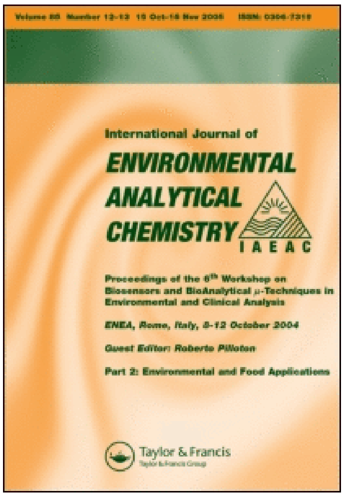

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METHODOLOGICAL APPROACH FOR THE HYDROLYSIS DEGRADATION OF ATRAZINE

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An approach by experimental design has been applied to measure the influence of different parameters in the hydrolysis of atrazine First, experiments were carried out in the laboratory under extreme conditions to reveal evolution phenomena. Then, a methodology was used to allow a representative equation of the degradation reactions. Three parameters were studied to evaluate their influence on hydrolysis: pH, water medium and temperature. Once the methodology had been validated in extreme pH conditions, this experimental design was applied to a neutral pH medium. The methodology was validated and the influence of the parameters was evaluated.

Keywords: s-Triazines; hydrolysis; experimental design; pH; temperature; natural water; HPLC.

INTRODUCTION

The fate of pesticides has been investigated extensively (1). Atrazine and other s-triazines are widely used for weed control in the cultivation of corn and other crops (2). Because of their widespread use, s-triazine herbicides have been the subject of numerous investigations into their degradation in soil and water and by plants and microbial microcosms (3–5). The difficulty lies in understanding the different ways in which these products degrade in natural water. The analysis of triazines in natural water is not straightforward since by-products may be trapped in organic materials. Experiments have therefore focused on hydrolysis under laboratory conditions.

The hydrolysis degradation pathway of atrazine is well known; the only reaction pathway is the substitution of hydroxyl by chlorine, whatever the different

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media are (6). There is also now general agreement on the different kind of factors which influence degradation, resulting in a more detailed understanding of the process. The following parameters are assumed to be important in the fate of pesticides: pH, salinity, ionic composition, temperature and concentration of humic and fulvic acids, organic and particular carbon, and oxygen (7). However, because degradation pathways are very slow, results for reaction rates are often dissimilar. For example, the half-life of the reaction rate for hydrolysis under natural conditions (natural water, pH neutral) can fall anywhere from one year to 1800 years (8), (9). In the same way, different parameters are not predicted to have the same effect according to different studies (12), (13).

The purpose of this investigation was to apply a methodology to the study of slow degradation processes of atrazine. The use of a particular experimental design for hydrolysis was studied here to find out if this methodology is appropriate and then to define the domains where it can be tested. The main objective was to make results for atrazine hydrolysis more coherent, in terms of the parameters considered to be the most influential. These were pH, temperature and the water medium. Experimental methodology was used to obtain more rigorous results. In this way, the number of experiments was reduced and the influence of the medium on degradation was calculated.

At first, experiments were carried out under extreme conditions in order to accelerate reaction rates, to assess phenomena and to validate the use of the methodology on the degradation of s-triazines. Then, the same methodology was applied under similar conditions to natural media. After validation of the modelling, the influences of the different parameters were estimated numerically, as well as any interference between these parameters.

EXPERIMENTAL DESIGN SOFTWARE

Modelling

The experimental matrix chosen for this study was a factorial 2^3 matrix (that is 3 factors for 2 levels). The three factors studied are the axes of a cubic experimental area. This experimental area is centered on the value 0, and the two levels take the code values: -1 and $+1$.

The guiding rule of the approach used in this study was to postulate a equation model in which the response is a first order polynomial with (n–1) variables, n being the number of experiments. These variables are the factors involved in the process. Response Y could be written as (15):

$$Y = B_0 + \Sigma_i B_i X_i + \Sigma_{ij} B_{ij} X_i X_j + \Sigma_{ijk} B_{ijk} X_i X_j X_k.$$

X_i: value of the parameter i (symbolized + 1 or - 1)

B_i: proportional coefficient for the influence of $X_i$on response Y, B_i is the weight of the variable

X_i (10). B_i can thus be calculated to determine the relative influence of each parameter.

