Adsorption of Methyl Orange from Wastewater by using Biochar

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Abstract

The biochar prepared from sawdust raw material was applied in this study for the treatment of wastewater polluted with methyl orange dye. The effect of pH (2-11), initial concertation (50-250 mg/L) and time were studied. The isotherm of Langmuir, Frendluch and temkin models studied. The Langmuir model was the best to explain the adsorption process, maximum uptake was 136.67 mg/g at $25C^o$ of methyl orange dye. Equilibrium reached after four hours of contact for most adsorbents. The values of thermodynamic parameters ΔG were negative at various temperatures, so the process spontaneous, while ΔH values were 16683 j/mol and ΔS values was 60.82 j/mol.k.

1- Introduction

Water is the most important source for human life, where the human use it for drinking, washing, agriculture and other uses to support his life. Water can be contaminated when the quality or composition of water is different due to the activity of humans.

Increasing industrial activities increase environmental pollution problems [1].

There are a lot of substances that can pollution water such as inorganic acids, salts, alkali, organic matter, and dyes. Wastewaters contaminated with dye represent the most amounts of the discharged industrial water.

Water polluted happened due to the use of large quantities of water in manufacturing processes and the first clear sign of water-polluting is color because of dyes [2].

Dyes are widely used by a human from antiquity and it was extracted from plants such as indigo and animals such as carmine, cochineal.

Humans depended on the natural sources of dyes until 1856, after that, William Henry Perkin trying to synthesize artificial quinine, in order to treat malaria and using allyltoluidine, has succeeded in produce aniline: a basic dye. This was the discovery of the first material synthetic dye [3].

Dyes are synthetic organic compounds with complex molecular structures and high molecular weights. These properties increase the difficulties of the treatment of dye wastewater.

In general, the main modes of classification of dyes are based either on their chemical constitution or on their methods of application to different substrates such as textile fibers, paper, leather, plastics, etc.

The different dye classes of these dyes are defined by their auxochromes, and are essentially, which is mordant dyes, direct dyes, disperse dyes, insoluble or developed azo dyes, vat dyes, reactive dyes, acidic or anionic dyes, and basic or cationic dyes. This classification allows dyers, to know the suitable dye required. It's clear that information like solubility in the dye bath, the affinity for the chosen fiber and the nature of the fixation are required for this kind of industry [4].

Dyes are widely used in sweets, fruit paste, green liquor, pastry both for cakes and pies as for biscuits syrup and lemonade; the cheese dairy, butter and margarine (yellow coloring) [5]. Releases of textile effluents, carrying dyes, into rivers, can greatly harm animals, plants, and micro-organisms living in these waters. This toxicity, therefore, could be related to the decrease of dissolved oxygen in these media. Moreover, their very low biodegradability, due to their high molecular weight and their complex structures, give them a character toxic that can be high or low.

As a result, they can persist for a long time in this medium, thus generating significant disturbances in the different mechanisms existing natural resources in the flora (decrease in the self-purification power of rivers, inhibition of the growth of aquatic plants and in wildlife (decimation of certain categories of fish, microorganisms) [6]. The dangers of textile waste are partly short-term (obvious dangers) and secondly, in the long run.

Depollution techniques most commonly fall into three categories: physical processes involving precipitation methods (coagulation, flocculation, sedimentation), reverse osmosis-filtration, adsorption (on biochar ,activated carbon, zeolite….etc) and then incineration; chemical processes, with oxidation (oxygen, ozone,

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oxidants such as NaOCl, H2O2), the complex metric methods, the use of the resin ion exchange and then the reduction (using for example Na2S2O); biological processes, using aerobic treatment (with oxygen) or anaerobic treatment (without oxygen) [7].

Among the above mention of methods, adsorption is a process of transferring the pollutant from its source environment or fluid phase (liquid or gaseous) to the surface of the adsorbent (solid). This mode of treatment remains very limited to the elimination of different dyes. Only, the cationic dyes, mordant dyes, dispersed, reactive and vat are eliminated by this technique[8].

