DOEHLERT EXPERIMENTAL DESIGN AND DENSITY FUNCTIONAL THEORY FOR THE REMOVAL OF BEZATHREN BLUE DYE FROM AQUEOUS SOLUTION

AFAF AMARA-REKKAB[*,**] and SARAH BOUHASSOUN[**]

[*]*Higher School of Applied Sciences of Tlemcen, BP 165, 13000 Bel Horizon, Tlemcen, Algeria*
[**]*Laboratory of Separation and Purification Technologies, Department of Chemistry, Faculty of Sciences, Box 119, University of Tlemcen, 13000, Algeria*
✉ *Corresponding author: A. Amara-Rekkab, amarafaf@yahoo.fr*

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Bezathren blue (BB) is a commonly used dye in the textile industry and it is difficult to remove during wastewater treatment. In this study, chitosan was used as an adsorbent and the process of liquid-solid extraction was employed to remove BB from an aqueous solution. The process parameters were optimized individually, using the Doehlert experimental design (DED). The DED predicts that the output will reach a maximum of 99.98% when slightly modified process conditions are used. This entails placing a mass of 0.095 g of chitosan in contact with the BB solution, which has a starting concentration of 45 ppm. The solution had an initial pH of 6.5, which is its normal pH, and this pH was maintained for 17.5 minutes. A study was conducted on the Mulliken atomic charges, focusing on the electronic properties using the density functional theory (DFT) technique. FMO (HOMO–LUMO), MEP, and ESP were all looked at as part of the study.

Keywords: dyes, wastewater, removal, optimization, Doehlert design, DFT, environment

INTRODUCTION

Several processing industries, such as textile, leather, printing, cosmetic, drug, and food sectors, widely utilize synthetic dyes.[1] Based on their structure, we can categorize synthetic dyes into 20–30 groups. However, the acid dyes make up the largest category of synthetic dyes in the color index. Mostly classified as azo, anthraquinone, or triarylmethane groups, these dyes are anionic chemicals. Anthraquinone-based dyes make up approximately 15% of colorants and contain structures derived from quinones. These dyes have high resistance to degradation and will retain their color for an extended period of time.[2]

Contamination of wastewater with dyes impairs ecological systems and poses a threat to environmental sustainability.[3] Several researchers have proposed a variety of techniques for eliminating and removing dyes from wastewater, including adsorption,[4-6] membrane separation,[7] cloud point extraction,[8,9] electro-oxidation,[10] coagulation,[11–13] reverse osmosis,[14] oxidation,[15] and heterogeneous photocatalysis.[16,17]

The seafood processing industry produces waste materials that yield chitosan (CS), a polysaccharide biopolymer. The primary by-products utilized as the raw material for chitosan production are the chitin shells of marine crustaceans. Industrial scale chitosan production involves deacetylating chitin in an alkaline environment.[18] Research on chitosan has been extensive. Key attributes of this substance are its prevalence in the natural environment, its ability to break down naturally, and its cost-effectiveness.[19] It has been applied in diverse domains, such as biomedical applications,[20] membrane separation,[21] the food sector,[22] and adsorption in chemical and environmental engineering.[23,24]

The design of experiments (DOE) is a collection of mathematical-statistical procedures that analyze the behavior of a system by examining different levels of variables. A matrix regulates the combination of levels, enabling a systematic and effective investigation of the

experimental environment. The relationship between the design of experiments (DOE) and response surface methodology (RSM) is a highly effective tool that enables cost-effective and efficient data collection. It also allows modeling of data behavior, resulting in the derivation of mathematical functions that can accurately describe the experimental region under study. This, in turn, facilitates statistical predictions and the identification of optimal conditions for conducting experiments. Design of experiments (DOE) and response surface methodology (RSM) must be put into practice in a series of steps, such as planning, carrying out experiments, analyzing the results, and checking the predictions' accuracy against the experimental values.[25] The Doehlert matrix is known for its cost-effectiveness, versatility, and efficiency in modeling experimental data. It also provides significant flexibility in selecting variable levels for investigation.[26,27] For this reason, this matrix was chosen for the optimization of the removal of Bezathren Blue by chitosan.

The objective of our work has been to remove Bezathren blue through liquid-solid extraction, utilizing chitosan as an adsorbent, and optimizing the significant parameters using a Doehlert experimental design. In order to obtain a more thorough understanding of the molecular interactions between Bezathren blue (BB) and chitosan, we utilized density functional theory (DFT) calculations. We were able to examine the adsorption sites and molecular-level mechanisms involved in the process of removing dye using computational tools.