Each experimental design was investigated to obtain an equation model representative of the responses. These for the code value 0 can be included in the calculation of the model and can be used to estimate the linearity of the responses. The modelling is proved valid if the values for the influences of each parameter are significant enough. Then, the influences of parameters can be mathematically estimated.

The response surface model was calculated using the NEMROD 3.0 software (New Efficient Methodology for Research using Optimal Design) developed by LPRAI (Laboratoire de Prospestive Réactionelle et d'Analyse de l'Information)-Marseille, France.

EXPERIMENTAL

Reagents

All organic solvents were of pesticide-grade. The standard, 99 % pure atrazine was obtained from Riedel-de Haën. Standard stock solutions for analysis were prepared in methanol and then diluted in water to obtain different concentrations. For the hydrolysis experiments, the atrazine solution was made directly in water. Water sampling were carried out on one site of a canal network (Prise au Rhône) managed by the Company BRL, Nimes, France, for irrigation and drinking water treatment.

Water medium

Two kind of water were used: ultra-pure water and natural water. The ultra-pure water was obtain by a Millipore process. The natural water came from the Rhône river. This water has been already the suject of investigations (16), (17), and some characteristic are given in Table I. These values are given oven one year.

TABLE I Characteristics of natural water used

Parameter	*Natural water (Rhône)*
Suspended mater	1 to 150 $mg.l^{-1}$
pH	7.5 to 8.5
Conductimetry	300 to 350 $\mu S.cm^{-1}$
TOC	< 5 $mg.l^{-1}$
TIC	25 to 30 $mg.l^{-1}$
TAT	3.6 $me^{-}.l^{-1}$

Hydrolysis procedure

All samples were prepared in 1 litre sterilized autoclaved flasks. Each sample of natural water was filtered through a 0.45 μm filter to remove suspended compounds. This was followed by a 0.22 μm filtration to eliminate microbacteria. Buffers were not used in order to avoid gram production. The pH was adjusted using HCl and NaOH solutions. Each sample was kept in continuous stirring at 100 rpm by a magnetic stirrer, and in the dark. The initial concentration of atrazine was 10 $mg.l^{-1}$ and an ultrasonic bath was used to make it dissolve better. Flasks were placed in rooms of different temperatures: 20, 25 and 30°C, with a variation estimated at ± 1°C. Samples were taken with a pipette through a little hole in the plug to avoid bacterial contamination. Three experimental domains were defined: acid, basic and neutral and the experimental design is described in Table II.

TABLE II Experimental matrix

experiment number	*pH*	*water medium*	*temperature*
1	−1	−1	−1
2	+1	−1	−1
3	−1	+1	−1
4	+1	+1	−1
5	−1	−1	+1
6	+1	−1	+1
7	−1	+1	+1
8	+1	+1	+1
9	0	0	0

Acid domain

level	*pH*	*water medium*	*temperature*
−1	2	ultra pure water	20°C
0	3	mixture : 50/50	25°C
+1	4	natural water	30°C

Basic domain

level	*pH*	*water medium*	*temperature*
−1	12	ultra pure water	20°C
0	11	mixture:50/50	25°C
+1	10	natural water	30°C

Neutral domain

level	*pH*	*water medium*	*temperature*
−1	6	ultra pure water	20°C
0	7	mixture: 50/50	25°C
+1	8	natural water	30°C

Experiments n* and n** were added to estimate the experimental variation, experiment n°9 was the centre point; this value was used to calculate the model equation, and to estimate its validity.

Analysis

Reversed-phase high-pressure liquid chromatography is a more appropriate analytical method than gas chromatography because it allows the quantification of atrazine and its byproducts without derivation. The HPLC measurements were carried on a Waters^{TM} 600 Controller liquid chromatograph equiped with a Varian 2550 variable λ detector. The wavelength selected for all measurements was 220 nm. The column was a Supelcosil LC–18, 25 cm × 4.6 mm particle size 5 µm. Elution was carried out with a gradient of phosphate buffer (pH7)-methanol (70:30, v/v) to phosphate buffer (pH7)-methanol (50:50, v/v), at a flow rate of 1 ml.min^{-1}. The run time was 35 min. The mobile phase was deaerated by the passage of a helium flow.

