Supplementary information

Eco-Friendly Adsorption of a Cationic Dye Using a Chemically Modified Industrial By-Product: Process Optimization and Modeling

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BB1 desorption study

(a) Number of BB41 adsorption cycles.

As depicted in Figure 1S. the results for treated Biomass (SA-OH) revealed a gradual reduction in BB41 adsorption over time. After Fifteen adsorption cycles. BB41 removal reached to 0% due to the complete saturation of all active sites on the surface of SA-OH.

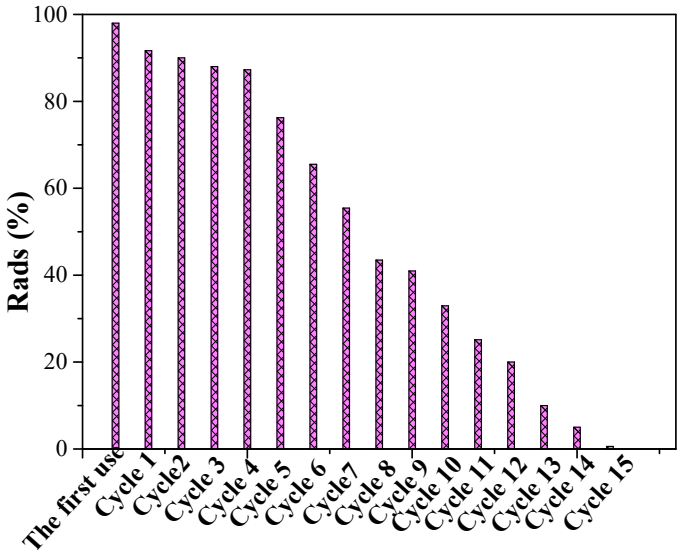

Figure 1S: Evolution of the adsorption capacity and efficiency of fluoride on treated Biomass (SA-OH) . ($m_{Brute\text{-}OH}$ = 2 g.L-1; $[BB41]_0$ = 200mg.L-1; T = 25°C; pH = 5.95; t = 60 min).

(b) Regeneration

The regeneration of the adsorbent is a crucial factor in assessing its long-term effectiveness.The adsorbent was examined for its regeneration potential.Figure S2 illustrates the release of BB41 from the surface as a function of the chemical agent. HCl proved to be the most effective agent. resulting in 98% BB41 desorption.

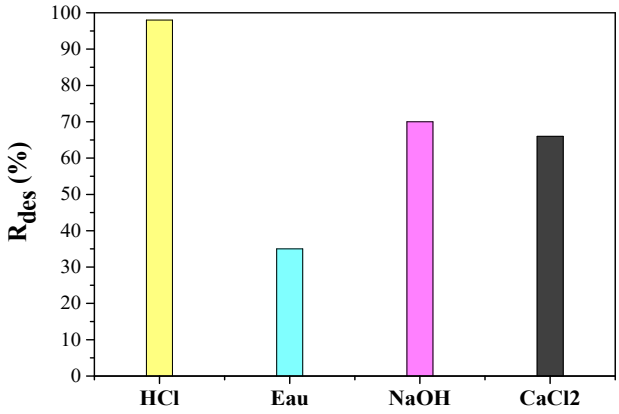

Figure.S2: Evolution of the adsorption capacity and efficiency of BB41 on SA-OH (m_{SA-OH} = 1 g.L-1. pH =6.15. T=23°C. t= 60 min)

C) Optimization of BB41 desorption operating parameters using HCl

The objective of this section is to study the effect of certain operating parameters that may influence the desorption phenomenon. namely: contact time. solid/liquid ratio. and the concentration of the desorption agent (HCl). To achieve this. the experimental research methodology was applied through the implementation of a designed experiment. maintaining the same previous experimental design. the "central composite design." with 16 trials.Therefore. the three process variables were chosen. each at five levels (−α. −1. 0. +1. +α) .The independent variables coded and actual values are presented in Tables S1 and S2.