EXPERIMENTAL

Materials

Bezathren blue, which has the chemical formula $C_{28}H_{14}N_2O_4$ (Fig. 1) was purchased from Complex Textile (Soitex) in Tlemcen, Algeria. Chitosan, sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Sigma-Aldrich. Distilled water was utilized in the preparation of the solutions.

Batch experiments

Batch tests were carried out to optimize the factors of the biosorption process. The experimental approach consisted of conducting batch investigations by adding an appropriate amount of chitosan (g/L) to a Bezathren blue solution at different concentrations held in a 20 mL Erlenmeyer flask at different times and pH. The mixture was agitated at a temperature of 20 °C using an orbital shaker set at a rotating speed of 250 rotations per minute.

The UV–Vis absorbance of Bezathren blue solutions was quantified using an SP-UV 200S UV–Vis spectrophotometer, at absorption band λ_{max} = 578 nm. The Adwa pH Metre was utilized for pH measurement. The percentage of BB elimination efficacy was determined using the following formula:[28-30]

$$\textbf{Removal Efficiency}\ (\%) = \frac{C_i - C_e}{C_i}\ .100 \quad (1)$$

where C_i is the initial concentration and C_e is the equilibrium concentration of BB.

The procedure for the organic pollutant extraction using the cloud point is shown in Figure 2.

Doehlert experimental design

Response surface methodology (RSM)[31] was employed to theoretically simulate and analyze the impact of various parameters on the extraction efficiency of the removal of Bezathren blue by chitosan.

The Doehlert matrix[32] was used in the experimental design to precisely evaluate the interactions between these parameters and their influence on the extraction yield. The link between the predictor variables and the examined responses was quantitatively described using a second-order empirical regression model, as represented by Equation (2).[33]

$$y\ (\%) = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} B_{ij} X_i X_j + \varepsilon$$

where B_0 represents the expected response, while B_i, B_{ii}, and B_{ij} represent constant coefficients. X_i and X_j represent the input components in coded values.

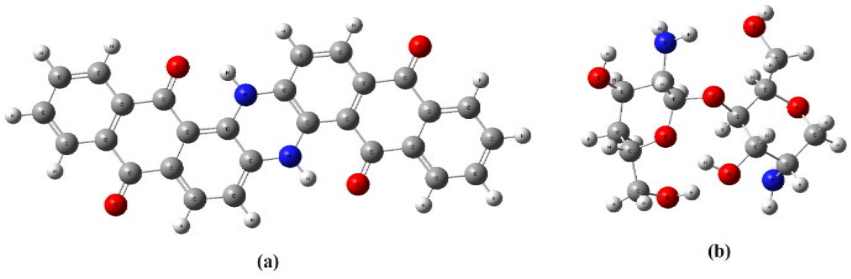

Figure 1: Chemical structures of (a) anionic Bezathren blue dye and (b) chitosan (by DFT calculation with the B3LYP functional and the 6–31G basis set)

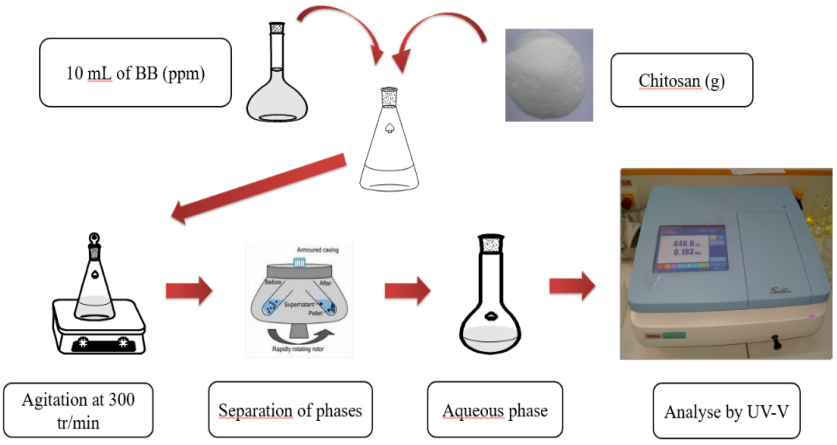

Figure 2: Scheme of liquid-solid extraction of BB dye by chitosan

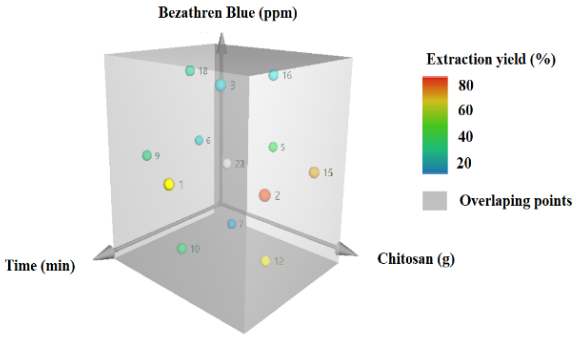

Figure 3: Design region of the removal of BB dye by chitosan

Table 1
Variables and their experimental ranges in the Doehlert design

Factors	Units	Range
Time	min	10 to 20
Chitosan	g	0.025 to 0.1
BB	ppm	20 to 70
pH		5 to 8

Ultimately, it refers to the whole inaccuracy. The statistical software MODDE 13-Pro generated response surface plots, contour plots, and performed statistical data analysis.

