The design of the experiments of arsenic removal from aqueous solutions onto Fe-XAD8-DEHPA

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Abstract

One of the main aims for a process is to find the optimum values of the parameters which assure the desired values of the process responses. This activity must be made in the minimum of the time and with the minimum use of consumable resources. The design of the experiments (DoE) assisted by the computer assures that this happens. In this paper, DoE was used to study the adsorption performance of Fe-XAD8-DEHPA in the removal process of As(V) ions from aqueous solutions. It was observed that the Adsorption Capacity and the Efficiency in the removal process of As(V) from the aqueous solution was significantly influenced by concentration and pH. The mathematical model of the process is very good. It includes the experimental data of over 99% in the case of adsorption capacity and over 97% in the case of efficiency. From the contour plots of adsorption capacity and efficiency can be seen that the chemical process is nonlinear. The DOE helped us to find the optimum values of the control factors (pH, contact time and arsenic initial concentrations from solutions) in order to obtain maximum values of Adsorption Capacity and Efficiency.
Keywords: arsenic adsorption, Fe-XAD8-DEHPA, design of experiments.

1 Introduction

In this paper, the design of experiments (DoE) was used to study the adsorption performance of Fe-XAD8-DEHPA in the removal process of As(V) ions from aqueous solutions.

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The presence of dissolved arsenic in groundwater has created significant concern on a global basis. Consumption of arsenic containing water causes serious health-related problems because of its toxicity [1–7]. Thus, choosing a technology for the removal of arsenic from drinking water often represents a challenge. Numerous methods are proposed to reduce arsenic level in natural waters. From all these methods, adsorption proved to be the most effective procedure in arsenic removal, even from very low concentration solutions. From the variety of the adsorbents studied by workers, the use of macro porous organic polymer supports, with a high surface area and good mechanical stability, is found more suitable for the removal of toxic elements from dilute solution, due to their faster kinetics, ease of regeneration and high adsorption capacity [1–10]. In this study the Amberlite XAD8 resin was impregnated, through the most widely used method (dry method), with di(2-ethylhexyl) phosphoric acid (DEHPA) [11–14]. Because the iron compounds in general were found to be very efficient adsorbents for arsenic removal from water due to the high affinity of arsenic towards iron, the XAD8-DEHPA was loaded with Fe(III) ions [2, 3, 6–10, 13, 14].

The use of statistical methods in industry is increasing. The goal of all technological process is to improve the quality and increase the productivity with the minimum of time and costs. The design of experiments has the role to achieve this goal, being centered around factors, responses and runs [15]. In the present paper the optimization of the adsorption process of As(V) from aqueous solution onto Fe(III)-loaded XAD8 impregnated resin, containing di(2-ethylhexyl) phosphoric acid (DEHPA), was studied by using the design of experiments, a statistical method based on the analysis of experimental adsorption data and not on theoretical models.

2 Experimental

The studied adsorbent is Amberlite XAD8 resin which was impregnated with di(2-ethylhexyl) phosphoric acid (DEHPA) and then was loaded with Fe(III) ions. In order to determine the adsorption performance of Fe-XAD8-DEHPA resin, in the removal process of As(V) from aqueous solution, the influence of different physicochemical parameters (pH, contact time and initial concentration of As(V) from solution) upon the adsorption capacity and removal efficiency was studied. The physicochemical parameters are called control factors, or variables and the adsorption capacity and removal efficiency are called process responses. The goal of our research was to find which are the optimum values of the control factor in order to obtain higher values of the adsorption capacity and efficiency in the removal process of As(V) from aqueous solution by adsorption onto Fe-XAD8-DEHPA resin. The advantage of use of the DOE in the adsorption process of As(V) from aqueous solution onto the studied resin is that the DOE can use simultaneous all the variables, in a wide range of values, in order to predict the responses. With the DOE is possible to find the best combination of the physicochemical parameters in order to obtain the higher values of adsorption capacity and efficiency.

Because there are only three control factors, Time, Concentration and pH, has been made a nonlinear experiment, using Response Surface Method (RSM) [16]. This RSM is useful for modeling and analyzing the problems in which the response is influenced by several variables and the main target is to optimize the response. In this case the first step is to find a suitable approximation for the functional relationship among the response and the set of the independent variables. Because usually the processes are nonlinear, then a polynomial of second order must be used in so called second-order model [16, 17].