Table S1 : Experimental factors and their ranges and standard deviations

Parameters	Units	Factor code	Coded levels and actual values				
			Low axial (−α = −1.68)	Low factorial −1	Central (0)	High factorial +1	High axial (+α =+1.68)
the desorption time	h	X_1	1	2.216	4	5.783	6.998
the concentration of the desorption solution	mg/L	X_2	0.0992	0.221	0.4	0.578	0.699
the mass of saturated SA-OH	mg/L	X_3	0.0992	0.221	0.4	0.578	0.699
$\alpha = (2^k)^{1/4}$	–	–	–	–	–	–	–

Table S2 :Central composite rotatable design matrix with experimental and predicted values

Runs	the desorption time (h)	the concentration of the desorption solution (mg.L-1)	the mass of saturated SA-OH	Coded values			Removal experimental (%) Y1 (SA)	Removal predicted (%)Y1 (SA)
				X_1	X_2	X_3		
1	3.9995	0.3995	0.099	0	0	a	70.5	76.967
2	2.216	0.221	0.221	-1	-	-	60.3	54.845
3	5.783	0.221	0.221	+1	-	-	92.1	87.999
4	2.216	0.578	0.221	-1	+	-	55.02	52.5
5	5.783	0.578	0.221	+1	+	-	90	83.874
6	3.9995	0.0992	0.3995	0	a	0	73	75.457
7	1.000022487	0.3995	0.3995	a	0	0	32.55	32.825
8	3.9995	0.3995	0.3995	0	0	0	45.3	46.291
9	3.9995	0.3995	0.3995	0	0	0	48.5	46.291
10	6.998977513	0.3995	0.3995	A	0	0	55.5	62.322
11	3.9995	0.6997	0.3995	0	A	0	58	62.641
12	2.216	0.221	0.578	-	-	+	48.27	49.376
13	5.783	0.221	0.578	+	-	+	56.09	53.336
14	2.216	0.578	0.578	-	+	+	39.18	38.261
15	5.783	0.578	0.578	+	+	+	45.75	43.185
16	3.9995	0.3995	0.699	0	0	A	35	35.630

d) Experimental design

Analysis of variance

The ANOVA results for the quadratic equations (Table S3) reveal that the Fisher values for all regressions are considerably high. indicating the model's strong ability to describe the variation in BB41 desorption.The calculated Fisher value for the regression model is 16.1481. which exceeds the critical Fisher value ($F_{9.6}$= 3.74).Furthermore. the exceptionally low probability values (ppp < 0.001) validate the statistical significance of the regression models at a 95% confidence level for BB41 desorption.

Both the actual and predicted dye desorption values presented in the table. along with the R^2= 0.96 et R^2ajs = 0.90 . demonstrate a strong correlation between the experimental and predicted responses.

Table S3 : ANOVA for response surface Quadratic model

Source	Degree of Freedom	Sum of Squares	Mean square	Rapport F	Prob > F
Regression	9	4249.6549	472.184	16.1481	0.0015
Résidus	6	175.4446	29.241		
Total	15	4425.0992			

Main interaction effects and Student's t test

The regression coefficients. their associated standard errors. Student's t-values. and their effects are presented in Tables S3 . By inserting the coefficient values from Tables S1 and S2 into Equation (1). the resulting expression is obtained.

$$Y=46.32123+ 8.58669X_1-3.99337X_2-12.10628X_3-0.07125X_1X_2-6.23625X_1X_3-1.19375X_2X_3 +0.38081X_1X_1+7.97336X_2X_2+3.46558X_3X_3 \quad (1)$$

As shown in Table S4. the desorption time (X_1). the concentration of the desorption solution (X_2). and the mass of saturated SA-OH (X_3) are statistically significant. because the absolute Student's t-value is less than the critical Student's t-value. with a probability of p-value less than 5%.The most impactful factor was X_3 (the mass of saturated SA-OH). followed by X_1 (the desorption time) and X_2 (the concentration of the desorption solution).Regarding second-order interactions. only X_1X_3 and X_2X_2 are significant. with p-values of 0.0172 and 0.0042. respectively. Third-order interactions are not included in the table. as they are not considered significantly important.

