - k_1 t \quad (2)$$

Pseudo-second order (PSO) is presented in its linear form in equation (3)

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{qe} \quad (3)$$

where qe and qt are the equilibrium adsorption capacity (mgg^{-1}) and the adsorption capacity (mgg^{-1}) at time t, respectively.

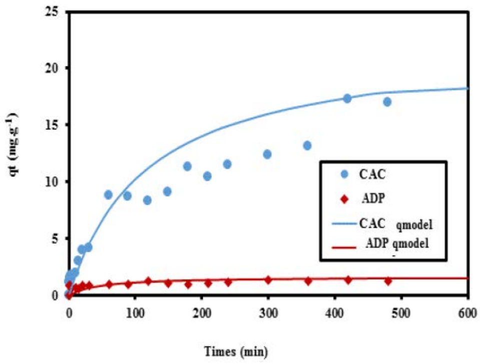

Fig. 4: - Adsorption kinetics of Methyl orange (MO) on (ADP) and (CAC) fitted by (PSO) model (C0: 25mg/L; pH: 7; SD: 1g/L; V: 0.200 L; T: 25°C)

Source: created by the authors

K_1 (min^{-1}) and K_2 ($gmin\ mg^{-1}$) are the kinetic constants, respectively. The parameters of the uptake kinetics models are listed in Table 1.

The results indicate that both activated date pits (ADP) and commercial activated carbon agree with the pseudo-first-order kinetic model (PFO), with a better R^2 correlation coefficient for expressing the order of the dye adsorption kinetics (MO).

Table 1. Kinetic parameters of Methyl orange (MO) onto activated date pit (ADP) and commercial activated carbon (CAC)

Kinetic model	Parameters	Adsorbent	
		ADP	CAC
Pseudo 1st Order **(PFO)**	$q_e(mgg^{-1})$	3.46	24.09
	k_1	0.0021	0.004
	R^2	0.981	0.992
Pseudo 2 sd Order **(PSO)**	$qe(mgg^{-1})$	3.55	20.77
	k_2	0.0011	0.00026
	R^2	0.886	0.949

Source: created by the authors

3.1.3 Isotherm

The equilibrium adsorption isotherms of (MO) on the activated date pit (ADP) and commercial activated carbon (CAC) are presented in Figure 1 (Appendix).

In this study, two empirical models were applied to illustrate and evaluate the experimental data. The principal methods are based on the [14], [15], equations which were used to predict adsorption capacity, which can be represented as follows:

$$\frac{1}{q_e} = \frac{1}{k_l q_m} + \frac{1}{c_e} + \frac{1}{q_m} \quad (4)$$

$$logq_e = \log K_F + \frac{1}{n}\ logC_e \quad (5)$$

Where q_m (mg/g) is the maximum sorption capacity, and K_L is a Langmuir constant (Lmg^{-1}), q_e is the amount sorbed at equilibrium (mg/g), and Ce is the equilibrium liquid-phase concentration (mg/L). Where K_F ((mg/g)(L/mg)1/n) and n are empirical constants related to the adsorption intensity, which depends on the heterogeneity of the material. Based on the R^2 value, it can be noted that the isotherm Freundlich model is more suitable than the isotherm Langmuir model, with the highest correlation coefficient of 0,897 and 0,818 for the Langmuir model. The maximum capacity q_m for MO adsorption obtained by activated date pits (ADP) reached 3 mg/g. This is why the Freundlich model confirms the heterogeneity of the sorbent surface, which means that the adsorption takes on an exponential character. The constant parameters for the two models are shown in Table 2 (Appendix). Comparing the obtained results with commercial activated carbon (CAC), it is shown that sorption of Methyl orange is closer to the Langmuir model and takes an asymmetric character with a maximum adsorption capacity equal to 67.11 mg/g and R^2 of 0.917. Additionally, the sorption capacity for (CAC) is assigned to the high specific surface area and adsorption via pore filling mechanisms, [16]. In this study, commercial activated carbon (CAC) with a specific surface area of 650 $m^2.g^{-1}$, was used as a reference to adsorb Methyl orange. The Langmuir model describes a monolayer adsorption that occurs on the biosorbent surface with identical homogeneous sites, an instantaneous and reversible reaction. However, under the studied conditions, the sorption capacity of (MO) onto (ADP) is considerably lower than that of other adsorbents obtained from agricultural waste. Several adsorbents are used for (MO) sorption, including a blend of carrot and potato peels, [17], waste orange and lemon peels, [18], bamboo hydrochar, [19], and raw fava bean peels, [20].