Adsorption occurs mainly in four stages. Below are the different areas in which the molecules can be found organic or inorganic adsorption processes: diffusion of the adsorbate, from the external liquid phase, to that located in the vicinity of the surface of the adsorbent; extra-granular diffusion of the material (transfer of the solute through the liquid film to the grain surface; intra-granular transfer of matter (transfer of matter into the structure porous outer surface of seeds to active sites; and adsorption reaction in contact with active sites. Once adsorbed, the molecule is considered immobiled [9], [10].

In the last years, biochar has become very important in agriculture in terms of improving the quality of soil and productivity of agricultural crops as well as in food preservation. Biochar is a granular and porous material, which is usually produced by the pyrolysis process of the raw materials at conditions that have no oxygen.

The surface area and the porosity of biochar are usually high, so it is used as an absorbent to adsorb the contaminants from aqueous solutions as in the activated carbon. In this study, biochar was prepared from low cost and locally available raw material represented by sawdust.

The characters surface area and total pore volume of the biochar were 58.845 m2/g and 0.061 cm3/g. Therefore, the biochar has great importance in addressing and controlling the environmental pollutants [11].

2- Experimental Work

2.1. Preparation of adsorbate

Anionic dye used was Methyl orange (Sodium4-{[4 (dimethylamino) phenyl]diazenyl}benzene-1-sulfonate) purity of 99.9% with molecular weight of 327.33 g/mol, was used as adsorbate. The chemical formula of Methyl orange was C14H14N3NaO3S. The solutions concentration were prepared by adding a known weight of dyes to 100 ml distilled water. The methyl orang in the aqueous solution was analyzed using UV-Visible Spectrophotometer. The wavelength corresponding to maximum absorbance was 466 nm.

2.2. Batch Experiments

The Methyl orange uptake experiments were conducted as follows: weighting 0.02g of biochar with particle size about 200 μm and then added to the flask containing 40 ml of dye solution. The flasks were put in a shaker at speed 150 rpm at room temperature.

After that, samples were filtered and the concentration of dye was calculated using UV-Visible Spectrophotometer. The adsorption variables study was: time (15-360 min), initial concertation (50-250 ppm) and pH (2-11). Also, the adsorption isotherm models Freundlich, Langmuir and Temkin, were used to fit data of experimental equilibrium isotherm data. The adsorption isotherms for the aqueous solution with various initial concentrations are 50,100, 150, 200, and 250 ppm for 24 hours. Thermodynamic parameters were studied at different temperatures (25-45 C°). The dye adsorption at equilibrium, q_e (mg/g), was calculated as following shown in Eq. (1) [12]:

$$qe = \frac{(C_o - Ce)V}{W} \tag{1}$$

Where: C_o (mg/l) is the primary concentration of dyes.

C_e (mg/l) is the equilibrium concentration of dyes.

V (l)is the dye solution volume.

W (g) is the weight of biochar.

3- Results and Discussion

3.1. FT-IR Analysis

The biochar was studied by infrared spectroscopy FTIR to determine the different chemical functions present on the surface of biochar before and after the adsorption process. It is a complementary technique that focuses in general on the study of samples at a molecular level.

Fig. **1** shows the FTIR spectra of biochar before and after adsorption of methyl orange. Generally, the bands are due to different surface groups. A broad absorption band around 3,423 cm-1 is attributed to the O-H stretching vibration of hydroxyl functional including hydrogen bonding due to adsorbed water. The disappearance of the hydroxyl group is due to the adsorption of the methyl orange on the surface of the biochar. The decrease of the intensity came from the extra layer of methyl orange which increases the absorption of the infrared spectrum, leading to a decrease in the transmission intensity.
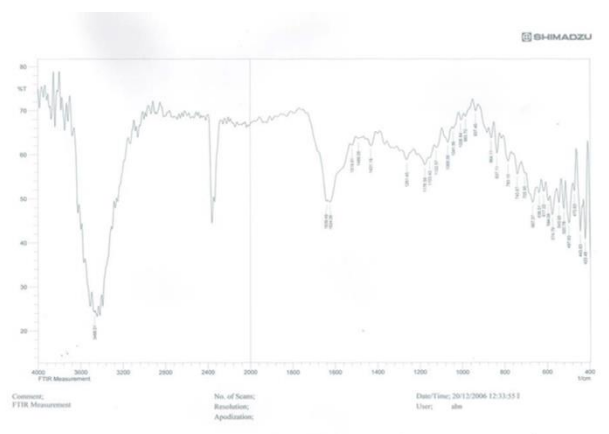
(a)
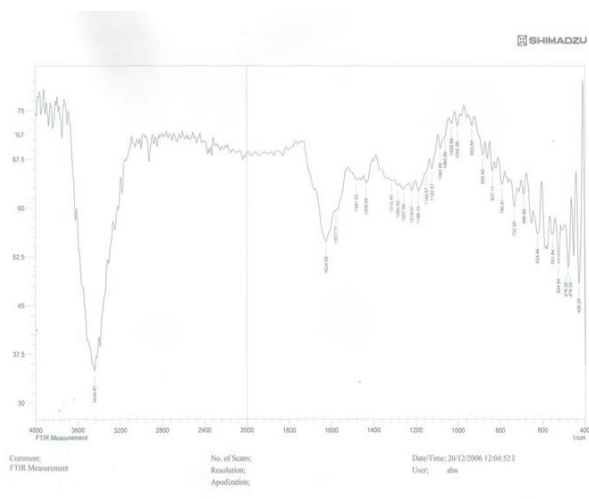
(b)

