Elimination of a cationic dye by adsorption on two natural materials, olive pomace and peanut shells

H. Baloul[1*], F. Abed[1], M. Touati [1]

[1]Food Technology Research Laboratory (LRTA) Faculty of Sciences Engineer
University of M'hamedBougara, Boumerdes, 35000 Boumerdes–Algeria

*Corresponding author: h.baloul@univ-boumerdes.dz; Tel.: +213 541 32 54 96

ARTICLE INFO

ABSTRACT/RESUME

Abstract: This study focuses on the recovery of agro-food waste "olive pomace and peanut shells" in the field of industrial liquid effluent treatment.

The two materials were chemically activated by phosphoric acid while mixing them in different quantities and this by fixing the mass of the olive residue and by varying that of the shell of peanuts in order to obtain a homogeneous solution and to improve their adsorptive capacity.

In order to test the performance of the various adsorbents prepared, we were interested in the cationic dye basic yellow considered as polluting. The effects of several parameters such as contact time, initial concentration of dye, the pH of the solution, the temperature were studied in a batch system.

The study of the adsorption in batch system, made it possible to note that the optimum pH range for the elimination of the cationic dye studied, correspond to pH values greater than 4, the maximum adsorption capacity is about 42.73 mg/g obtained in the case of adsorbent (50% OP-50% PS) at a pH 8, and at a temperature of 40 °C.A modeling of the experimental results was carried out using the models Langmuir and Freundlich isotherms as well as a kinetic study using the equation of Pseudo-second order which has been found to be more consistent with experimental results.

I. Introduction:

Many industries, such as textiles, paper, plastics and the dye industries consume large volumes of water, and also use chemicals and dyes during the manufacturing process **[1-4]**. As a result, they produce a considerable amount of polluted wastewater. Their toxic effluents are a major source of aquatic pollution and will considerably damage receiving waters if they are not treated **[5-9]**, the World Health Organization (WHO) considers that 80% of the diseases that affect the world's population are directly transmitted by water, which requires their treatment.

Several treatment methods, biological, physical and chemical, have been used for the treatment of industrial textile effluents, including microbial biodegradation **[10-14]**, membrane filtration, oxidation, the process of electric discharge, precipitation, extraction with solvents. However, many of these technologies are expensive, especially when applied to high throughput effluents, therefore the adsorption technique appears to be well suited to the textile industry **[15-21]**, thanks to its proven effectiveness in removing organic pollutants and also for economic considerations research has therefore focused on treatment processes using natural materials such as olive pomace and peanut shells **[22]**, especially in recent years, various studies have demonstrated the potential of various natural adsorbents for the adsorption of textile dyes.

Research has therefore focused on treatment methods using natural materials such as olive pomace, peanut shells, clays, etc. due to their availability and low costs of treatment.

The present study therefore has a double objective, namely, the study of the discoloration of a colored liquid waste by adsorption, and the recovery of a natural waste; olive pomace, peanut shells.

Kinetic and adsorption isotherms have been modeled to better understand the dye adsorption mechanism.

II. Material and method

II.1. Raw material preparation:
II.1.1. Olive pomace (OP)
The olive pomace used in this study was collected from the Lakhdaria region during the olive growing period.

Washed several times under running water to remove dust and adhering impurities, as well as water-soluble substances, until clear washing water is obtained, then rinsed with distilled water.

Brought into contact with hexane for 48 hours, to remove residual oils, and finally washed with distilled water several times and dried in an oven at 105 °C.

II.1.2. Peanut shells (PS)
The peanut shells come from China. The crushed peanut shells undergo the following stages:

Washing: washed several times under running water to remove dust and adhering impurities, until clear washing water is obtained, then rinsed with distilled water.

Drying: takes place in an oven up to constant weight (about 48 hours) at 105 °C.

II.2. Chemical activation
Once dried, we prepare different samples based on a mixture of the two materials, before going on to chemical activation.

To do this, we mix the two materials as follows:

Sample1: 7.275 g of olive pomace + 2.425g of peanut shells (7.275g OP -2.425g PS).

