MODELING AND OPTIMIZATION OF A REAL TEXTILE EFFLUENT TREATMENT BY SORPTION ONTO SAWDUST AS ‘LOW COST’ SORBENT

MODELAREA ŞI OPTIMIZAREA EPURĂRII UNUI EFLUENT TEXTIL REAL PRIN SORBȚIE PE RUMEGUŞ CA SORBENT,IEFTIN’

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Abstract. *An experimental planning of sorption on sawdust (as ‘low cost’ sorbent) applied for a real textile effluent (i.e. collected after the dyeing and rinsing steps of cotton fabrics manufacturing) is discussed using a 2^3 central compositive rotatable planning. It was elaborated an empirical model considering the sorbent concentration, pH and temperature of textile effluent as indepen-dent variables, while the decoloration degree (color removal) was chosen as optimization criterion. The highest decoloration degree was 65.815 % after 24 hours of continuous static sorption. The proposed model was found adequate for the real effluent treatment by sorption on sawdust as primary treatment step.*
Key words: *decision variables, empirical model, experimental planning (2^3), optimization criterion, real textile effluent, sawdust, sorption*

Rezumat. *În lucrare este discutată o programare experimentală a unui proces de sorbție pe rumeguş aplicat unui efluent real textil (i.e. colectat după treptele de vopsire şi clătire de la fabricarea țesăturii de bumbac), bazată pe aplicarea unei planificări central compozițional rotabile de ordinul 2^3. A fost elaborat un model empiric considerând concentrația de sorbent, pH-ul şi temperatura ca variabile independente, în timp ce gradul de decolorare (îndepărtarea culorii) din efluentul textil a fost ales drept criteriu de optimizare. Cel mai mare grad de decolorare găsit a fost de 65.815 % după 24 ore de sorbție statică continuă. Modelul propus a fost găsit adecvat pentru epurarea efluentului real folosind sorbția pe rumeguş ca procedeu primar de epurare.*
Cuvinte cheie: *variabile de decizie, model empiric, planificare experimentală (2^3), criteriu de optimizare, efluent real textil, rumeguş, sorbție*

INTRODUCTION

The avoidance, minimization or reduction of pollution is a necessary action for assuring the sustainable management of water resources, or the conservation of natural aquatic environment for future generations. In order to reduce pollution is required the treatment of final effluents, among others, either individually or mixed with domestic wastewaters, in a modern and performant treatment plant.

All industrial sectors are discharging final effluents, either in the urban sewage system or in different natural receptors. The environmental protection requirements directed researches to development of new production processes

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with lower consumption level of water and raw materials, and also efficient treatment of individual and/or mixed final effluents for in-side recycling (Zaharia et al., 2012). The removal of pollutants from industrial effluents by adsorption on „low cost" materials became an interesting objective (*i.e.* a relative simple and cheap 'end-of-pipe' solution, fulfilling the strict demands imposed by the environmental regulator of industrial effluent quality) (Zaharia, 2012b).

Numerous studies concluded that the adsorbents which contain high quantities of celluloses adsorb different organic substances, dyes, heavy metals, etc., by processes of physical ('physical sorption'), chemical (‚chemisorption') or biological nature (‚biosorption'), respectively complex mixed processes of all these (Zaharia and Suteu, 2012a). From economic and performance reasons (costs-adsorption performance), the cheap adsorbents which contain either high quantities of carbon in their chemical structure of inorganic nature (*i.e.* ash, sludge) (Zaharia and Suteu, 2012b; Zaharia et al., 2012) or prevalent inorganic material of carbonate, phosphate type (*i.e.* rests of marine carcasses, seashells) or organic material of ligno-cellulosic type (*i.e.* sawdust, peat, wasted raw coal, industrial lignin, rests of non-living vegetal – dead algae, branches, leafs, fibrous trunks or stalks, rests of pips, seeds), available in nature or as production wastes, were applied for removal of polluting loads from different industrial effluents (Zaharia et al., 2012; Zaharia and Suteu, 2012b).

This paper is a continuation of authors' researches in which is presented a study of modeling and classic optimization applied for the sorption step on sawdust (one-single stage treatment) of a real textile effluent. An experimental central compositive rotatable design of three order (2^3) was applied in the experimental laboratory researches.

MATERIAL AND METHOD

1. Materials, reagents and characteristics of the studied sorption process

The principal materials, chemical reagents, analysis apparatus and characteristics of textile effluent and of sorption process are synthesized below (Zaharia C. et al., 2012, Zaharia C., Suteu D., 2012a).