Fig. 1. FTIR peaks of biochar, (A) before adsorption, (B) after adsorption

3.2. PH Effect

The aqueous solution pH parameter is an important factor affects the dye adsorption capacity. Therefore, methyl orange dye adsorption on the biochar was tested in the pH value range (2-11). The results of the initial pH effect on the dye uptake are shown in Fig. **2** Figure 2 shows that the adsorption is favored by decreasing the initial pH. For initial pH values ranging from 3 to 5, sorption is accompanied increase by the initial pH decrease. On the other hand, when the initial pH varies from 6 to 11, the sorption is accompanied decrease by an increase in initial pH. This may be referring to the competition from available excess OH –ions with the dye anionic molecule for the active sites. While, acidic conditions are favorable for the adsorption between the dye and adsorbent because in case exist high electrostatic, attraction between the anionic dye and the surface charger positively of the adsorbent under acidic conditions [13].
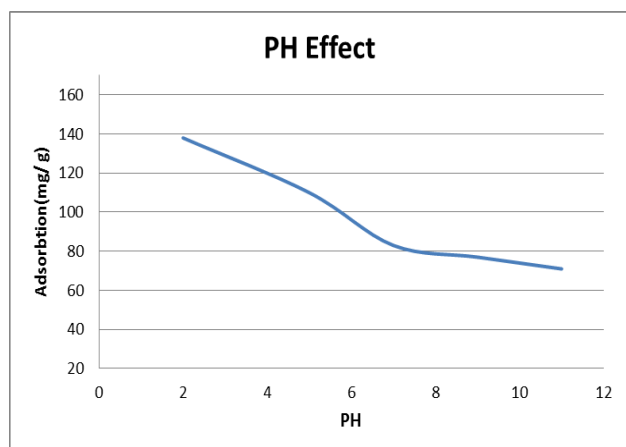

Fig. 2. pH effect on the adsorption of MO (W=0.02 g/40 ml, initial concentration = 100 mg/l, T= 25˚C, speed= 150 rpm, time=240 min, biochar particle size= 200 μm)

3.3. Initial Concentration Effect

The capacity of adsorption for the biochar at various initial methyl orange concentrations is shown in Fig. **3**

When the initial dye concentrations increased up to 250 mg/L, it is observed that the amounts of uptake increased. This may be due to the concentration that provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phase.

Hence a higher initial concentration of dye will enhance the adsorption process, this agrees with [12], [13],[14].

The amounts of adsorption of MO increased from 48 to 121 mg/g, when the initial dyes concentration increased from 50 to 250 mg/L.
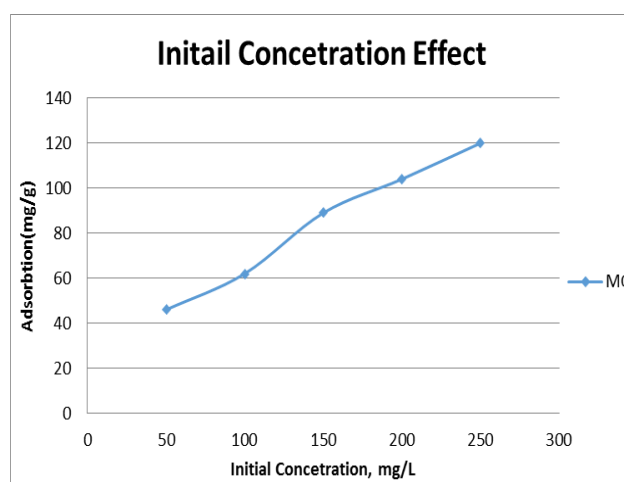