Sample2: 7.275 of olive pomace + 4.85g of peanut shells (7.275g OP -4.85g PS).

Sample3: 7.275 g of olive pomace + 7.275g of peanut shells (7.275g OP -7.275 g PS).

Sample4: 7,275 g olive pomace +12. 125 g peanut shells (7.275 g OP -12 .125gPS).

Sample5: 7,275 g of olive pomace (7,275 g OP).

Sample 6: 7,275 g of peanut shells (7,275 g PS).

These samples will be crushed using an electric mill, then sieved using a stack of sieves of different mesh openings. The choice of the desired particle size is between (80 μm and 630 μm).

The samples prepared are impregnated in an aqueous solution of phosphoric acid (3N), at a mass ratio equal to 2 g of acid/1g of adsorbent.

The temperature of the solution is kept constant T = 100 °C., with a total reflux of the vapors for 3 h.

The impregnated adsorbents are separated by simple filtration of the solution.

Washing: After cooling, the samples are washed several times with distilled water in order to remove the excess activating agent until the pH of the solution is neutralized.

Drying: The final step is to dry the adsorbents prepared at 105 °C, to constant weight. Then store in desiccators until needed.

II.3. Characterization of adsorbents:
II.3.1. Humidity
Humidity is a ratio expressed as a percentage, it is determined by drying the adsorbent in an oven at 105 °C until its weight remains constant, it is calculated by the following relationship (1) :

$$H (\%) = \frac{(M_0 - M_1)*100}{M_0} \qquad (1)$$

With:

H: humidity in mass percentage (%)

M_0: mass of adsorbent before drying (g)

M_1: mass of adsorbent after drying (g)

II.3.2. The ash rate
It allows to know the share of mineral matter in the adsorbent.

Procedure: Weigh one gram of dry adsorbent and put it in a calcination crucible, p_1 the weight of adsorbent put in the crucible. The crucible is then placed in an oven at 600 °C for 45 min. After cooling, the crucible is weighed again, p_2 the weight of the ashes in the crucible. We express the ash rate by the equation (2) :

$$C (\%) = \frac{p_2}{p_1} \times 100 \qquad (2)$$

II.4. The dye basic yellow (BY^+)
The dye used in this study is a cationic dye which is basic yellow (BY^+), the chemical structure of which is shown in figure 1.

Its molecular formula is $C_{20}H_{25}N_2$. Its molar mass is 293 g/mol and λ_{max}(nm) = 416 nm
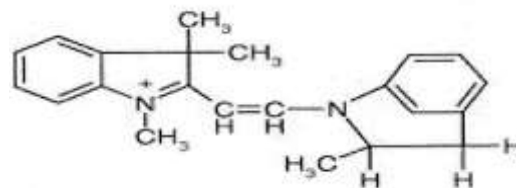

Figure 1. *Chemical structure of basic yellow (BY^+)*

II.5. Adsorption test
II.5.1. Effect of the solid / liquid ratio
Masses of adsorbent (0.025 g; 0.05 g; 0.1 g; 0.15 g; 0.2 g) are added to 50ml of basic yellow solution with a concentration of 30mg/l at 250 rpm until equilibrium is reached; the initial pH is 7.28, stirring was carried out for 180 min

II.5.2 Effect of contact time
The tests are carried out in batch at room temperature in beakers, by stirring (using a magnetic stirrer) with a fixed mass of 0.1 g of

Algerian Journal of Environmental Science and Technology
Month edition. Vol.X. N°X. (YYYY)
ISSN   : 2437-1114
www.aljest.org

adsorbent in a volume of 50 ml with concentration 15 mg/L and 30 mg/L at 250 rpm until equilibrium is reached.

The initial pH is 7.28.

The samples are taken at predetermined time intervals and are separated from the solid by filtration on a 0.45 μm diameter cellulose filter paper, then the concentration is measured by a visible UV spectrophotometer.

The amount of dye fixed per gram of adsorbent is given by the following relationship(3) :

$Qt = (Ci - Ct) \times V / M$ (3)

Or :

V: is the volume of the solution in (L).

