Chemical Bulletin of "Politehnica" University of Timisoara, ROMANIA
Series of Chemistry and Environmental Engineering
Chem. Bull. "POLITEHNICA" Univ. (Timisoara) *Volume 56(70), 1, 2011*

Optimization Study of Orange 16 Dye Sorption from Aqueous Systems Using Sawdust Wastes

C. Zaharia* and D. Suteu**

* Department of Environmental Engineering and Management, 'Gheorghe Asachi' Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 71A Prof. D.Mangeron Blvd, 700050 Iasi, Romania
e-mail: czah@ch.tuiasi.ro

** Department of Organic and Biochemical Engineering, 'Gheorghe Asachi' Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 71A Prof. D.Mangeron Blvd, 700050 Iasi, Romania
e-mail: danasuteu67@yahoo.com

Abstract: The application of sawdust waste as adsorptive material into an aqueous system containing the textile Orange 16 reactive dye is studied. The main treatment step is based on sorption followed by solid/liquid separation by sedimentation and filtration. All experiments are performed on a laboratory scale set-up in order to establish the optimal operational parameters (e.g., sawdust quantity, pH, sorption time, temperature) for high removal efficiencies of textile synthetic reactive dye - Orange 16. Variables concerning the sawdust quantity (0.2-0.7 g per 25 mL), pH (0.3-4), and sorption time (12-150 min) are considered in order to appreciate the sorption efficiency. An empirical model is proposed by a central composite rotatable design of third order (2^3), considering these variables as independent ones (x_i), while the dye removal is chosen as optimization criteria (Y, %). The optimal values are in good agreement with the experimental data (i.e. the data average deviation is lower than ±10%).

Keywords: Orange 16 reactive dye, sawdust, sorption, optimization, central composite rotatable design 2^3 type

1. Introduction

All industries discharge potential contaminants into public sewerage systems or different emissars and have the obligation to report to the local enironmental protection agency and/or local authority of water management each exceeding of the maximum admissible concentration or hourly load. To avoid the pollution of water resources it is necessary the individual or combined industrial wastewater treatment with municipal wastewater.

The industrial wastewater treatment must be in consence with the viable procedures of the production water management: (i) minimization of water use; (ii) the development of new processes and the optimization of existing or new ones with the aim of saving water, materials and energy, and (iii) the reuse and recycling of wastewater [1, 2].

An industrial effluent treatment can be applied into descentralized treatment systems with or without reuse or central wastewater treatment. For a high wastewater flow rate and a high COD concentration, an estimation of the treatment costs lets us know whether it is better to treat it in an end-of-pipe plant or in a decentralized effluent treatment system.

The interest towards an entire production process respecting the requirements of environment protection must direct all efforts to develop new production processes with reduced consumption levels of water and raw materials (i.e. dry processes or others electrochemical, physical ones), with reduced production of wastewater and to treat efficiently the individual or final effluents [2].

Among the physical-chemical processes in use for removal of organic dissolved compounds are adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, coagulation-floculation, extraction and gas stripping etc. [3-9]. In practice adsorption is limited to the accumulation of organic compounds at an interface liquid-solid or the dispersion away from interfaces depending on their relative strength of attraction for themselves or for the solvent (i.e. the use of activated carbon for the removal of non-polar dissolved compounds).

Also, many organic compounds are both hydrophobic and hydrophilic tending to become oriented at the surface with hydrophobic portion at the interface and the hydrophylic portion remaining in solution. Their function is to produce wetted surfaces without being removed themselves (i.e. detergents are the best known and common example of these compounds) [1, 2].

The removal of organic compounds by adsorption onto low-cost materials has recently become the subject of considerable interest (i.e. a potentially simple and economic 'end-of-pipe' solution to the challenges set by new legislation covering effluent discharges, especially textile effluents) [10-18].