Table S4: Statistical analysis of coefficients from the cubic model

Coefficient		Estimate parameter	Standard error	Student tvalue	p-value
Constant	a_0	46.321231	3.812455	12.15	<0.0001*
$\mathbf{X_1}$	a_1	8.5866879	1.463252	2.87	0.0011
$\mathbf{X_2}$	a_2	-3.993371	1.463252	5.87	0.0342
$\mathbf{X_3}$	a_3	-12.10628	1.463252	8.27	0.0002
$\mathbf{X_1}$* $\mathbf{X_2}$	a_{12}	-0.07125	1.911831	0.04	0.9715
$\mathbf{X_1}$* $\mathbf{X_3}$	a_{13}	-6.23625	1.911831	3.26	*0.0172
$\mathbf{X_2}$* $\mathbf{X_3}$	a_{23}	-1.19375	1.911831	0.62	0.5553
$\mathbf{X_1}$* $\mathbf{X_1}$	a_{11}	0.3808051	1 .776609	0.21	0.8374
$\mathbf{X_2}$* $\mathbf{X_2}$	a_{22}	7.9733642	1.776609	4.49	*0.0042
$\mathbf{X_3}$* $\mathbf{X_3}$	a_{33}	3.465584	1.776609	1.95	0.0990
p. probability * significant critical student t-test= 2.71					

Optimization of independent parameters

The 3D response surface plots (Figure S3) demonstrate clear interactions between the studied variables and adsorbent regeneration efficiency. Figure S3a presents the response surface plot of the adsorbent regeneration efficiency as a function of desorption time (X_1) and desorption agent concentration (HCl) (X_2).The results indicate that the regeneration efficiency significantly increases with increasing contact time and HCl concentration.The results show that regeneration efficiency improves with increasing contact time and HCl concentration. reaching an optimal threshold where desorption is most effective. A prolonged contact time enhances the interaction between the desorption agent and the adsorbent's active sites. facilitating pollutant release. Similarly. an increase in HCl concentration initially boosts regeneration by breaking the bonds between the adsorbed molecules and the biomass surface. However. beyond a certain concentration. excessive HCl reduces efficiency. likely due to the degradation of active sites or structural damage to the adsorbent. Therefore. optimizing both contact time and HCl concentration is essential to maximize regeneration while preserving the adsorbent's integrity for future reuse.