M: the mass of adsorbent used (g)

Qt: the amount of dye fixed in mg per gram of adsorbent.

Ci and Ct: are respectively the initial and instantaneous concentrations of the dye in (mg/L)

II.5.3. Effect of pH

It has been studied by mixing 0.1 g of adsorbent with 50 ml of colored solution at an initial concentration of 30 mg/L and at a temperature of 20 °C.

The pH range chosen is [2-4-6-8-10-12]. The initial pH of the solution was adjusted with solutions of NaOH at (0.1N) and HCl at (0.1N). Agitation was carried out for 120 min with an agitation speed of 250 rpm.

II.5.4. Temperature effect

To study the effect of temperature, the experiments were carried out at 20-30-40 and 50 °C. A quantity of 0.1 g of adsorbent was brought into contact with 50 ml of colored solution at an initial concentration of 30 mg/l immersed in a water bath to keep the studied temperature constant with stirring for 120 min at a speed of 250 rpm and a pH of 7,28.

II.5.5. Effect of the initial concentration

A mass of 0.1 g of adsorbent is added to 50 ml of basic yellow solution. The initial concentrations of dye tested are: (20.40, 60.80,100,120,140,160 mg/L). The experiments were carried out at 40 °C for 120 min.

II.5.6. Isothermal adsorption

Adsorption isotherms are important in describing how solutes interact with adsorbents and are essential in optimizing the use of the adsorbent. The Langmuir and Freundlich isotherms were used in this study.

III. Results and interpretations

III.1.Characterization of adsorbents
III.1.1. Humidity and ash rate

The results of the humidity rate and the ash rate are shown in table 1

Table 1. Humidity and ash rate

Properties	75% OP+ 25% PS	60% OP+ 40% PS	50% OP+ 50% PS	37.5% OP+ 62.5% PS	100 %OP	100 %PS
humidity %	4.77	4.66	4.75	5.1	4.9	5.55
The ash rate	3.45	3.18	3.22	3.37	3.4	3.2

The results obtained are close to those of the literature [22].

III.2. Adsorption test

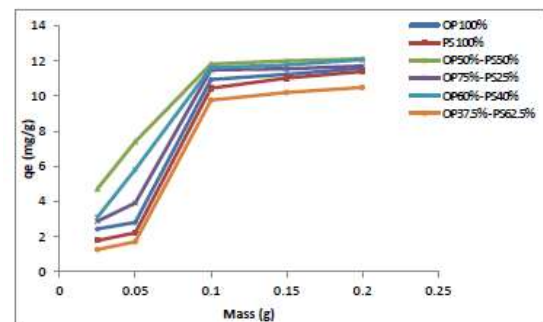### III.2.1. Effect of the solid / liquid ratio on adsorption

Figure 2. Effect of the report: mixture of olive pomace peanut shells / basic yellow solution, on the adsorption capacity of basic yellow (T = 20°C, pH = 7.28, ω = 250 rpm)

From the figure 2, we notice the existence of two intervals of evolution of the adsorption capacity of basic yellow, the first shows an increase in the adsorption capacity with the increase in the amount of adsorbent introduced up to 0.1 g; and in the second (amount of adsorbent > 0.1g), we have a fixed retention of basic yellow. Hence the optimal value of the order of 0.1 g/L.
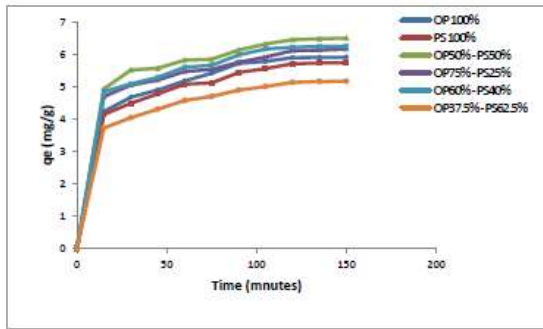
III.2.2. Effect of contact time on adsorption