RESULTS AND DISCUSSION

Methodological approach

Methodology

The aim of our investigation was to obtain results more coherent, and a strict methodology was therefore necessary. An experimental design was elaborated in order to quantify accurately the influences of medium parameters whereby atrazine is degraded. The use of only one experimental design over the entire pH scale was not possible. The matrix chosen involved a first order polynomial equation, and a linear response. It was already known that the influence of pH is not linear over the entire pH scale, as the studies of Erickson *et al.*(3) demonstrate. It was therefore decided to investigate over smaller pH bands in which responses were assumed almost linear. This hypothesis has to be confirmed by comparing calculated (given by equation model) and experimental mid-points. To start with, hydrolysis was studied using this methodology at extreme pH levels: acid and basic. At these levels, reaction is more rapid, and degradation rates are more accurate. Once the methodology was considered effective under these conditions, the experimental design was applied to a pH level that was close to that of natural conditions.

Hydrolysis by experimental design

Chosen responses for experimental design interpretation

For each domain, several experimental responses were studied. The aim is to validate a model equation to obtain values for the influences of parameters. The choices of the responses are listed in Table III.

TABLE III Chosen responses for the experimental domains

Domain	*N° of response*	*Chosen responses*
Acid	2	- half-life - % remaining at 30 days
Basic	2	- half-life - % remaining at 15 days
Neutral	4	- half-life - % remaining at 10, 20 and 30 days

For all three domains, half-lives were chosen as a response. And in addition, the degradation rate was estimated to give an other kind of response. The degradation rate was calculated according to the time at which the shortest degradation curve was near to the time axis. For the acid domain, this time was 30 days. For the basic domain, it was only 15 days. For the neutral domain, however, three different times were chosen because the phenomenon is less obvious and the effects of parameters less marked. The longest time was 30 days, because the lack of experimental data after this time makes linear regression inaccurate. The shortest was 10 days, before which variation was insufficient. A middle value of 20 days was also taken.

For each assay, the degradation kinetic of atrazine was considered as a first order reaction. Kinetic parameters could therefore be calculated.

The percentage of atrazine remaining is estimated with a linear regression applied to the degradation rate.

Modelling of the answers

For both kinds of response, a first-order polynomial model was calculated according to the following equation:

$$Y = B_0 + B_1(PH) + B_2(H_2O) + B_3(T°) + B_{12}(pH.H_2O) + B_{13}(pH.T°) \\ + B_{23}(H_2O.T°) + B_{123}(pH.H_2O.T°)$$

- B_0: value of the response when each parameter takes the code value: 0. B_0 represents the experimental mid-point.
- B_i, B_{ij}, and B_{ijk}, i, j, k ∈ [1,3]: coefficients according to the influence of the pH, water medium (H_2O), and temperature (T°), of the interaction two by two parameters, and the influence of the interaction between the three paramaters.

Acid experimental domain

(a) Kinetics and degradation rate. An example of the kinetic parameters (constant rate and half-life) and degradation rates (% atrazine remaining) obtained is given in Figure 1 for assay number 3.F

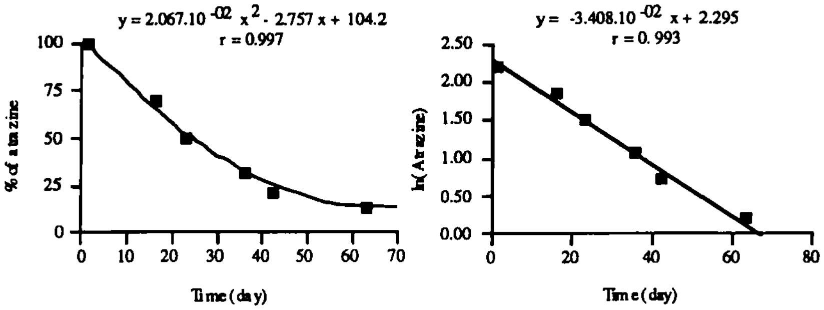

FIGURE 1 Percentage of atrazine remaining in the media and kinetic exploitation: assay n° 3

The results obtained for each assay are given in Table IV.