An important category of compounds into textile effluents is represented by the textile dyes. Numerous research studies indicate that adsorbents which contain high concentrations of cellulose irreversibly adsorb basic dyes through coulombic attraction and ion exchange processes. Acid dyes are mostly adsorbed in a reversible process involving physical adsorption (combination of van der Waals attraction, hydrogen bonding and coulombic attraction that generates a negative surface charge of the adsorbent in contact with water) [2, 5].

The adsorption capacities of dyes onto non-biological waste material, such as carbon, coal ash, fly ash, modified coal ash depend on the surface charge of the adsorbent on contact with water. For carbon, the surface charge will be neutral, the physical adsorption will predominate and a high adsorption capacity for both acid and basic dyes will be achieved.

The principal criteria for choosing an adsorbent to remove organic dyes are the cost effectiveness, availability and adsorptive properties. Taking these criteria into consideration, many researchers have investigated the adsorptive properties of unconventional adsorbents for the removal of some organic pollutants from aqueous environment [10-19].

In this paper, all experiments were performed for textile Orange 16 reactive dye by sorption onto Romanian wasted sawdust (i.e. tests using adsorbent quantities of 0.20-0.72 g per 25 mL). Our previous studies were indicated higher dye removals when were used sawdust quantities of 1-25 $g{\cdot}L^{-1}$, pH of 1-4, and a sorption time of 5-160 minutes [14], [16]. This study of sorption modeling and optimization is an additional one that was performed in order to find some different optimal treatment conditions.

The results of an other previous optimization study by sorption onto wasted sawdust applied for Orange 16 reactive dye indicate the possibility to improve the sorption efficiency extending the experimental data field of two selected variables (i.e. sorbent quality and pH) [2]. This new additional study was considering these extended experimental variation fields keeping the same experimental variation field only for sorption time (the same as into our previous studies [2]).

A central composite rotatable design of 2^3 type was applied for all experiments performed at laboratory scale set-up [20-31].

2. Experimental

2.1. Materials and reagents

All experiments were performed with the Orange 16 reactive dye (MW = 617.54; λ_{max} = 495 nm; C.I. 17757) used as commercial salt (Figure 1). Working dye solutions (24.7-197.6 mg/L) were prepared by appropriate dilution with bidistilled water of the stock dye solution (600 mg/L). It was used HCl 1M solution for pH adjustment.

Reactive dye - Orange 16

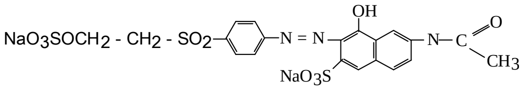


Figure 1. Chemical structure of textile Orange 16 reactive dye

The sorbent for laboratory scale-up experiments was the Romanian wasted material from the conifer wood processing (i.e. conifer sawdust) dried in air, and sieved. It was worked with fractions having particle size of 1-2 mm. The major constituents of sawdust are cellulose, hemicelluloses and lignin; the humidity was of 9.85% (i.e. chemical composition of conifer wood was of 49.9% C, 6.4% H, 43.0% O and 1.0% N), density of 1211 $Kg.(m^3)^{-1}$ and caloric power of 2035 $kcal.Kg^{-1}$.

The pH of zero charge (pH_{pzc}), determined by method proposed by Nouri and Hagesersht, was of 4.6 [2, 14].

2.2. Sorption experiments

The sorption experiments were performed using 'batch' technique at room temperature (18°C): samples of sawdust (0.20-0.71 g per 25 mL) were mixing with 25 mL of aqueous solution containing 80 $mg{\cdot}L^{-1}$ Orange 16 reactive dye, in 100 mL Erlenmeyer flasks, under an intermittent agitation.

The pH of solutions was adjusted to a desired value (0.3-4) by addition of HCl 1M solution and measuring the pH value with an HACH One Laboratory pH meter.

After an established sorption time (12-150 minutes), the concentration of the reactive dye in supernatant was determined by absorbance measurement with a VIS Spectrophotometer, model SP 830 Plus, Metertech Inc. Version 1.06.