Figure 3. *Evolution of the adsorption capacity of basic yellow as a function of contact time (Co = 15 mg/L, T = 20 °C, pH = 7.33, ω = 250 rpm)*
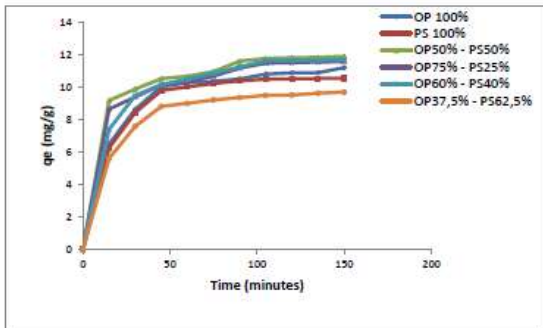

Figure 4. *Evolution of the adsorption capacity of basic yellow as a function of contact time (Co = 30 mg/L, T = 20 °C, pH = 7.33, ω= 250 rpm)*

According to figures 3 and 4 the curves show the same trend:

Rapid adsorption followed by spreading with similar saturation at the same time intervals. The first phase, a rapid increase in the elimination rate of the dye, takes place in a few minutes (15 to 60 minutes), which can be explained by the availability of active sites on the surface of the various adsorbents.

In the second stage, we observe a second slower phase which can last from (60 to 120 minutes), which may be due to the decrease in the contact surface after occupying the majority of the active sites.

On the other hand, the more the initial concentration of the dye increases, the more the number of ions in solution increases, implies a higher adsorption capacity.
Based on these graphs, an equilibrium time of 2 hours (120 minutes) will be used.

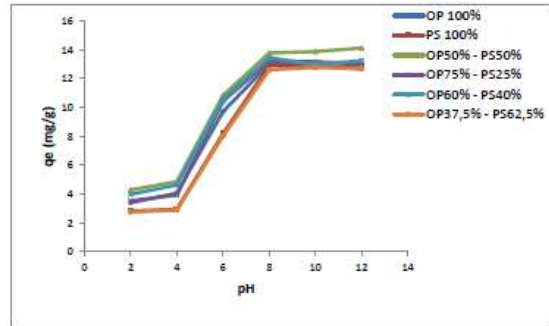### III.2.3. Effect of the pH of the solution on the adsorption

Figure 5. *Evolution of the adsorption capacity of basic yellow as a function of the initial pH (Co = 30 mg/L, T = 20 °C, ω= 250 rpm)*

The best results are observed for basic pH from pH = 8
The results show that the acid pH (pH <4) is unfavorable for adsorption, this is due to the presence of the H^+ ions in excess, which compete with the dye cations BY^+, for adsorption sites, which causes the decrease in adsorption capacity [23-25].

At high pH, above 4, the surface of the adsorbent can become negatively charged, which improves the electrostatic attraction forces, between the surface of the adsorbent and the cations of BY^+. So the basic pH is favorable for the adsorption of basic yellow.
It is therefore clear that an increase in the pH favors the development of a negative electrical charge on the surface of the adsorbent [26]. , this charge has, towards the basic yellow, an electrostatic attraction due to the positive charge which they carry in solution.

III.2.4. Effect of temperature on adsorption
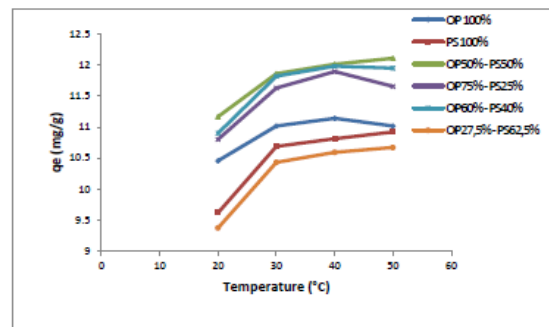

Figure 6. *Effect of temperature on the adsorption of basic yellow (pH = 7.28, ω = 250 rpm)*

According to Figure 6 in the range of 20 to 40 °C, there is an increase in the adsorption capacity for all adsorbents [27].