TABLE IV Hydrolysis assays in acid media: response results and correlation coefficients

	Kinetic parameters			Degradation rate	
		Response 1		Response 2	
N° of assay	*k: constant rate (d^{-1})*	*$t_{1/2}$: half-life (day)*	*Correlation coefficient*	*% remaining (30 days)*	*Correlation coefficient*
1	3.101.10–2	22.3	0.992	40.75	0.996
2	5.153.10–4	1345.1	0.952	97.76	0.993
3	3.408.10–2	20.3	0.993	40.08	0.997
4	3.948.10–4	1755.6	0.762	96.80	0.948
5	1.195.10–1	5.8	0.992	3.18	0.991
6	5.648.10–4	1227.2	0.941	99.27	0.973
7	1.221.10–1	5.6	0.989	3.50	0.991
8	2.100.10–3	330.0	0.959	94.89	0.997
9	1.606.10–2	43.15	0.961	59.90	0.978

Half-lives values are scattered from almost 6 to 1755 days. The fastest reaction corresponds to assay n°7, carried out at 30°C, in natural water and at pH=2.

(b) Modelling of the answers. In this domain, the half-life did not give very significant results, although the levels of significance of coefficients are more accurate for the percentage of atrazine remaining in the solution.

In initial investigations, in terms of the model, the factor B_2 (water medium) was considered not very significant. The B_{23} interaction was also insignificant and has been left out. Values of the remaining factors are given in Table V, with their level of significance: "% error".

TABLE V Factor and interaction effects

factor	*effect*	*error %*
B_0	59.6	< 1‰
B_1	37.54	< 1‰
B_2	–0.64	24%
B_3	-9.19	< 1‰
B_{12}	–0.71	< 5%
B_{13}	9.14	< 1‰
B_{123}	–0.61	5.6%

The final model can be described:

$$\textbf{\% atrazine remaining} = 59.6 + 37.54(pH) - 0.64(H_2O)$$

$$- 9.19(T°)\ 0.71(pH.H_2O) + 9.14(pH.T°) - 0.61(pH.H_2O.T°)$$

This last equation allowed the response value for all points in this experimental domain to be calculated using the coded variables (+1 and – 1).

The experimental and calculated results arising from the model are set out in Table VI.

Table VI Experimental and calculated results

experiment number	*atrazine % exp.*	*atrazine % cal.*	*residual error*
1	40.75	41.11	0.36
2	97.76	97.93	0.17
3	40.08	39.85	0.23
4	96.80	96.46	0.34
5	3.18	3.05	0.13
6	99.27	99.05	0.22
7	4.10*	4.41	0.31
8	94.89	95.18	0.29
9	59.90	59.63	0.27

*: average of the different assays

Each model had to be validated. It appeared necessary to estimate:

- the relative experimental error for the responses (10), (11),
- the error due to the model.

The model was considered linear if the experimental mid-point corresponded with the theoretical one.

The standard deviation in the model was estimated from the residual error according to the following equation:

$$\mathrm{SD(m)} = \sqrt{\frac{\Sigma(x_{i\,\mathrm{exp}} - x_{ical})^2}{\alpha}}$$

α: degree of liberty : number of experiments - number of coefficients .

The calculated value in this case is: SD(m) = 0.76 % (estimation from the 8 assays).

This standard deviation is the consequence of the error due to the model itself and also perhaps to the experimental error.

The standard deviation in experimental errors was estimated by repeating experiment n°7, and was calculated by the following equation:

$$\mathrm{SD(exp)} = \sqrt{\frac{\Sigma(x_i)^2 - n(\bar{x})^2}{n-1}}$$

In this case, the experimental standard deviation is: SD(exp) = 0.67 %

Residual values are low, and the experimental mid-point is very close to the theoretical one. This seems reason enough to accept the validity of the equation model put foward for hydrolysis in this experimental domain. For this reason, the same methodology was applied to a basic pH domain.

Basic experimental domain

(a) Kinetics and degradation rate. In this domain, the results obtained for each assay are give in Table VII.

Half-life values are less scattered compared to the acid domain. They range from 3 to 77 days. The fastest reaction corresponds to assay n°8, carried out at 30°C, in natural water and at pH=12.