The factors examined were the contact time (min), the mass of chitosan, dye concentration ([BB]) and initial pH, as presented in Table 1. The number of experiments needed for this design was calculated by adding k^2, k, and cp, where k represents the number of variables and cp represents the number of replicates of the central point.[34,35]

Fifteen experiments were conducted in our investigation. The value of E (%) represents the percentage of extraction yield (%) of BB by chitosan.

The model was assessed using Fischer's test, p-value, and the coefficient of determination R^2.

RESULTS AND DISCUSSION

Experimental design study

Based on the combinations chosen using Doehlert modeling, the experimental matrix in Table 2 consists of 23 experiments. By employing this methodology, we have determined the four factors that were assessed as the most important variables and their synergistic interrelationships.

Table 2 displays the matrix at the tree-level created by DED using the experimentally acquired responses for the extraction of the dye.

The table clearly indicates that the highest extraction yield was achieved when all parameters were set to their central values. There is an electrical affinity between the negatively charged anion of Bezathren blue and chitosan.[36]

Based on these observations, the empirical correlations between the response of DED and chosen factors were established as follows:

Removal efficiency (%) = 55.4467 + 13.014 Time + 28.2174 Chitosan -11.6555 [BB] + 6.68824 pH + 9.32832 Time*Time + 7.49832 Chi*Chi -27.0392 BB*BB -12.1882 pH*pH - 2.08424 Time*Chi -16.2259 Time*BB + 9.90268 Time*pH -37.9823 Chi*BB + 30.4161 Chi*pH - 39.165 BB*pH

The results demonstrate a strong correlation between the response variable and the independent variable in the proposed equation.[37,38]

Table 2
Experimental results on the adsorption of BB by chitosan

N° exp.	Time (min)	Chitosan (g)	BB (ppm)	pH	Removal efficiency (%)
1	20	0.062	45	6.5	79.24
2	17.5	0.094	45	6.5	96.00
3	17.5	0.073	65.41	6.5	28.00
4	17.5	0.073	50.10	7.68	65.19
5	10	0.062	45	6.5	50.31
6	12.5	0.030	45	6.5	29.00
7	12.5	0.051	24.58	6.5	21.00
8	12.5	0.051	39.89	5.31	34.81
9	17.5	0.030	45	6.5	41.82
10	17.5	0.051	24.58	6.5	44.87
11	17.5	0.051	39.89	5.31	46.00
12	15	0.084	24.58	6.5	78.50
13	15	0.084	39.89	5.31	44.88
14	15	0.062	60.30	5.31	39.37
15	12.5	0.094	45	6.5	86.79
16	12.5	0.073	65.41	6.5	31.83
17	12.5	0.073	50.10	7.68	46.17
18	15	0.040	65.41	6.5	37.15
19	15	0.040	50.10	7.68	22.07
20	15	0.062	29.69	7.68	73.93
21	15	0.062	45	6.5	54.40
22	15	0.062	45	6.5	54.40
23	15	0.062	45	6.5	57.54

Coefficient diagram

The coefficient diagram displays the regression coefficients along with their confidence intervals. This graph allows for the interpretation of the coefficients. The coefficient is considered significant when the confidence interval does not include zero. Our coefficient diagram is derived directly from the mathematical analysis of the test results (Fig. 4).

There are four individual effects of four factors (X_1; X_2; X_3; X_4), and it has been observed that the effect of factor X_2 (chitosan mass) is more significant compared to the others. It is undeniable that there are many important and meaningful interactions, specifically, BB*BB, pH*pH, Time*BB, chi*BB, chi*pH and BB*pH. The interactions BB*pH, chi*BB, BB*BB and Time*BB have a key role. It can also be asserted that there are four non-significant interactions. Specifically, this includes the relationships between time and temperature (Time*chi), time and time (Time*Time), time and pH (Time*pH), and chi and chi (chi*chi).