Sawdust. It is a fibrous production waste (produced in the mechanical processing of conifer wood), which contains different functional groups and organic compounds (10-16% hemicelluloses, 48-57% cellulose, 27-33% lignin with polyphenolic groups and ionizing carboxylic groups (uronic acids) as the most important adsorptive constituents). Sawdust (humidity of 4%) is dried in air, breaked in pieces, mortared and sieved in two fractions: SD-1 (particles of 1-2 mm) and SD-2 (dust, < 0.1 mm). It was worked with SD-1 sawdust fraction.

pH adjustment. It was performed with 0.05N H_2SO_4, and 0.01N NaOH.

Dyestuff. The dyestuff contains 2 textile dyes (Remazol Arancio 3 R, 33 g/L, Remazol Rose RB, 22 g/L), Kemapon FRD (tensioactive agent, 3 g/L), pH buffer solution (Na_2CO_3, 20 g/L), additives (NaOH, 5 g/L) and other auxiliaries (electrolyte, anti-crust agent, reducing agents). The dyestuff bath capacity is 3.69 m^3/day.

Textile effluent. It is a real textile effluent collected from a private textile unit from NE Romania after dyeing and rinsing of cotton fabrics. The average flow of textile effluent collected individually and treated is of 15-16 m^3/day. *Principal characteristics of textile effluent* are: pH-7.30, color (A_{436}=0,614), suspended solids-289 mg/L, turbidity-93 FTU, COD_{Cr}-665 mg O_2/L, BOD_5-386 mg O_2/L, chlorides-98 mg/L, sulfates-365 mg/L, total N-23.12 mg/L, total P-14.54 mg/L, phenol-26.23 mg/L, extractable substances in solvents-45 mg/L, detergents-1.56 mg/L, total heavy metal ions < 4 mg/L.

Laboratory installations and apparatuses. Digital HACH One Laboratory pH-meter, VIS SP 830 Plus 1.06 spectrophotometer (Metertech), UV-VIS multifunctional DRELL 2000 spectrophotometer (HACH Company, SUA) with kits, water bath, distilation installation, thermo-oxidation installation for COD_{Cr} determination, Partner WPS 510/C/2 digital balance, TZS First heating range, Austria.

Sorption working methodology. It was used the cvasi-static ‚batch' technique, in which is considered the sorption as a physical-chemical process-*sorption* (*i.e. physical* – by van der Waals, hydrogen, hydrophobic, coulombic forces, and *chemical* –electrostatic attraction, ionic exchange and complexation). *Working conditions*: sorbent doses of 16-40 g/L, pH of 0.35-4.0, temperature of 5°-40°C, and 24 h of sorption.

2. Modeling methodology and experimental planning

It is considered that the principal real variables which influence the decoloration process by sorption on sawdust are: quantity of sorbent (Z_1, g per 25 mL), pH (Z_2, pH unit), and sorption temperature (Z_3,°C). As optimization criterion (decision function) was chosen the decoloration degree or color removal (Y, %). It was used a mathematical model of "n=3" variables, and an experimental central compositive rotatable planning of 2^3 order (equation (1)) (Zaharia C., Suteu D., 2009, 2011).

$$Y= b_0+\sum b_i x_i + \sum b_{ii}x_i^2+\sum b_{ij}x_ix_j \quad (1)$$

where: *Y* represents the decission function (optimization criterion); x_i, x_j, x_{ii}, x_{ij} are the coded model variables, and b_0, b_i, b_j, b_{ij} are the model coefficients (i, j= 1, 2, 3), calculated with the response surfaces methodology in 20 experimental points, using the central compositive rotatable design of 2^3 order (Macoveanu M., Nicu V., 1989; Zaharia C. et al., 2006, 2007).

In table 1 are indicated the values attributed to coded variables (*i.e.* $X_i = (Z_i-Z_{i0})/\Delta Z_{i0}$; ($Z_{i0}$) – basic values of real variables and (ΔZ_{i0}) – variation step).

Table 1

Codification of independent variables in experimental adopted planning (2^3)

Variable \ Value	Coded variable (X_i)	Real variable (Z_i)	Real basic variable (Z_{i0})	Variation step (ΔZ_{i0})
Sorbent concentration, g per 25 mL	X_1	Z_1	0,75	0,15
pH	X_2	Z_2	2	1
Temperature, °C	X_3	Z_3	20	10

The values of coded variables are: 0, ±1, ±α_i (*i.e.* ±1.682 for experimental central compositive rotatable planning of 2^3 order). The Fisher constant, multiple correlation coefficient or Fisher test are calculated, and applied for establishing the correlation between the three independent variables (Z_i) and dependent decission function (*Y*, decoloration degree, %). The average deviation of calculated values with the proposed model in comparison with the experimental ones must be between +10% and -10% for a good agreement of all processed data.