Fig. 3. Effect of initial concentration on the uptake of MO (W=0.02 g/40 ml, T= 25˚C, speed= 150 rpm, time=240 min, biochar particle size= 200 μm)

3.4. Contact Time Effect

The contact time effect was studied at time range of (0.15–6 h) at an initial dye concentration of 100 mg/L is explained in Fig. **4**.

The amount of adsorbed increased rapidly in initial stage up to 2 hrs, and then gradually decreased with further process of the adsorption.

Finally, equilibrium achieved after 4 hrs and adsorption uptake for MO was 75 mg/g. The rapid adsorption in initial stage can be attributed to higher availability of active sites on adsorbent surface.

With the passage of time, these active sites are gradually occupied by dye molecules which lead to decrease in number of active sites available for the residual dye molecules in solution. Similar behavior has been reported in previous literature [13], [15].
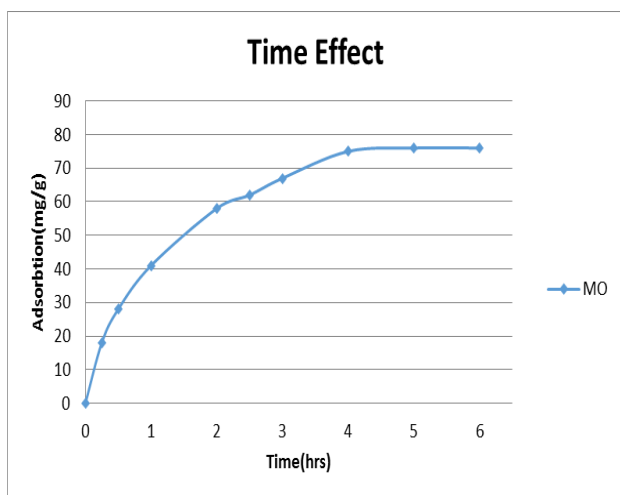
Fig. 4. Effect of agitation time on the uptake of MO (W=0.02 g/40 ml, initial concentration = 100 mg/l, T= 25˚C, speed= 150 rpm, biochar particle size= 200 μm)

3.5. The Thermodynamic Parameters

The change of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are the characteristics of thermodynamics of the adsorption system.

The value of Gibbs's free energy, enthalpy, and entropy obtained from the intercept and slope of drawing data of LnKc versus 1/T as shown in Fig. **5** where thermodynamic parameters calculated from Eq. (2) and Eq. (3).and the Kc calculated from Eq. (4) [16].

The thermodynamic parameters tabled in Table **1**. The positive values of enthalpy for Methyl Orange indicate that the adsorption is endothermic and this value is less than 20 KJ/mol which refers to phsicosorption process, while the value of entropy is positive reflects the affinity of MO for the biochar where the degree of disorder increases.

The value of free energy of the thermodynamic process (ΔG) at the different temperatures was negative and rise with heating, which mean spontaneous and favorable adsorption at high temperature.

$$\ln K_C = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \quad (2)$$

$$\Delta G^{\circ} = -RT\ ln K_c \quad (3)$$

$$K_C = \frac{Cad}{Ce} \quad (4)$$

Where: Kc: is the equilibrium constant, C_{ad} is the concentration of MO adsorbed on the adsorbent per liter of the solution (mg.l^{-1}), Ce: is equilibrium concentration of MO in the solution (mg.l^{-1}), R: is the universal constant gas (8.314 J/mole. K), T: is the solution temperature (K)
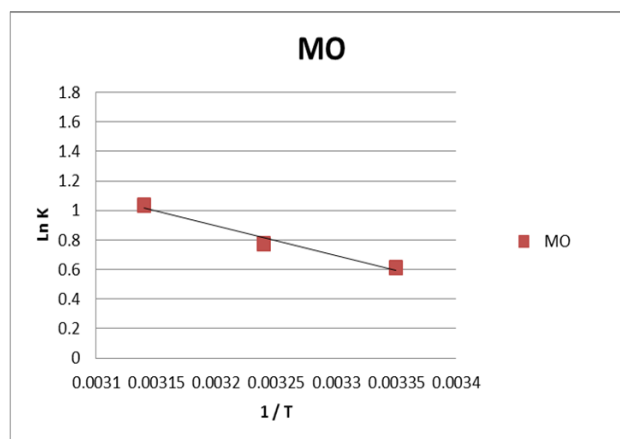

Fig. 5. Thermodynamic adsorption of MO on biochar.