The nonlinear experiments are used when we are at a point on the response surface that is remote from the optimum. The objective is to lead rapidly and efficiently along a path of improvement toward the general vicinity of the optimum (Figure 1). A second order experiment type central composite was design using software MINITAB 15. This design is presented in table 1.

Table 1: Central composite design.

Time, min	Concentration, μg/L	pH	Adsorption capacity, μg/g	Efficiency, %
8	10	9	1.09	43.8
24	300	4	47.06	63.5
16	155	6.5	18.18	47.16
8	300	9	48.79	66.03
24	10	4	0.69	28
8	300	4	44.6	60.53
16	155	6.5	18.18	47.16
24	10	9	0.84	33.8
8	10	4	0.97	39.1
24	300	9	49.31	66.47
16	155	6.5	18.18	47.16
16	155	6.5	18.28	47.35
16	155	4	14.15	36.71
16	155	6.5	18.23	47.29
16	300	6.5	48.17	65.9
16	155	9	14.81	38.9
24	155	6.5	18.86	48.9
16	155	6.5	18.18	47.16
8	155	6.5	17.83	46.43
16	10	6.5	0.86	34.5

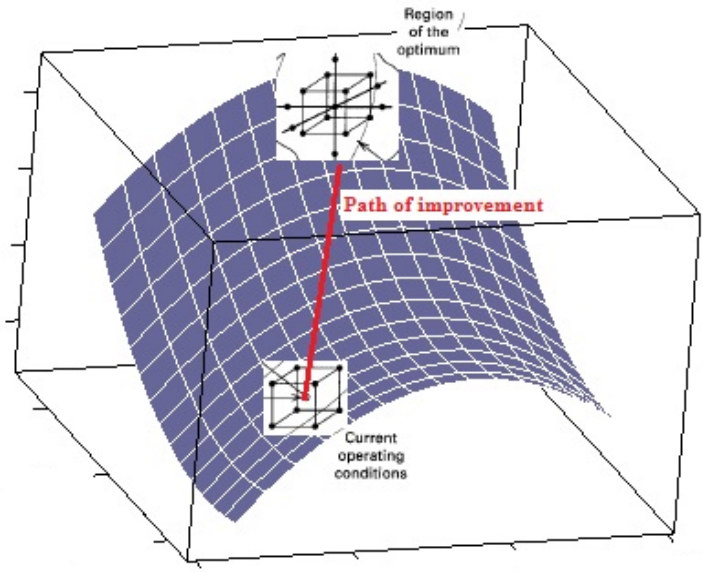

Figure 1: The path of improvement.

3 Results and discussions

The analyses of the experiment, using coded units estimated regression coefficients for Adsorption Capacity are presented in table 2 and for Efficiency are presented in table 3.

Table 2: Estimated regression coefficients for adsorption capacity.

Term	Coefficient	SE coefficient	T	P
Constant	17.7358	0.2622	67.637	0.000
Time	0.3470	0.2412	1.438	0.181
Conc.	23.3481	0.2412	96.797	0.000
pH	0.7354	0.2412	3.049	0.012
Time*Time	1.3150	0.4600	2.859	0.017
Conc*Conc	7.4873	0.4600	16.278	0.000
pH*pH	-2.5463	0.4600	-5.536	0.000
Time*Conc	0.4390	0.2697	1.628	0.135
Time*pH	-0.2400	0.2697	-0.890	0.394
Conc*pH	0.7733	0.2697	2.868	0.017
S = 0.762762 PRESS = 36.2545 R-Sq = 99.9% R-Sq(pred) = 99.37% R-Sq(adj) = 99.81%				

Table 3: Estimated regression coefficients for efficiency.