RESULTS AND DISCUSSIONS

The textile effluent samples of 25 mL were treated with different quantities of sawdust at different values of pH and temperature in order to study the decoloration performance by sorption on sawdust according to an experimental central compositive rotatable planning of 2^3 order. The results are synthezed in table 2. The proposed model is presented in equation (2), and the calculation of model coefficients was achieved with specific calculation formulas from statistics and described in previous papers (Zaharia et al., 2006, 2007).

Table 2

Experimental matrix in the central compositive rotatable planning of 2^3 order

Exp. No.	Z_1	Z_2	Z_3	X_1	X_2	X_3	Y_{exp}	Y_{calc}	Deviation
1	0.60	1	10	-1	-1	-1	5.69	23.12	-3.06
2	0.90	1	10	1	-1	-1	0	19.78	0
3	0.60	3	10	-1	1	-1	1.57	17.06	-9.878
4	0.90	3	10	1	1	-1	0	20.30	0
5	0.60	1	30	-1	-1	1	57.76	52.74	0.087
6	0.90	1	30	1	-1	1	63.65	63.44	0.003
7	0.60	3	30	-1	1	1	37.92	33.42	0.119
8	0.90	3	30	1	1	1	52.85	50.70	0.041
9	0.498	2	20	-1.682	0	0	29.67	23.12	0.221
10	1.002	2	20	1.682	0	0	49.901	34.84	0.302
11	0.75	0.318	20	0	-1.682	0	65.815	54.18	0.177
12	0.75	3.682	20	0	1.682	0	48.33	38.37	0.206
13	0.75	2	3.18	0	0	-1.682	43.418	7.37	0.830
14	0.75	2	36.82	0	0	1.682	43.418	57.85	-0.332
15	0.75	2	20	0	0	0	49.312	50.61	-0.026
16	0.75	2	20	0	0	0	53.242	50.61	0.0495
17	0.75	2	20	0	0	0	46.758	50.61	-0.0823
18	0.75	2	20	0	0	0	51.277	50.61	0.0131
19	0.75	2	20	0	0	0	50.491	50.61	-0.0023
20	0.75	2	20	0	0	0	48.919	50.61	-0.0345

$$Y=50.606+3.485X_1-4.698X_2+15.005X_3-7.644X_1^2-1.531X_2^2-6.360X_3^2+1.645X_1X_2+3.510X_1X_3-3.312X_2X_3 \quad (2)$$

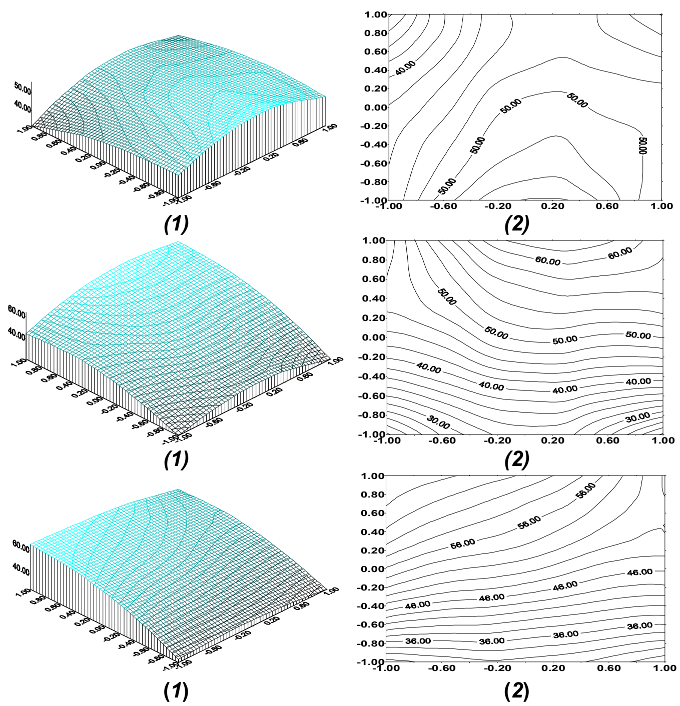
The value of Fisher constant is F= 18337.82 for Y in comparison with statistic value from tables, F_{tab}= 4.6 (α=99, ν_1=n-1=19 and ν_2=k-1=2, in which: n– number of experiments, and k– number of independent variables) (Macoveanu M., Nicu V., 1989). Because $F>F_{tab}$ is considered that the deviation of experimental values from the average value is not the results of experimental errors, but is determined by the influence of independent variables on decision function (Y).