Table 1. The thermodynamic parameters for the sorption of MO on biochar

Adsorbent	T,*K*	ΔG ,*Kj/mol*	ΔH,*Kj/mol*	ΔS, *j/mol.k*
Methyl Orange	298	-1440.67		
	308	-2048.86	16683.7	60.82
	318	-2657.1		

4- Adsorption Isotherm Models

The adsorptive capacity of dye by biochar was studied using the initial concentration of dyes. The experimental conditions are identical to those used previously.

The results obtained were fitted to by three empirical models: Langmuir, Freundlich and temkin. These three models are a widely used tool for the adsorption mechanism and the quantification of the adsorbent / adsorbate affinity.

These linear models are plotted in Fig. **6**, listed in Table **2** and the results are shown in Table **3**.

It is observed that the adsorption of methyl orange by bio char is satisfactorily described by the Langmuir model with R^2 (0.9958) which is higher than the value that given by the Freundlich model with R^2(0.9778) and Temkin with R^2(0.9578).

This means monolayer coverage of methyl orange molecules on biochar surface. The max absorption capacity for MO on bio char was 136.67 mg/g.
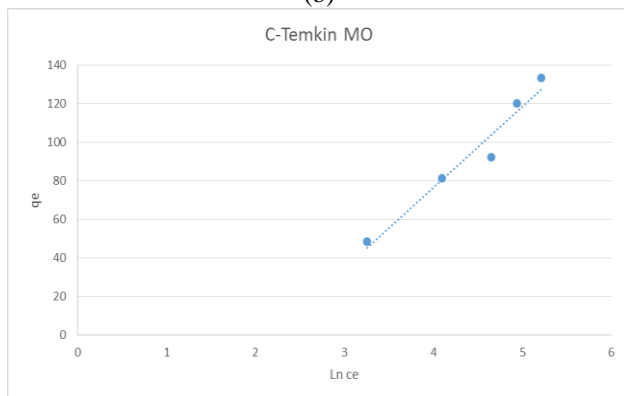
The maximum adsorption uptake for Langmuir model for methyl orange is compared with the other different source of adsorbates as shown in Table **4**.
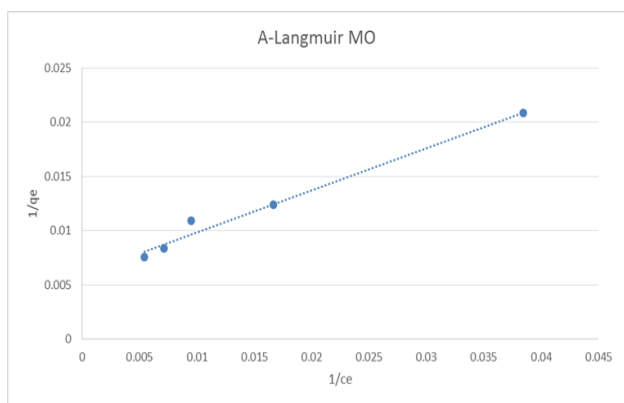
(a)
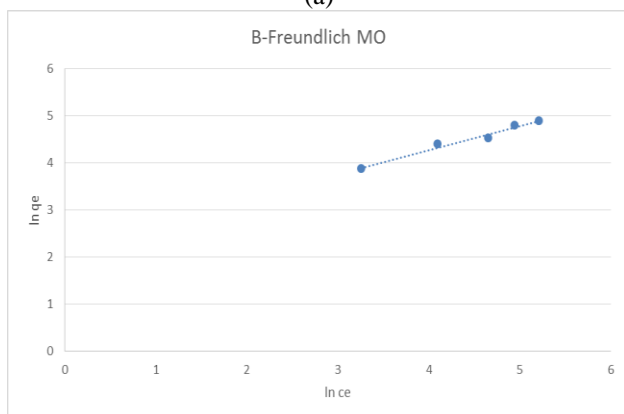
(b)