(b) Modelling of the answers. In initial investigation, a study of these responses is satisfactory only in terms of the half-life: levels of significance are higher in this case.

As with the acid domain, B_2 (water medium) seems to be insignificant, and the model was better when the B_{12} interaction was left out. Finally, the influences of the different factors are given in Table VIII.

TABLE VII Hydrolysis assays in basic media: response results and correlation coefficients

	Kinetic parameters			*Degradation rate*	
		Response 1		*Response 2*	
N° of assay	*k: constant rate* (d^{-1})	$t_{1/2}$: *half-life (day)*	*Correlation coefficient*	*% remaining (15 days)*	*Correlation coefficient*
1	8.95.10–3	77.4	0.919	95.59	0.925
2	6.82.10–2	12.3	0.991	30.76	0.987
3	1.10.10–2	62.8	0.973	91.97	0.977
4	7.89.10–2	8.8	0.995	51.27	0.997
5	2.47.10–2	28.1	0.996	81.21	0.998
6	2.18.10–1	3.2	0.992	14.94	0.982
7	1.33.10–2	51.9	0.962	91.66	0.964
8	2.32.10–1	3.0	0.989	23.01	0.977
9	2.09.10–2	33.1	0.975	67.40	0.976

TABLE VIII Factor and interaction effects

factor	*effect*	*error %*
B_0	31.18	< 1 ‰
B_1	-24.11	< 1 %
B_2	0.69	63 %
B_3	-9.39	< 5 %
B_{13}	5.66	< 5%
B_{23}	5.21	< 5%
B_{123}	-4.39	7.1 %

The final model can thus be given:

$$t_{1/2} = 31.18 - 24.11(pH) + 0.69(H_2O) - 9.39(T°) + 5.66(pH.T°) + 5.21(H_2O.T°) - 4.39(pH.H_2O.T°)$$

The experimental and calculated results arising from the model are set out in Table IX.

SD(exp) = 0.19 (day) (estimation on the assay n° 8),

SD(m) = 4.63 (day) (estimation from the 8 assays).

This time, residual values are not so good as for the previous domain, but error of coefficients are acceptable. The experimental centre point is very close to the theoretical centre. For these reasons the validity of the model equation put foward for hydrolysis in this experimental domain can be accepted.

TABLE IX Experimental and calculated results

experiment number	*half-life time exp.*	*half-life time cal.*	*residual error*
1	77.39	79.25	1.86
2	12.30	10.93	1.37
3	62.84	61.43	1.41
4	8.78	10.67	1.89
5	28.06	29.95	1.89
6	3.18	1.83	1.35
7	51.88	50.53	1.35
8	3.01*	4.85	1.84
9	33.10	31.18	1.92

* : average of the different assays

These two experimental designs were useful for understanding the hydrolytic phenomenon, and because this methodology seemed appropriate to hydrolysis, the following neutral domain was studied in the same way.

Neutral experimental domain

(a) Kinetics and degradation rate. The results obtained for each assay are give in Table X.

In this case, half-life values are all of the same order. They range from 79 to 108 days, that is faster that expected in reference to the literature (9).

Table X Hydrolysis assays in neutral media: response results and correlation coefficients

	Kinetic parameters			*Degradation rate*			
		Response 1		*Responses 2, 3 and 4*			
N° of assay	*k: constant rate (d^{-1})*	*$t_{1/2}$: half-life (day)*	*r*	*% at 10 days*	*% at 20 days*	*% at 30 days*	*r*
1	7.73.10–3	89.6	0.945	88.9	81.4	77.0	0.971
2	6.38.10–3	108.6	0.942	98.1	92.2	86.3	0.946
3	7.31.10–3	94.7	0.908	86.6	79.8	75.8	0.922
4	6.95.10–3	99.7	0.906	88.3	81.6	78.3	0.970
5	8.75.10–3	79.1	0.940	86.5	78.1	74.9	0.980
6	8.33.10–3	83.2	0.995	91.9	84.4	78.1	0.997
7	8.53.10–3	81.3	0.919	87.8	79.9	75.5	0.944
8	6.85.10–3	101.2	0.948	91.2	84.6	80.8	0.972
9	7.66.10–3	90.4	0.972	90.0	83.0	79.1	0.976

(b) Modelling of the answers. In this domain, response variations were less prononced and they were of the same order as experimental error. Nevertheless, of the four responses, the one showing the percentage of atrazine remaining at 10 days gave good results (error % of coefficients are low). Only this model was considered worth developing. All the factors are set out in Table XI. to compare the influences of the parameters given by each model.