Term	Coefficient	SE coefficient	T	P
Constant	45.9186	0.8611	53.323	0.000
Time	-1.5223	0.7921	-1.922	0.084
Conc.	14.3233	0.7921	18.082	0.000
pH	2.1160	0.7921	2.671	0.023
Time*Time	3.6907	1.5105	2.443	0.035
Conc*Conc	6.2261	1.5105	4.122	0.002
pH*pH	-6.1674	1.5105	-4.083	0.002
Time*Conc	3.0625	0.8856	3.458	0.006
Time*pH	-0.1792	0.8856	-0.202	0.844
Conc*pH	-0.2542	0.8856	-0.287	0.780
S = 2.50494 PRESS = 388.230 R-Sq= 97.47% R-Sq(pred) = 84.35% R-Sq(adj) = 95.19%				

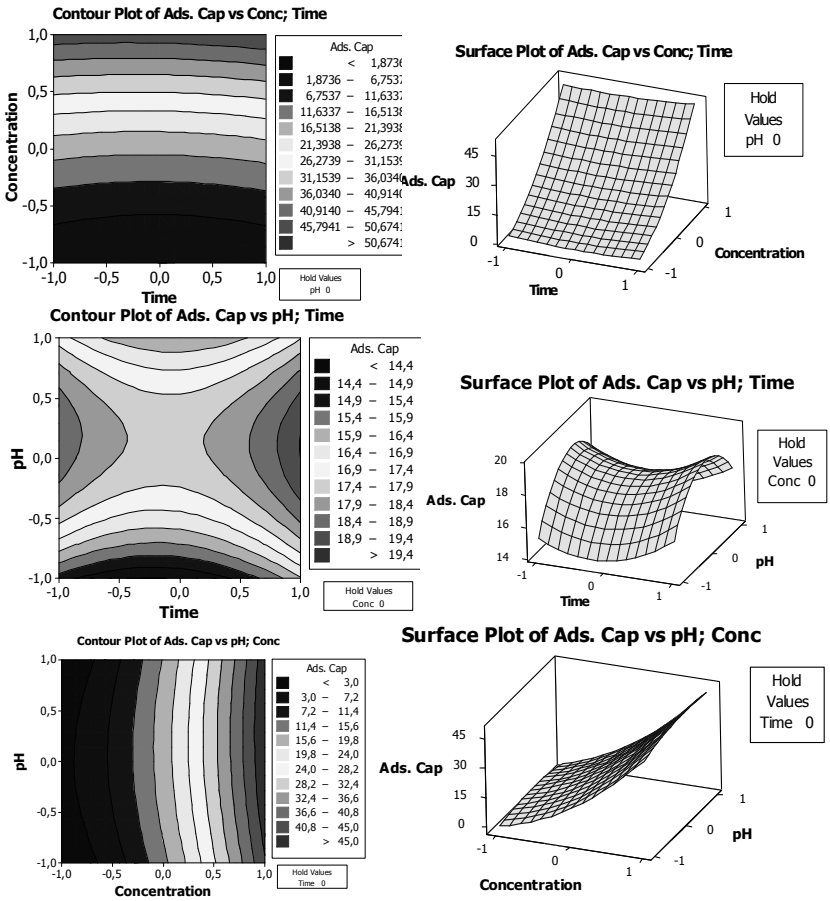

Figure 2: Contour and surface plots for adsorption capacity.

The Adsorption Capacity is significantly influenced by the Concentration, pH and by the second order interactions Conc*Conc, pH*pH, Time*Time, and Conc*pH. The mathematical model in this case is very good, over 99% of the experimental data are inclusive in this mathematical model.

Efficiency is significantly influenced by Concentration and pH. It is also significantly influenced by the second order interaction pH*pH, Conc*Conc, Time*Time, and Time*Conc. This mathematical model is also very good, over 97% of the experimental data are inclusive in this mathematical model.

Adsorption Capacity and Efficiency show that significant weight have had the interaction of the second order. That means we must be very careful when we draw conclusions.

The contour plots and surface plots for Adsorption are presented in figure 2.

Both contour plot and surface plot show the nonlinear influence of the control factors upon adsorption capacity. The contour plot and surface plot for pH and Time put in evidence the saddle form of the surface. All other dependences are a surface which assure maximum of adsorption capacity for maximum values for Concentration.