For Temperature between 40 and 50 °C, there is a decrease for (OP50% -PS50%), (OP75% -PS25%) and the others continue to increase.

The maximum capacity observed, is at a temperature of 40 °C, for the adsorbent (OP50% - PS50%) which has the following value 12.015 mg/g.

III.3. Kinetic and adsorption isotherm modelling

III.3.1. Kinetics of adsorption
Several kinetic models are used to test the experimental data
We applied and tested the models.
The results obtained are presented in the tables below

- ➢ Pseudo first order
- ➢ Pseudo second order

III.3.1.1. Modeling of pseudo first order kinetics

The figures represent the evolution of the function ln $(q_e - q_t)$ as a function of time.
C = 15 mg /L

Table 2. *First order pseudo kinetics (C = 15mg/l)*

Adsorbent	Kinetics of pseudo-first order	
	K1(g/mg,min)	R^2
(OP37,5% - PS62 ,5%)	0,053	0,4059
(PS100%)	0,055	0,423
(OP100%)	0,061	0,3538
(OP75% - PS25%)	0,044	0,4149
(OP60% - PS40%)	0,056	0,4191
(OP50% - PS50%)	0,047	0,4159

Table 3. *First order pseudo kinetics (C = 30 mg/L)*

Adsorbent	Kinetics of pseudo-first order	
	K1 (g/mg,min)	R^2
(OP37,5%- PS62 ,5%)	0,069	0,4797
(PS100%)	0,070	0,4956
(OP100%)	0,035	0,6369
(OP75% - PS25%)	0,0596	0,5343
(OP60% - PS40%)	0,0617	0,5538
(OP50% - PS50%)	0,0451	0,5389

From the results obtained, we find that the experimental data and the data obtained by the model are very divergent. The speed constant also has a very low value for all the mixtures used. The variation of ln $(q_e$-$q_t)$ as a function of time was not found to be very linear, and the regression coefficients R^2 are not satisfactory, since their values do not exceed 0.6369.Finally, we can conclude that the kinetics do not respond to the Lagergren model (Pseudo first order kinetics).

III.3.1.2. Modeling of pseudo second order kinetics
The kinetic model of the pseudo second order is as follows (4)

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t \right)^2 \qquad (4)$$

After integration we obtain the equation (5):

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \qquad (5)$$

k: The speed constant for an order pseudo-scond kinetics ((g / mg.min)).
q_t : The adsorption capacity at time t (mg/g)
q_e : Adsorption capacity at equilibrium (mg/g)
The plot of **t/q_t** as a function of time t will give a straight line with a slope equal to **1/q_e** and an ordinate at the origin equal to **1/$k_2\,q_e^2$**

Table 4. *Second order pseudo kinetics (C = 15 mg/L)*

	Kinetics of pseudo-second order		
Adorbent	q_e(mg/g)	k2(g/mg,min)	*R²*
(OP37,5% - PS62 ,5%)	5 ,367	0,025	0,9957
(PS100%)	5,966	0,022	0,9951
(OP100%)	6,157	0,0223	0,9956
(OP75% - PS25%)	6,33	0,0245	0,9958
(OP60% - PS40%)	6,46	0,0248	0,9962
(OP50% - PS50%)	6,68	0,024	0,9964

Table 5. *Second order pseudo kinetics (C = 30 mg/L)*

	Kinetics of pseudo-second order		
Adsorbant	q_e(mg/g)	k₂(g/mg,min)	*R²*
(OP37,5% - PS62 ,5%)	10,08	0,0143	0,9966
(PS100%)	11,01	0,0149	0,9974
(OP100%)	11,52	0,012	0,9962
(OP75% - PS25%)	11,94	0,014	0,9971
(OP 60% - PS40%)	12,19	0,0116	0,9967
(OP 50% - PS50%)	12,22	0,0153	0,9974