The correlation coefficient is $R_{YX1X2X3}$= 0.772, and demonstrates that all independent variables are important for dependent function - decoloration degree of textile effluent in the whole experimental variation domain.

The value of Fisher test is F_{calc}= 7.84, comparing with F_{tab} = 6.59 from statistic data (freedom degree of ν_1 = n-k-1=16, and ν_2 =k=3), value higher than statistic one, providing that the independent variables have a significant influence on dependent function. It is considered that a good agreement exists between the experimental and calculated data, the average deviation being of -0.568 %.

Analysis of proposed model. The application of classical optimization method leads to conclusion that the Y function has a *local maximum* at $X_1^* = 0$, $X_2^* = -1.608$ and $X_3^* = 0$ (Y= 65.815 %). Transposed in real variables, these values correspond to some optimal values of the independent variables as follows: sorbent concentration (sawdust) of 30 g/L (*i.e.* 0.75 g per 25 mL textile effluent), pH of 0.392, temperature of 20°C, after 24 h of sorption. Because in practice is difficult to work at pH ≤ 0.40, it is usually worked at pH ≅ 2.

The analysis of Y decision function concludes that all X_i independent variables (quantity of sawdust, pH and temperature) are important for the decoloration of textile effluent. The figures 1(a-c) illustrate the dependence of effluent decoloration (Y) on each two of independent variables (X_i, X_j, j=1, 2, 3).



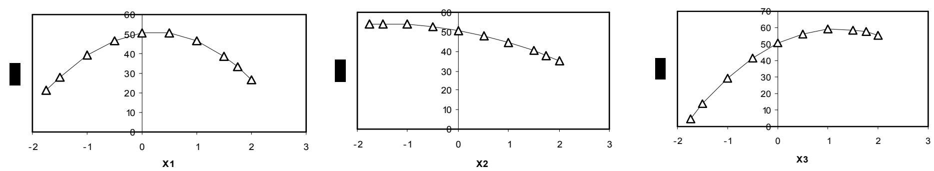
(a) Variation of Y vs. X_1, X_2:
(1) $Y=Y(X_1,X_2,0)$,
(2) Isoline

(b) Variation of Y vs. X_1, X_3:
(1) $Y=Y(X_1,0,X_3)$,
(2) Isoline

(c) Variation of Y vs. X_2, X_3:
(1) $Y=Y(0,X_2,X_3)$,
(2) Isoline

Fig. 1 - Influence of each two X_i, X_j independent variables vs. decoloration degree (Y)

The decoloration variation vs. sorbent concentration can be observed in the graphical representation of Y vs. X_i (Fig. 2(a-c)). Thus, it exists a *distinct decoloration maximum* (51.003 %) for $\boldsymbol{X_1^*} = 0.228$ (*i.e.* a sorbent quantity of 0.784 g per 25 mL, at pH= 2 and $T_{sorption}$= 20°C) (Fig. 2(a)), or a *local decoloration minimum* (35.085%) for $\boldsymbol{X_2^*} = +2{,}00$ (*i.e.* a local minimum at pH= 4.00, sawdust concentration of 30 g/L, and temperature of 20°C) (Fig. 2(b)), or a *distinct decoloration maximum* (59.456 %) for $\boldsymbol{X_3^*} = +1.1796$ (*i.e.*, a sorption temperature of 31.80°C, pH=2 and sorbent concentration of 30 g/L)(Fig. 2(c)).



(a) Y=Y(X_1,0,0) **(b) Y=Y(0,X_2,0)** **(c) Y=Y(0,0,X_3)**

Fig. 2 - Influence of each X_i independent variable vs. effluent decoloration degree (Y)

The best decoloration efficiency of a single-stage sorptive treatment of the real textile effluent with sawdust corresponds to a relative high sorbent concentration of 30 g/L, at pH of 0.392 (in practice is used pH ≅ 2), and t=20°C.

CONCLUSIONS

1. The decoloration of textile effluent by sorption on sawdust (“low cost” sorbent) represents a viable removal alternative of colored pollutants.

2. An empirical modeling by 2^3 central compositive rotatable planning was used, and the optimal values of decision variables correspond to 30 g/L sawdust, pH= 0.392, $t_{sorption}$=20°C, for decoloration of 65.815 %.

3. The graphical representations permit the localization of optimal variation domain, in specific operating conditions of textile unit.

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