4 Conclusion

A comprehensive study was conducted to understand the sorption properties of Methyl orange on activated date pits waste using phosphoric acid activation. The activation was performed at 600°C for 180 min under an airflow condition. Complete batch sorption was carried out involving optimization of the parameters (pH, contact time). The equilibrium data were best described with the Freundlich model for (ADP) and the Langmuir model for (CAC), with a sorption capacity of about 3 mg/g for (ADP) and 67.11 mg/g for (CAC). Kinetics of Methyl orange sorption followed a pseudo-first order model for (ADP) and (CAC), indicating that physisorption was the dominant mechanism. FT-IR characterization allowed the functional groups before and after (MO) sorption. Comparison of the maximum Methyl orange onto (ADP) with the (CAC) indicates that alternative operational conditions should be investigated to overcome the materials limitations, particularly in enhancing porosity, increasing the specific surface area, and improving the maximum adsorption capacity of (MO). Furthermore, this work opens numerous possibilities related to the research and development of new adsorbents derived from natural and renewable sources, aimed at treating low-color effluents from the textile industry.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- F-N Allouche: Conceptualization-Methodology–Investigation-Writing-Original draft-Visualization.
- S. Ait Saadi: Investigation.
- S. Roumane: Investigation.
- A. Guezloun: Visualization.

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Conflict of Interest

The authors have no conflicts of interest to declare.

APPENDIX

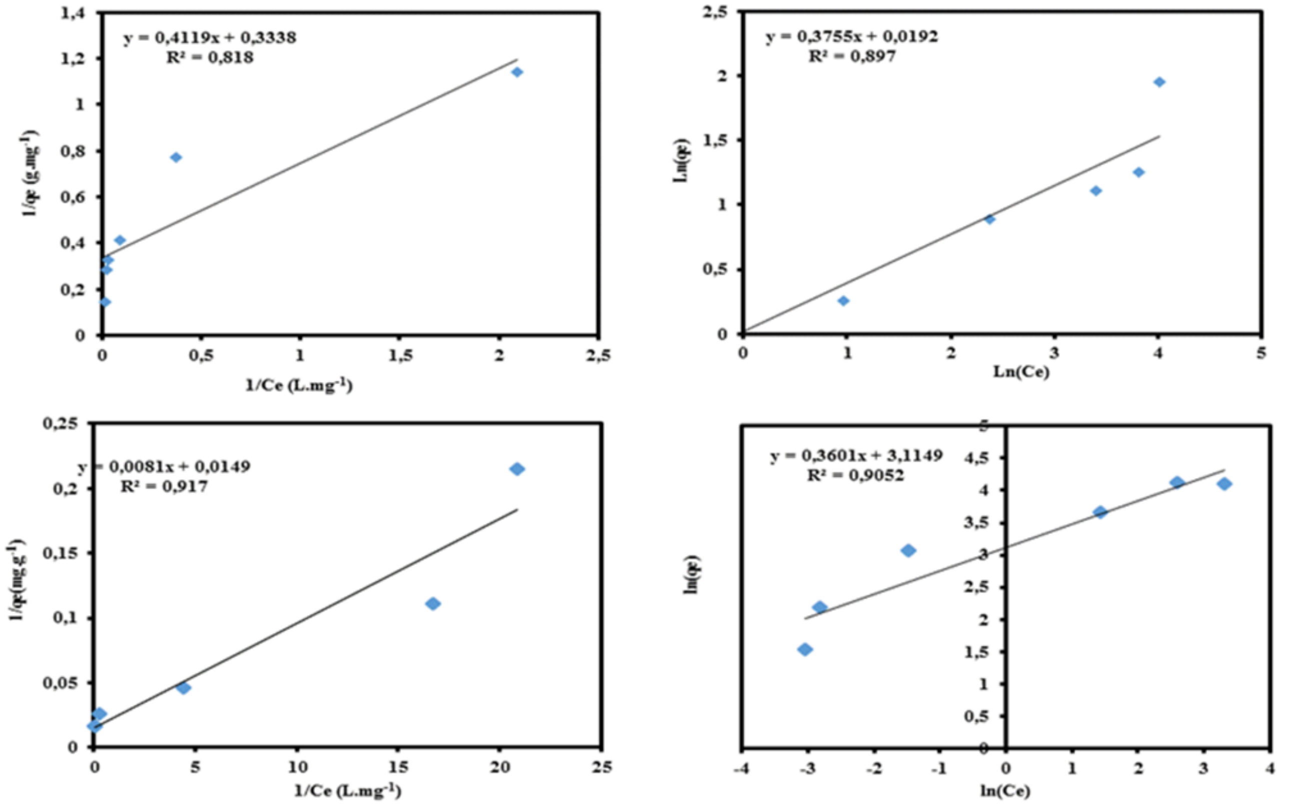

Fig. 1: Plots of the linear regression of Langmuir and the Freundlich isotherm models for the sorption of Methyl Orange (MO) onto activated date pits (ADP) and Commercial Activated Carbon (CAC)
Source: created by the authors

Table 2. The constants of Langmuir and Freundlich parameters on (MO) sorption by (ADP) and (CAC)

Langmuir				**Freundlich**		
Material	q_m	K_L	R^2	K_F	n	R^2
	($mg.g^{-1}$)	($Lm.g^{-1}$)		($mg.g^{-1}$)		
(ADP)	3	0.81	0.818	1.019	2.67	0.897
(CAC)	67.11	1.84	0.917	2.51	2.77	0.905

Source: created by the authors