TABLE XI Factor and interaction effects

factor	*half-life time*	*error %*	*% at 10 days*	*error %*	*% at 20 days*	*error %*	*% at 30 days*	*error %*
B_0	92.09	< 1	90.03	< 1	83.57	<5	78.49	< 1
B_1	5.88	6.9	2.34	< 1	1.58	51.9	2.47	5.9
B_2	2.18	18.9	-1.26	< 1	-2.40	39.1	–0.66	22.1
B_3	-5.86	6.9	–0.41	< 5	-2.13	42.7	–0.94	16
B_{12}	0.10	89.7	-1.31	< 1	–0.20	92.3	–0.66	22.1
B_{13}	–0.13	87	–0.41	< 5	0.93	67.3	–0.49	28.7
B_{23}	3.12	13.3	1.74	< 1	3.15	31.7	1.64	9.1
B_{123}	3.60	11.6	0.59	< 5	–0.45	82.5	1.04	14.5

The final model can be given:

$$\textbf{\% atrazine remaining} = 90.03 + 2.34(\mathrm{pH}) - 1.26(\mathrm{H_2O}) - 0.41(\mathrm{T^\circ})$$
$$- 1.31(\mathrm{pH.H_2O}) - 0.41(\mathrm{pH.T^\circ}) + 1.74(\mathrm{H_2O.T^\circ}) + 0.59(\mathrm{pH.H_2O.T^\circ})$$

The experimental and calculated results arising from the equation model are set out in Table XII.

TABLE XII Experimental and calculated results

experiment number	*atrazine % exp.*	*atrazine % cal.*	*residual error*
1	88.89	88.79	0.10
2	98.09	98.09	0.00
3	86.59	86.59	0.00
4	88.30	88.29	0.01
5	86.51	86.49	0.02
6	91.87	91.79	0.08
7	88.93*	88.89	0.04
8	91.24	91.31	0.07
9	90.01	90.03	0.02

*: average of the different assays

The standard deviation can only be calculated if assay n°9 is included, giving as many coefficients as assays.

The calculated value in this case is: SD(m) = 0.15 %

The standard deviation due to experimental errors was estimated: SD(exp) = 4.34 % (estimation from assay n° 7).

As with the other experimental designs, residual values were very low, and the experimental centre point is very close to the theoretical centre, there are good reasons to accept the validity of the model put forward for hydrolysis in this experimental domain.

Since the models given by the experimental design have been validated for each domain, the influence of parameters can be discussed.

Discussion

(a) Reaction rate. In terms of the responses given by plotting the kinetics, the degradation rates in the acid domain were slower than those in the basic domain.

At pH 7, half-lives were between 79 days and 108 days according to temperature and water medium. Which means that the reaction rate is more rapid than had been envisaged.

(b) The influences of parameters. To illustrate the influences of the parameters, Table XIII. summarises the relative influence of the different factors in each experimental domain for the responses chosen: expressed as a percentage.

TABLE XIII Influence of paramaters and interactions percentage

factor	*acid domain*	*basic domain*	*neutral domain*
B_0 (average)	50.7%	38.6%	91.7%
B_1 (pH)	**31.9 %**	**29.9 %**	**2.3 %**
B_2 (water medium)	**0.5 %**	**0.8 %**	**1.2 %**
B_3 (temperature)	**7.8 %**	**11.6 %**	**0.4 %**
B_{12}	0.6%	-	1.3%
B_{13}	7.7%	7.0%	0.4%
B_{23}	-	6.4%	1.7%
B_{123}	0.5%	5.4%	0.6%

Not surprisingly, extreme pH conditions considerably accelerate degradation compared to neutral pH. The effect of pH was almost the same in the basic domain as in the acid one. And the same effect of pH was found within the neutral domain; the degradation rate was a little more rapid at pH 6 than at pH 8.