(c)

Fig. 6. Isotherm of MO on biochar (A) Langmuir (B) Freundlich(C)Temkin

Table 2. Equations for the adsorption isotherm models

Model	Equation used	Reference
Langmuir Isotherm	$\frac{1}{q_e} = \frac{1}{q_m\,kl\,C_e} + \frac{1}{q_m}$	[17]
Freundlich Isotherm	$Log\ q_e = \log K_f + \frac{1}{n}\ \log C_e$	[17]
Temkin isotherm	$q_e = B \ln A + B \ln C_e$	[17]

Table 3. Parameters of isotherms model for adsorption of MO

Type of isotherm	parameters	Methyl Orange
Langmuir	q_m	136.67
	K_L	0.021
	R^2	0.9958
Freundlich	k_f	9.297
	n	1.958
	R^2	0.9778
Temkin	A	0.112
	B	42.202
	R^2	0.9578

Table 4. The maximum adsorption capacities of MO Comparison with various adsorbents

Adsorbent	Capacity of Adsorption (mg/g)	References
Acid modified carbon coated monolith	147.06	[18]
Activated carbon	238.1	[19]
Chitosan	34.83	[20]
Biochar	136.67	The current study
Modified Chitosan	89.30	[21]

5- Conclusions

The results obtained show that the biochar could be applied as a good adsorbent for methyl orange dye removal from an aqueous solution. It is observed that the adsorption of methyl orange by biochar is described by the Langmuir model with R2 (0.9958) which is higher than the value that given by the Freundlich model and Temkin .pH is the most important variable for adsorption anionic dyes on biochar. Methyl orange uptake was 138.2 mg/g at initial concertation 100 ppm. The thermodynamic parameters (ΔG°, ΔH°, and ΔS°) at temperature range of 298-318 k explained that the process of adsorption is endothermic. The sorption process was phsicosorption process, spontaneous and favorable adsorption at high temperature.

Nomenclature

A: Temkin constant (L/g).
B: Heat of adsorption (J/mol).
C_{ad}:   Adsorbed concentration, mg/L
C_e: Concentration at equilibrium, mg/L
C_i: Initial concentration, mg/L
ΔG°:   Gibbs free energy, KJ/mole
ΔH°:   Enthalpy change, KJ/mole
K_C :   Equilibrium constant
K_f :   Freundlich's constant., mg/g
K_L: Langmuir Adsorption constant coefficient
M: Mass of adsorbent, g
1/n: Constant indicative of the intensity of the adsorption

q_e: Sorbed dyes molecules on the adsorbent, mg/ g
q_m: The maximum sorption capacity for monolayer coverage, mg/ g
R: Universal gas constant
$\Delta S°$: Entropy change, J/K. mole
T: Temperature, K
V: Volume, L

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امتزاز صبغه المثيل البرتقالي من المحلول المائي باستخدام الفحم الحيوي

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الخلاصة

تم استخدام الفحم النباتي المحضر من نشارة الخشب في هذه الدراسة لمعالجة المياه الملوثة بصبغة المثيل البرتقالي. تمت دراسة تأثير الأس الهيدروجيني (2−11) وتأثير التركيز الأولي (50−250 ملغم / لتر) والوقت. كما تم دراسة موديلات الايزوثيرم لانكماير وفرندليش وتيمكن. لوحظ ان افضل موديل ينطبق لشرح عملية الامتزاز هو لانكماير . وكان الحد الأقصى للامتصاص 136.67 ملغم / جم عند 25 درجة مئوية لصبغة المثيل البرتقالي. تم الوصول إلى التوازن بعد أربع ساعات من اجراء عملية الامتزاز . كانت قيم الديناميكا الحرارية ΔG سالبة في درجات حرارة مختلفة ، لذلك كانت العملية تلقائية ، في حين كانت قيم ΔH / j 16683 mol وكانت قيم ΔS mol.k / j 60.82 .

الكلمات الدالة: الامتزاز ، الاسترجاع ، الاصباغ ، ماص للحرارة