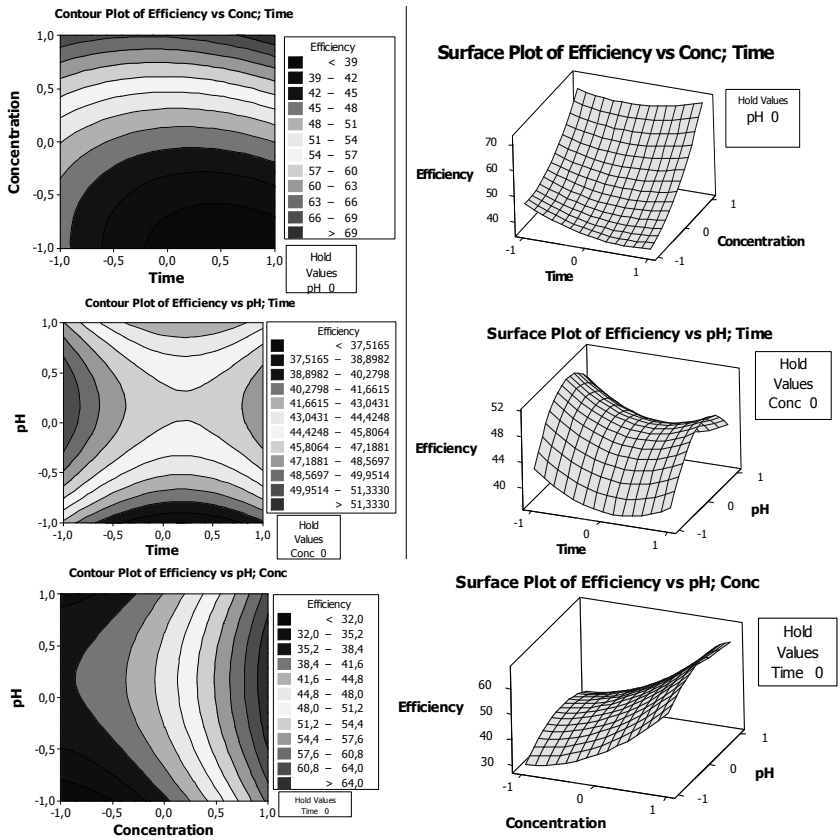

Figure 3: Contour and surface plots for efficiency.

The contour and surface plots for Efficiency are presented in figure 3. From figure 3 can be seen that the chemical process is nonlinear. The maximum values for Concentration will assure a maximum for efficiency. In the case of Efficiency the surfaces are in the form of a saddle in the case of Time-pH and also a light in the case of pH-Conc.

For our process it is important to have maximum values for Adsorption Capacity and Efficiency. For this reason in figure 6 the overlaid contour plot of Adsorption Capacity and Efficiency has been shown. The aim was to see the domain of control factor setting for having the maximum values of responses.

Figure 4 shows that for maximum values of the process responses the Concentration must be set at a maximum value, pH in the middle of the setting domain and Time can be anywhere in the setting domain.

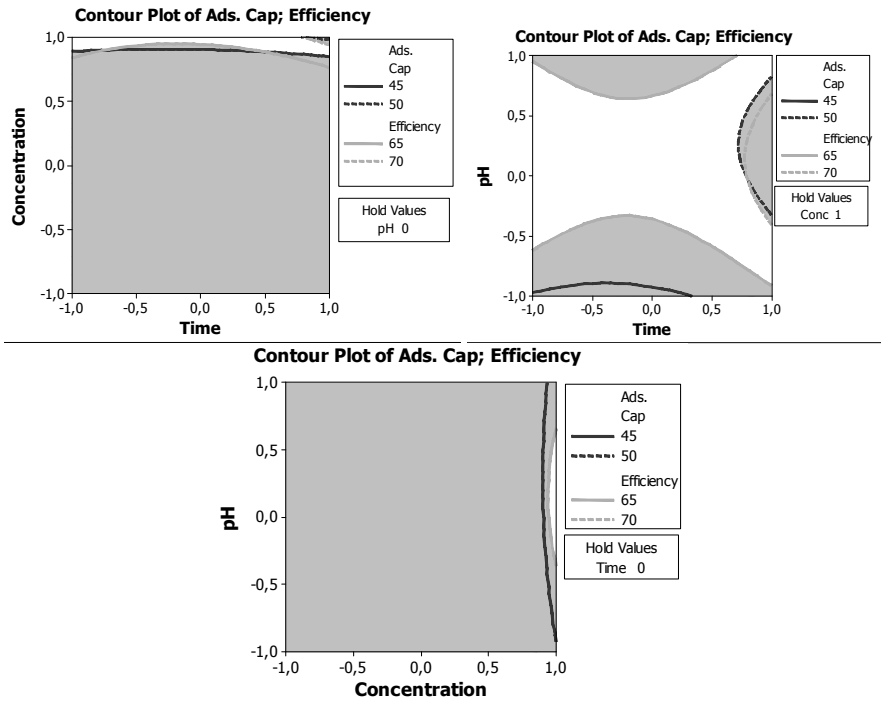

Figure 4: Overlaid contour plot for adsorption capacity and efficiency.