In the described experimental domain, the influence of the water medium was not so marked. With the neutral experimental design, the influence was weak, but a more rapid degradation in natural water was predicted. Nevertheless, a study of the other two experimental designs did not prove the influence of the water medium to be significant. This result is in agreement with a study comparing atrazine hydrolysis in ultra-pure water and well water (12). The influence of the water medium thus needs further investigation. This is certainly one reason why authors have found contradictory results. Maybe it would be interesting to study the effects of different natural water media (14).

Some authors do not consider the effect of the temperature below 30°C as very significant (12). In our case, the influence of temperature was notable. For the acid and basic domains, temperature had a similar influence. However, in the neutral domain, the influence of temperature was not so pronounced: the ratio was smaller. On the other hand, in the modelling, the effect of temperature was still seen to be significant.

(c) The influences of interactions. In this study, only the interaction between pH and temperature at the two extreme pH domains could be explained for his important coefficient. The effect of pH is stronger at 30°C in the acid domain whereas in the basic domain, the influence of pH is stronger at 20°C. This phenomenon could be explain by the Nernst relation.

For a temperature above 25°C, the value of the pH could be over-estimated. That may explain why in the acid domain the influence of the pH is greater (values may be more extreme), and in the basic domain, the influence of the pH is less strong at 30°C (values of pH may be lower that expected).

The other interactions gave no more information that could be interpreted in a physico-chemical way. In preliminary stage, interactions were given in order to adjust the model.

(d) Diagrams of the responses. Each experimental domain can be represented by a cube. The following diagrams in Figure 3 represent the influence of parameters in the three experimental domains studied. For each parameter, the importance of the influence is symbolised by the difference in the size of the sphere between the level (+1) and (−1). In this way, it can be visualised immediately that in the acid and basic domains, the influence of pH is predominant. On the other hand, no factor is predominant in the neutral domain, the spheres are almost identical.

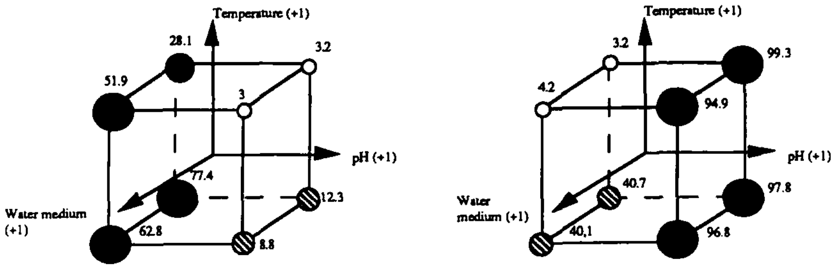

FIGURE (a): % atrazine remaining (30 days)

FIGURE (b): atrazine half-life (days)

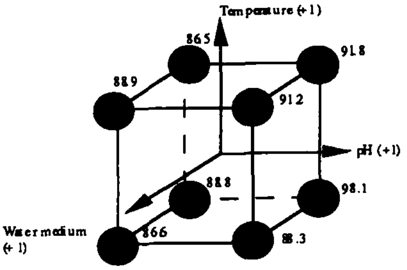

FIGURE (c): % atrazine remaining (10 days)

FIGURE 2 Diagrams of the responses: (a); acid domain, (b); basic domain, (c); neutral domain

CONCLUSION

Rates of degradation of atrazine by hydrolysis were investigated using an effective methodology: experimental design. The first approach by this methodology gives additional results on the hydrolysis of atrazine. For the three experimental designs presented, degradation rates of atrazine by hydrolysis were quantified, and the influence of parameters was abble to be assessed. The following conclusions were obtained:

- half-lives of atrazine were calculated as between 79 and 108 days in a neutral pH domain, depending on the water medium (ultra-pure or natural) and temperature (20 or 30°C).
- in these experimental conditions, the water medium has a minor influence on hydrolysis. In the neutral pH domain, natural water accelerated atrazine degradation,
- temperature has a weak but significant influence on degradation rates in all pH domains.
- as expected, pH was an important parameter in degradation by hydrolysis.

This study is a startingpoint for further investigations of slow degradation phenomena of atrazine.

This methodology seems to give an accurate measure of influence of different factors on these degradation rates.

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