The correlation coefficients of the kinetic equation of the pseudo - second order, are high and the theoretical values q_e obtained from this equation are close to those experimental which allows us to suggest that the adsorption of basic yellow on the different adsorbent is better represented by the kinetic process of pseudo - second order. As can be seen, the values of the adsorption capacity in the case of the adsorbent mixture are better for the majority of the proportions by comparing them with the two separate adsorbents (PS100%), (OP100%) except in the case of mixing. (OP37.5% -PS62.5%). The maximum capacity obtained in both cases (C = 15mg/l), (C = 30mg / l) with the mixture (OP50% - PS50%) q_e = 6.68 mg/g, q_e = 12.22mg. With (R² = 0.9964, R² = 0.9974) The kinetic constant (K2) increases in the case of mixing more than in the separated state.
This allows us to conclude that the mixture between the two adsorbents improves their adsorption capacity. The adsorption of basic yellow on the various adsorbents is best represented by the kinetic process of the pseudo-second order.

III.3.2. Modeling of adsorption isotherms
III.3.2.1. The effect of initial concentration
The isotherm obtained is of type L corresponding to an adsorption of a mono molecular layer, hence the possibility of applying both the Langmuir law and that of Freundlich.

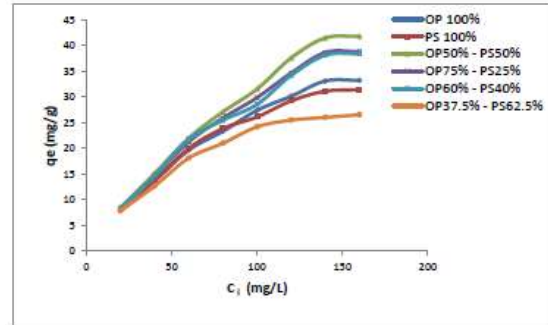The experimental conditions used are specified in the following table:

Figure 7. *The effect of initial concentration on adsorption (T = 40°C, pH = 8, ω = 250 rpm)*

From the results obtained, it can be seen that the mixture of the two adsorbents makes it possible to improve their adsorption capacity such as for (OP50% -PS50%) (42.82 mg/g) compared to OP100%, PS100% (33.24mg/g and 31.395 mg/g respectively).

III.3.2.2. Adsorption isotherms (adsorption equilibrium)

III.3.2.2.1. Langmuir isotherm

Linearization of the Langmuir equation (6)

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bC_e\, q_{max}} \tag{6}$$

Or

b: is the equilibrium constant

q_{max}: The maximum adsorption capacity.

by tracing $\frac{1}{q_e}$ function of $\frac{1}{C_e}$
A slope line $\frac{1}{bq_{max}}$ Ordinate at origin $\frac{1}{q_{max}}$

Table 6. Langmuir parameters for the different types of adsorbents used:

Constant / Adsorbent	R^2	q_{max} (mg/g)	B	R_L(1620)	R_L(160)
OP37,5% -PS62,5%	0,964	27,472	0,0868	0,365	0,067
PS100%	0,9683	31,847	0,0897	0,357	0,65
OP100%	0,9705	34,013	0,0739	0,403	0,078
OP75% - PS25%	0,972	39,525	0,075	0,4	0,0769
OP60% - PS40%	0,9795	40	0,071	0,413	0,0809
OP50% - PS50%	0,9795	42,73	0,076	0,396	0,0759

As expected, the mixture of olive pomace with peanut shells in different proportions gave an improvement in the adsorption properties of the adsorbent, giving it better fixation of the basic yellow.
Indeed, with a mixture of (50% OP, 50% PS), increases the adsorption capacity of basic yellow to (42.73 mg/g) compared to the use of olive cake only (34.013 mg/g), peanut shells alone (31.847 mg / g).
The values of q_{max} determined by the Langmuir model increase with the increase in the rate of olive cake in the mixture,
The value of q_{max} goes from 34.013 mg/g to 42.73 mg/g, when 50% of peanut shells are added to olive pomace (50 OP, 50% PS).
The value of q_{max} decreases from 34.013 mg/g to 27.472 mg / g when 62.5% of peanut shells are added to olive pomace (OP37.5% -PS62.5%).
The viability of an adsorption can also be defined from the dimensionless separation factor R_L

$$R_L = \frac{1}{1 + b.C_0} \qquad (7)$$

If $R_L > 1$ the adsorption conditions are unfavorabl
If $R_L < 1$ the adsorption conditions are favorable
If $R_L = 0$ the adsorption is irreversible.