The sorption capacity of sawdust was evaluated by percentage of dye removal (*R*),

$$R = [(C_0-C)/C_0]\cdot 100\ (\%) \qquad (1)$$

where, C_0 and C are the initial and final concentration (residual concentration) of Orange 16 reactive dye in solution after a specific *t* sorption time ($mg.L^{-1}$).

2.3. Experimental modelling and design

The principal variables that influence dye sorption onto conifer sawdust are considered to be: quantity of sawdust (Z_1, g per 25 mL), pH (Z_2, pH unit) and sorption time (Z_3, min). As optimization criteria or response function were chosen the percentage of dye removal (Y, %) [2].

A mathematical model of a central composite rotatable design with "n" variables is used and expressed by following equation (2) [2], [20-31].

$$Y= b_0+\sum b_i.x_i+ \sum b_{ii}x_i^2+\sum b_{ij}x_ix_j \qquad (2)$$

where, *Y* represents the response function or optimization criteria; x_i, x_j, x_{ii}, x_{ij} are the coded variables of the system, and b_0, b_i, b_j, b_{ij} are the model coefficients (i, j= 1, 2, 3).

The model coefficients are estimated using a least square fitting of model (empirical model) obtained in the design points (20 experimental points). The central composite rotatable design has the advantage of no excessive experiments in comparison with the number of coefficients to be determined (i.e. 20 experiments: $N_F=2^3$ factorial experiments, performed at the corner of cube, that represents the experimental data area; N_a= 2x3 axial experiments, carried out on the axes, at a distance of $\pm \alpha_i$ from the centre, calculated as to obtain rotability; N_0=6 experiments at the centre of experiment field in order to allow calculation of an independent estimation of "pure" experimental error variance or reproducibility variance) [18-28].

Tables 1 and 2 indicate the levels attributed to each independent Z_i variable (quantity of sawdust, pH and sorption time) that correspond to a basic value Z_{i0} and a variation step ΔZ_{i0}. Adding the variation step to the basic value the upper level is obtained, while the subtraction of the step value lead to the lower level of variable. The coded value of Z_i denoted as X_i is calculated with relation (3):

$$X_i = (Z_i - Z_{i0})/\Delta Z_{i0} \quad (3)$$

The coded values can have one of the following value: 0, ±1, $\pm\alpha_i$ (i.e. α_i=±1.682 for a central composite rotatable design of 2^3 type).

The Fisher constant, the multiple correlation coefficient, or the Fisher test were calculated and applied in order to establish the correlation between the dependent variable (optimization criteria or response function), and the three independent variables [20-31]. The deviation of the calculated values with the proposed model and experimental data must be between +10% and -10% for a very good accordance.

3. Results and Discussion

The real and coded basic values for the three studied independent variables of dye sorption were presented into Table 1, together with their variation steps. The aqueous dye solutions of 25 mL (80 $mg \cdot L^{-1}$ dye) were treated with different quantities of sawdust wastes at different pH values. After temperature stabilization and the adjustment of pH there were performed sorption experiments according with the designing matrix presented in Table 2. The room temperature was of 18°C and all samples were initially agitated for few minutes (50 rpm).

The matrix of this experimental design is synthetically presented into Table 2.

The equation of the proposed model is expressed by formulae considering that the coefficient calculation is made according to some specific formulae [2], [20-31] well known into statistic and experimental design modelling.