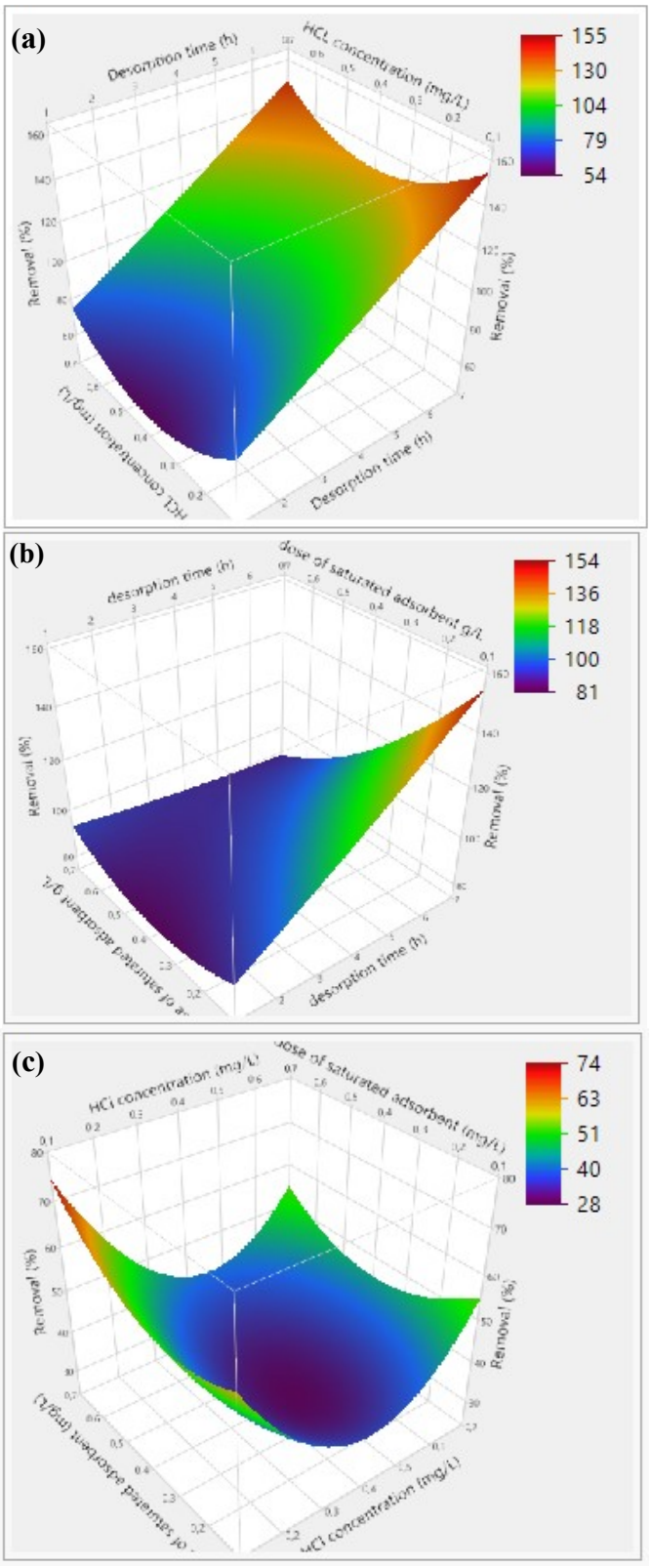

Figure. S3: Response surface plots (3D) of BB41 removal versus the effects (desorption time.HCl concentration and dose of saturated adsorbent).

The response surface plot (figure S3a). illustrates the effect of desorption time X1 (1 to 7h) and the dose of saturated adsorbent X_3 (0.221 to 0.0992 $g.L^{-1}$) on regeneration efficiency. while keeping the initial concentration of HCl (0.4 $g.L^{-1}$) (desorbing agent) constant .The results show that regeneration efficiency increases with contact time. A extended contact time enables a prolonged interaction between the adsorbent and the desorbing solution. which in turn enhances the regeneration efficiency by facilitating the gradual release of adsorbed molecules. Additionally. the regeneration efficacy is initially enhanced by increasing the adsorbent mass. as a greater quantity of biomass contributes to a greater number of active desorption sites. Nevertheless. the efficacy seems to stabilize beyond a specific threshold. which is likely the result of mass transfer constraints.The process's overall efficacy is ultimately restricted when the adsorbent concentration is excessively high. as the desorbing agent's diffusion through the particles becomes less effective. resulting in delayed desorption kinetics. Figure S3C illustrates a response surface plot that depicts the effect of HCl concentration (X_2) and the amount of saturated adsorbent (X_3) on regeneration efficiency. with contact duration held constant.Increasing HCl concentration initially enhances desorption; however. beyond a specific threshold. the effectiveness either stabilizes or declines. potentially due to damage to active sites. An increased adsorbent mass initially improves regeneration; however. excessive amounts lead to a plateau. likely due to mass transfer limitations or saturation effects.The response surface plot demonstrates that the peak regeneration efficiency attained was 74%. occurring at an initial HCl concentration of 0.1 g.L-^{1} and a saturated adsorbent mass of 0.7 $g.L^{-1}$.The predicted desorption efficiency for BB41 reached 90.93%. under ideal conditions. which included a desorption time of 5.9 hours. an initial HCl concentration of 0.22 $g.L^{-1}$. and a saturated adsorbent mass of 0.2 $g.L^{-1}$.