The dimensionless separation factor is less than 1, for all the mixtures used, hence adsorption is very favorable.

III.3.2.2.2 Freundlich isotherm

Freundlich's equation is expressed by the relation (8)
$$\text{Ln } q_e = \text{Ln } K_f + 1/n \text{ Ln } C_e \qquad (8)$$
Where k_F and n are dimensionless constants.
The results obtained are represented according to the Freundlich model, by plotting
Ln q_e = f (Ln C_e), hence the slope of the line is 1/n and Ordinate at origin Ln K_f.
The intensity parameter, 1/n, indicates the deviation of the linearity adsorption isotherm. When 1/n = 0, the adsorption is linear, it is to die that the sites are homogeneous and that there is no interaction between the adsorbed species.
When 1/n < 1, the adsorption is favorable, the adsorption capacity increases and new adsorption sites appear.
When 1/n>1 the adsorption is not favorable, the adsorption bonds become weak and the adsorption capacity decreases.

Table 7. Freundlich parameters for the different types of adsorbents used

Constant / Adsorbent	R^2	K_f (mg/g)	1/n
OP37,5% - PS62%	0,9653	4,55	0,4015
PS100%	0,9743	4,93	0,4276
OP100%	0,9881	4 ,297	0,4722
OP75%- PS25%	0,9885	4,57	0,5077
OP60%- PS40%	0,98	4,66	0,4975
OP50%- PS50%	0,988	4,75	0,5271

From the results obtained in the table above, we find that the ratio 1/n is less than 1, so the Freundlich isotherm is favorable for the absorption of basic yellow for any proportion of OP and PS.

IV. Conclusion

The study of the adsorption in batch system, made it possible to note that the optimum pH range for

the elimination of the cationic dye studied, correspond to pH values greater than 4, the maximum adsorption capacity is about 42.73 mg / g obtained in the case of adsorbent (50% OP-50% PS) at a pH 8, and at a temperature of 40 °C.

During our study, we found that the adsorption rate increases with the increase in the peanut rate in the mixture

The Langmuir isotherm as well as the Freundlich isotherm are favorable for the adsorption of basic yellow on the various adsorbents, with $R^2 > 0.964$ for the Langmuir linearization, with a better representation of the linearization with a $R^2 = 0.9795$.

The Freundlich model with an $R^2 > 0.9653$, , with a better representation of the linearization with a $R^2 = 0.9885$.

While the kinetic study of the experimental results using the pseudo-first order and the pseudo-second order equations, has shown that the latter coincides better indicating that adsorption is a second order reaction.