TABLE 1. The codification of independent variables into central composite rotatable design (2^3)

Variable/ value	Real variable (Z_i)	Coded variable (X_i)	Real basic variable (Z_{i0})	Variation step (ΔZ_{i0})
Sawdust content, g per 25 mL	Z_1	X_1	0.45	0.15
pH	Z_2	X_2	2	1.0
Sorption time, min	Z_3	X_3	80	40

TABLE 2. The matrix of experimental central composite rotatable design(2^3) applied for Orange 16 dye sorption

No. exp.	Z_1	Z_2	Z_3	X_1	X_2	X_3	Y
1	0.30	1	40	-1	-1	-1	65.038
2	0.60	1	40	1	-1	-1	71.956
3	0.30	3	40	-1	1	-1	22.180
4	0.60	3	40	1	1	-1	23.530
5	0.30	1	120	-1	-1	1	93.320
6	0.60	1	120	1	-1	1	90.404
7	0.30	3	120	-1	1	1	24.594
8	0.60	3	120	1	1	1	28.949
9	0.198	2	80	-1.682	0	0	29.294
10	0.702	2	80	1.682	0	0	48.353
11	0.45	0.318	80	0	-1.682	0	72.563
12	0.45	3.682	80	0	1.682	0	39.662
13	0.45	2	12.72	0	0	-1.682	25.555
14	0.45	2	147.28	0	0	1.682	49.741
15	0.45	2	80	0	0	0	40.846
16	0.45	2	80	0	0	0	41.770
17	0.45	2	80	0	0	0	41.967
18	0.45	2	80	0	0	0	40.925
19	0.45	2	80	0	0	0	40.586
20	0.45	2	80	0	0	0	40.925

The proposed model is presented below considering all coefficients (Eq.4) or in the case of no consideration (insignificance) of X_1X_2 term (Eq.5) (Student test application, Table 3).

$$Y=40.897+3.058X_1-.269X_2+6.974X_3+0.887X_1^2+7.001X_2^2-0.471X_3^2+0.213X_1X_2-0.854X_1X_3-4.862X_2X_3 \quad (4)$$

The calculated value for the Fisher constant is F = 21089.21 for Y and the comparative value from statistical table is F_{tab} = 4.6 (α=99, ν_1=n-1=19, ν_2=k-1=2, where n is the number of experiments and k is the independent variable number). Because $F>F_{tab}$ it can be considered that the deviation of experimental values from the average value is not the result of experimental errors, but is determined by the influence of independent variables on response function.

The correlation coefficient is of $R_{YX1X2X3}$ = 0.9167, and demonstrates that all independent variables are important for the variation of dependent variable (optimization criteria) into the studied experimental field.

The calculated Fisher test value was found to be: F_{calc} = 28.071. In comparison with with F_{tab} = 6.59 from statistics for freedom degree of ν_1 = n-k-1=16 and ν_2 =k=3, it resulted that the calculated values are higher than the statistical value. This fact demonstrates that the independent variables have a significant influence on the dependent variable.

$$Y=40.897+3.058X_1-.269X_2+6.974X_3+0.887X_1^2+7.001X_2^2-0.471X_3^2-0.854X_1X_3-4.862X_2X_3 \quad (5)$$

The correlation between the experimental and calculated data with the proposed model is synthetically illustrated into Table 4.

TABLE 3. The results of Student test application

Model coeff.	Coefficient value		t	$t_{critical}$	Sign
b_0	40.897	0.12495	327.306	2.571	+
b_1	3.058		24.4746		+
b_2	-20.269		162.213		+
b_3	6.974		55.815		+
b_{11}	0.887		7.100		+
b_{22}	7.001		56.032		+
b_{33}	0.471		3.773		+
b_{12}	0.213		1.704		-
b_{13}	-0.854		6.832		+
b_{23}	-4.862		38.912		+

TABLE 4. The experimental and calculated values of response function (Y) into all experiments