A better optimization can be achieved using the optimizer of the MINITAB. To do this some target values for Adsorption Capacity (Adsorption Capacity =52) and Efficiency (Efficiency = 75) must be selected. The result of optimization is presented in figure 5.

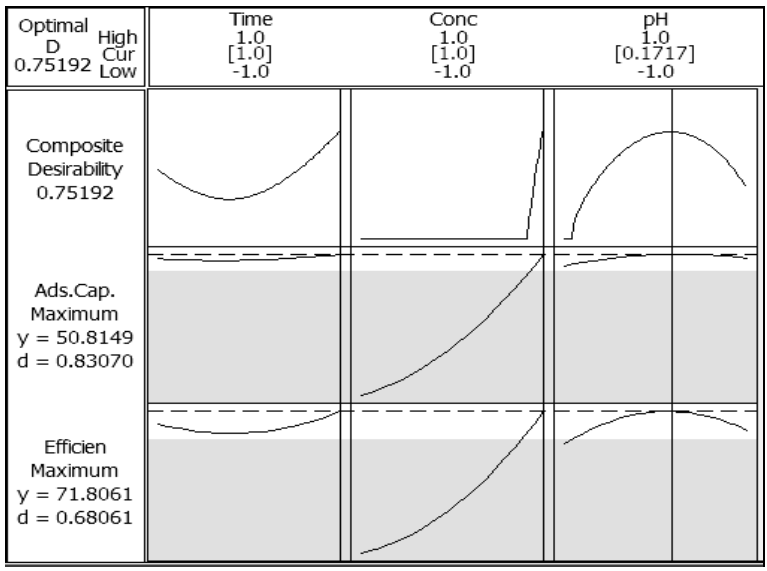

Figure 5: Optimal values for control factors.

The optimal values for control factors can be seen in the top row of figure 5. These optimal values are presented in table 4.

Table 4: Response optimization.

Parameters						
	Goal	Lower	Target	Upper	Weight	Import
Ads. Cap.	Maximum	45	52	52	1	1
Efficiency	Maximum	65	75	75	1	1
Global Solution Time = 1 Conc. = 1 pH = 0.171717						
Predicted Responses Ads. Cap. = 50.8149, desirability = 0.830700 Efficiency = 71.8061, desirability = 0.680605						
Composite desirability = 0.751916						

It can be seen that for maximum values of Adsorption Capacity and Efficiency, Time and Concentration must be set on the maximum values in the setting domain and pH nearly the middle of the setting domain.

4 Conclusions

One of the main aims for a process is to find the optimum values of the parameters which assure the desired values of the process responses. This activity must be made in the minimum of time and with a minimum of consumable resources. The design of the experiments (DoE) assisted by the computer assures that this happens. In this paper the optimization of the chemical process of As(V) removal from aqueous solutions by adsorption onto Fe-XAD8-DEHPA resin is presented. It was observed that the Adsorption Capacity and the Efficiency in the removal process of As(V) from aqueous solution was significantly influenced by concentration and pH. The mathematical model of the chemical process is very good, over 99% in the case of adsorption capacity and over 97% in the case of efficiency of experimental data are include in model. In these conditions the regression coefficients were estimated. From the contour plots of adsorption capacity and efficiency it can be seen that the chemical process is nonlinear. The DOE helped us to find the optimum values of the control factors (pH, contact time and arsenic initial concentrations from solutions) in order to obtain maximum values of Adsorption Capacity and Efficiency. For maximum values of Adsorption Capacity and Efficiency (called process responses), Time and Concentration must be set on the maximum values in the setting domain and pH nearly the middle of the setting domain.

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