V. References

1. Maurice, R. The Discovery of Aniline Purple, 1856-1976: A History of Chemists, Companies, Products and Changes, *Dye-Makers of Great Britain*, Manchester. (1987) 94-101.
2. Quesneville, C., le Moniteur Scientifique, *Journal des sciences pures et appliquées*. TOME II, 1865.
3. Messina, P.V.; Schulz, P.C. Adsorption of Reactive Dyes on Titania-Silica Mesoporous Materials. *Journal of Colloid and Interface Science 299 (2006) 305-320.
4. Yener, J.; Kopac, T.; Dogu, G.; Dogu, T. Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite. *Journal of Colloid and Interface Science* 294 (2006) 255-264.
5. Koller, E. Traitement des pollutions industrielles eau, air, déchet, boues. Dunod France ,2004.
6. Hemsas, S. Contribution à l'étude de la décoloration des eaux sur grignons d'olives valorisés. étude dynamique. Magister thesis ;university of Boumerdes. 2008.
7. Zawlotzki Guivarch, E. Traitement des polluants organiques en milieu aqueux par procédé électrochimique d'oxydation avancée, électro-fenton, application à la minéralisation des colorants synthétiques. Doctoral thesis, University of Marne-La- Vallée, 2004.
8. Teng, C.L.; and Wang, F.S. Intermittent contiguous method for recovering refined activated carbon from waste tires and the like and the device therefore, *US Patent*, ,1999.
9. Lounici, H. Nouveau procédé de défluoruration des eaux potables: l'électrocoagulation et l'électrosorption, Application aux eaux de Sahara Septentrional Algérien, Doctoral thesis, Ecole Nationale Polytechnique, 2002.
10. Pagga, U.; Taeger, K. Development of a method for adsorption of dyestuffs on activated sludge. *Water* Research 28(5) (1994)1051-1057.
11. Hitz, H.R.; Huber, W; Reed, R.H. Publication Sponsored by ETAD The Adsorption of Dyes on Activated Sludge. *Journal* of the *Society* of *Dyers and Colourists* 94 (2) *(*1978) 71-76
12. Weber,E. ; Wolfe, N.L. Kineticc studies of reduction of aromatic azo compounds in anaerobic sediment/water systems. *Environmental Toxicology and Chemistry* 6 (12) (1987) 911-920.
13. Carliell, C.M.; Barclay, S.J.; Naidoo, N. Microbial decolourasition of a reactive azo dye under anaerobic conditions. *Water SA*. 21(1) (1995) p 61-69.
14. Venceslau, M.C. ; Tom, S.; Simon, J. Characterization of textile wastewaters- a review. Journal of Environmental Technology 15 (1994) 917-929.
15. Raghavacharya, C. Colour removal from industrial effluents: a comparative review of available technologies. *Chemical Engineering World* 32 (1997) 53-54.
16. El-Geundi, M.S. Colour removal from textile effluents by adsorption techniques. *Water Research* 25 (3) (1991) 272-273
17. Chitiour, C.E. Physico-chimie des surfaces. Vol. 2, O.P.U.Alger. 1992.
18. Mekaoui, M. Etude de l'adsorption, de la persistance et de la photodégradation de l'herbicide Tribenuron Méthyle (TBM) dans le sol et l'eau, Doctoral thesis. University. Mohammed V, Faculty of Sciences-Rabat 2001.
19. Timothy, B and al, « Carbon Materials for advanced Technologies », First edition , Timothy, Burcchell,(1999).
20. Giles, C.H.; Smith,D.; Huitson, A. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *Journal of Colloid and Interface Science* 47 (3) *(*1974) 755-765.
21. De Flora S.; Wetterhahn K.E. ,Mechanisms of chromium metabolism and genotoxicity. *Life Chemistry Reports,* (1989)169- 244.
22. M. Gueye, J. Blin, C. Brunschwing. Etude de la synthèse des charbons actifs à partir de biomasses locales par activation chimique avec H_3PO_4. Journées Scientifiques du 2iE. Campus 2iE Ouagadougou, 6 ème édition 4-8 avril 2011.
23. Subramani, A. Adsorption of organic pollutants on to natural adsorbents. Magister thesis, University of Mississippi, (2002).
24. Fabre, B. ; Ayele, J.; Mazet, M. ; Lafrance, P. Adsorption du pentachlorophenol sur divers matériaux : Influence de co-adsorbats organiques (Substances humiques et Lindance) *Revue des Sciences de L'eau.* 3(3) (1990) p 277-292
25. Daifullah, A.A.M.; Girgis, B.S. Removal of some substituted phenols by activated carbon obtained from agricultural waste. *Water. Research*, 32 (4) (1998)1169-1177.
26. Babakhoya, N.; Boughrara, S.; Abed F.; Abai, N.; Midoune, S. Etude du potentiel d'utilisation des déchets agroalimentaires, les grignons d'olives et les noyaux de date pour récupération et adsorption des métaux lourds. *Algerian Journal of Environmental Science and Technology* . 1 (1) (2015) 04-10.
27. Cardot, C. Les traitements de l'eau, procédés physico-chimiques et biologiques. seconde édition ellipses, 2010.