No. exp.	X_1	X_2	X_3	Y	Y_{calc}	Deviation %
1	-1	-1	-1	65.038	52.835	18.763
2	1	-1	-1	71.956	60.659	15.699
3	-1	1	-1	22.180	22.021	0.717
4	1	1	-1	23.530	29.845	-26.838
5	-1	-1	1	93.320	78.215	16.186
6	1	-1	1	90.404	82.623	8.607
7	-1	1	1	24.594	27.953	-13.658
8	1	1	1	28.949	32.361	-11.786
9	-1.682	0	0	29.294	38.263	-30.617
10	1.682	0	0	48.353	48.550	-0.407
11	0	-1.682	0	72.563	94.796	-30.40
12	0	1.682	0	39.662	26.611	32.905
13	0	0	-1.682	25.555	27.834	-8.919
14	0	0	1.682	49.741	51.295	-3.124
15	0	0	0	40.846	40.897	-0.125
16	0	0	0	41.770	40.897	2.090
17	0	0	0	41.967	40.897	2.549
18	0	0	0	40.925	40.897	0.068
19	0	0	0	40.586	40.897	-0.766
20	0	0	0	40.925	40.897	0.068

In general, an acceptable accordance between the experimental values and calculated values exists (average deviation of calculated data with the proposed model in comparison with the experimental data is of -1. 461% being into admissible limits).

Analysis of the proposed model. The application of classical optimization method leads to the conclusion that the *Y* function has *a distinct maximum* which corresponds to X_1* = +2.156, X_2* = -1.608, and X_3* = -0.897 (Y=90.319%). Transposed to real variables, these values correspond to the next optimal independent variables: a sawdust content of 0.773 g per 25 mL, a pH of 0.392, and a sorption time of 44.10 min.

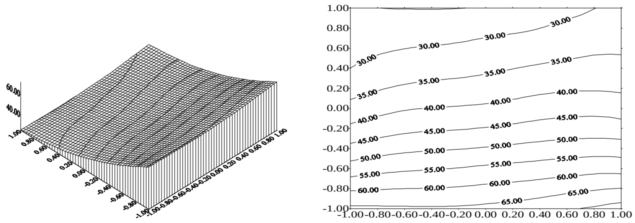
The *Y* analysis leads to the conclusion that all X_i variables (sawdust content, pH, and sorption time) have an important influence on the textile dye removal, fact that is also demonstrated by values of all coefficients much higher than the unit. The influence of X_2 variable is almost 6.628 times higher than of X_1 and 2.906 times than of X_3 for *Y* function, and its effect is contrary (the X_2 decreasing increases the dye removal).

The Figures 2, 3 and 4 show the dependence of the dye removal (*Y*) vs two variables (one variable kept at the basic value) (i.e. $Y=Y(X_1,X_2,0)$, $Y=Y(X_1,0,X_3)$, $Y=Y(0,X_1,X_2)$).

The increase of dye removal with the increase of adsorbent quantity can be found from variation of *Y* versus X_1 (Fig. 5a). Thus, exists a minimum dye removal (48.803%) for $X_1^* = 1.723$ (i.e. a local maximum point for a sawdust content of 0.708 g per 25 mL, pH= 2 and $t_{sorption}$ = 80 minutes).

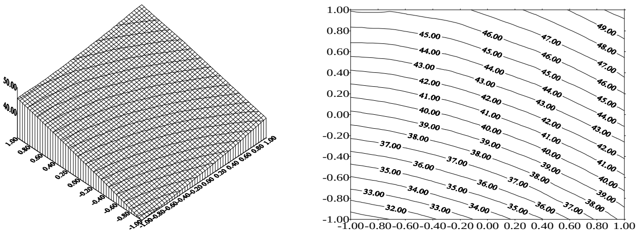
The dependence of dye removal vs X_2 (X_1 and X_3 encoding values are 0) indicates a minimum removal (26.227 %) for $X_2^* = +1.448$ (i.e. a minimum point for a sawdust content of 0.45 g per 25 mL, pH= 3.448 and $t_{sorption}$ = 80 minutes) (Fig. 5b). Exist a local maximum for the highest value of X_2 (extreme negative value).

The dependence of dye removal vs. X_3 (X_1 and X_2 encoding values are 0) indicates a maximum dye removal (66.713 %) for $X_3^* = +7.403$ (e.g., a local maximum point for sorption time of 376 minutes, pH=2 and adsorbent quantity of 0.45 g per 25 mL) (Fig. 5c).



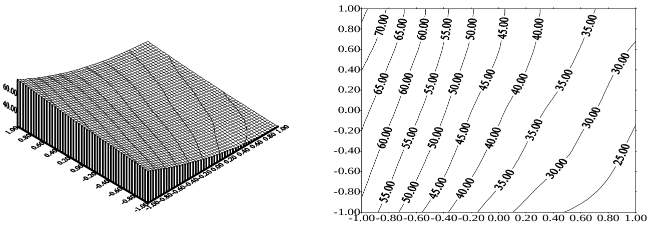
(a) (b)

Figure 2. Variation of *Y* function vs. X_1 and X_2: (a) $Y_1=Y(X_1,X_2,0)$, (b) Isoline



(a) (b)

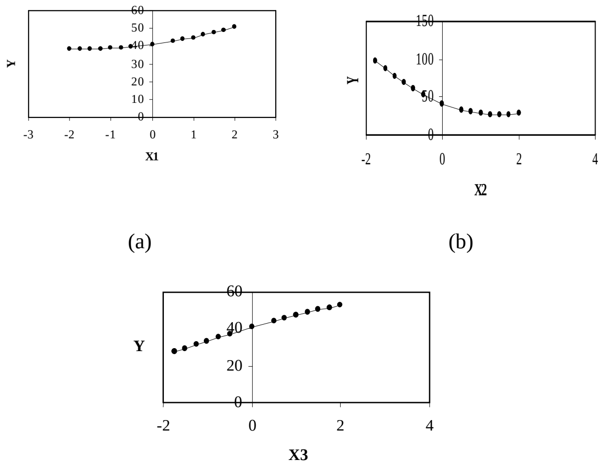
Figure 3. Variation of *Y* function vs. X_1 and X_3: (a) $Y_1=Y(X_1,0,X_3)$, (b) Isoline



(a) (b)

Figure 4. Variation of *Y* function vs. X_2 and X_3: (a) $Y_1=Y(0,X_2,X_3)$, (b) Isoline

In this paper, our researches were concentrated to determine the optimal values when it is worked with a relative high quantity of sawdust (in case of combined physico-mechanical steps for dye-containing effluent treatment). Thus, it seems that high dye removals will be obtained for relative high sorbent quantities (i.e. > 0.70 g per 25 mL sample), low pH value (i.e. pH< 1.50) and a minimum sorption time of 45 minutes.



(a) (b)

(c)

Figure 5. Dependence of *Y* vs. each variable: (a) $Y=Y(X_1,0,0)$; (b) $Y=Y(0,X_2,0)$ and (c) $Y=Y(0,0,X_3)$.

These representations permit to observe into the experimental admissible field the variation on isoline, and the maximum point for high dye removal efficiency. There were used the WinSurf and Excel graphical representations.

4. Conclusions

The Orange 16 reactive dye removal from aqueous environments by *sorption* onto wasted sawdust can be applied with very good results.

An empirical model is proposed by a central compositional rotatable design (2^3), considering quantity of sawdust, pH and sorption time as independent variables, while Orange 16 dye removal efficiency is chosen as optimization criteria (response function). The distinct optimum variables correspond to a sawdust content of 0.773 g per 25 mL, a pH of 0.392, a sorption time of 44.10 minutes for a maximum dye removal of 90.319 %.

The graphical representation permits the localization of the optimal field and to find the best parameters using a simulated aqueous environment containing textile Orange 16 reactive dye treated by sorption with a ‘low cost’ sorbent (wastes of conifer sawdust). This optimization study can also be considered as a preliminary application of a valorization procedure of natural wastes from an important economic sector – conifer wood processing - into the treatment of aqueous contaminated systems or final aqueous effluent.

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Received: 06 April 2011
Accepted: 26 May 2011