Analysis of variance

To ascertain the major primary and combined effects of dye extraction parameters, an analysis of variance (ANOVA) was conducted,[39] as shown in Table 3. The model's F-value of 22.8714, compared to the critical F-value of 3.24 at a significance level of 0.05 and degrees of freedom of 14 and 8, suggests that the model is statistically

significant. The likelihood that this enormous cloud's F-value is due to noise is extremely low, at only 0.01%. The lack of fit F-value of 11.4881 suggests that the lack of fit is not statistically significant when compared to the pure error (0.05, 6, 2) = 19.33. The forecasted R^2 value of 0.976 is in good agreement with the corrected R^2 value of 0.933. That is the discrepancy is smaller than 0.2.

Q^2 is the percentage of the response's variance that is accurately predicted by the model during cross validation. Q^2 provides an assessment of the model's ability to accurately forecast new data.[40] Our model has a high Q^2 value. The model validity was assessed. The model validity bar is larger than 0.25, which means that the model error is in the same range as the pure error. The reproducibility bar is near 1.0 (the pure error is weak). This means that, under the same conditions, the values of the response would be identical (Fig. 5).

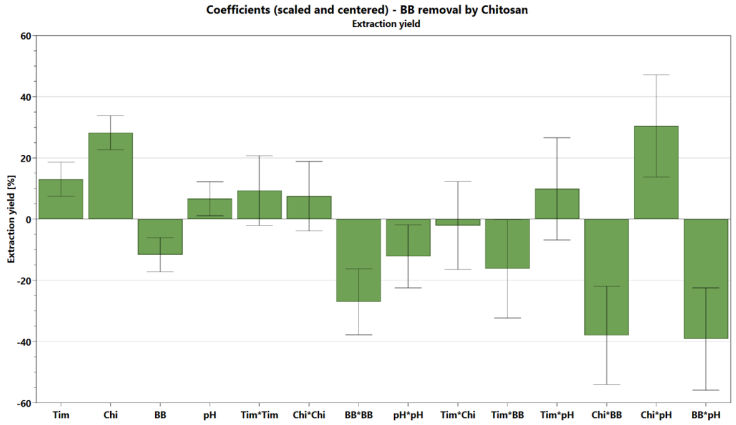

Figure 4: Graphical presentation of significant and insignificant interactions of parameters on the extraction of BB by chitosan

Table 3
ANOVA for the DED-quadratic model

Extraction yield	DF	SS	MS (variance)	F	p	SD
Total	23	68398	2973.82			
Constant	1	58834.7	58834.7			
Total corrected	22	9563.33	434.697			20.8494
Regression	14	9330.21	666.444	22.8714	0.000	25.8156
Residual	8	233.11	29.1387			5.39803
Lack of Fit	6	226.537	37.7561	11.4881	0.082	6.1446
Pure error	2	6.57306	3.28653			1.81288

Response surface diagram

In the surface diagram, the evolution of the yield depending on different factors can be observed. Level lines can be used to identify areas of the response surface where the response is maximum or minimum,[41] as illustrated in Figure 6. Figure 6 demonstrates that the extraction efficiency rises with higher pH values and an increased mass of chitosan. Furthermore, we observed that extending the contact time beyond 17.5 minutes significantly enhances the BB removal efficiency. When the concentration of BB dye fluctuates between 20 and 45 parts per million (ppm) and the mass of chitosan is around 0.094 grams, we achieved an optimal range.

Optimization of the response

To determine the optimal values for the variables that maximize or minimize the response, the computer tool known as the response optimizer is essential for achieving this point quickly and accurately.[42] Table 4 below displays the various values of our experimental parameters. The experiment was carried out under the specified conditions and yielded a 99.98% extraction rate, which is the best extraction yield.

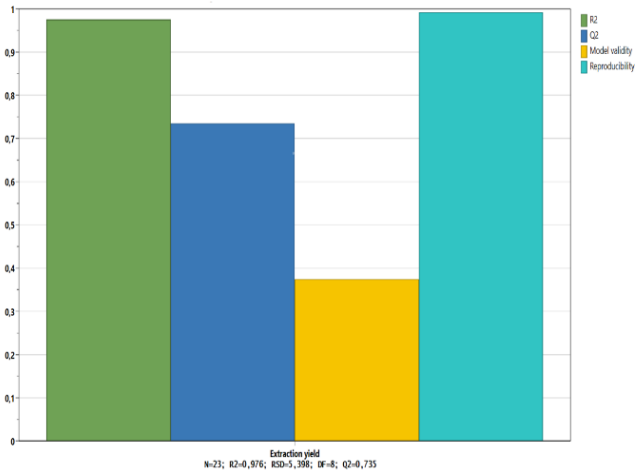

Figure 5: Summary of fit for removal of BB by chitosan

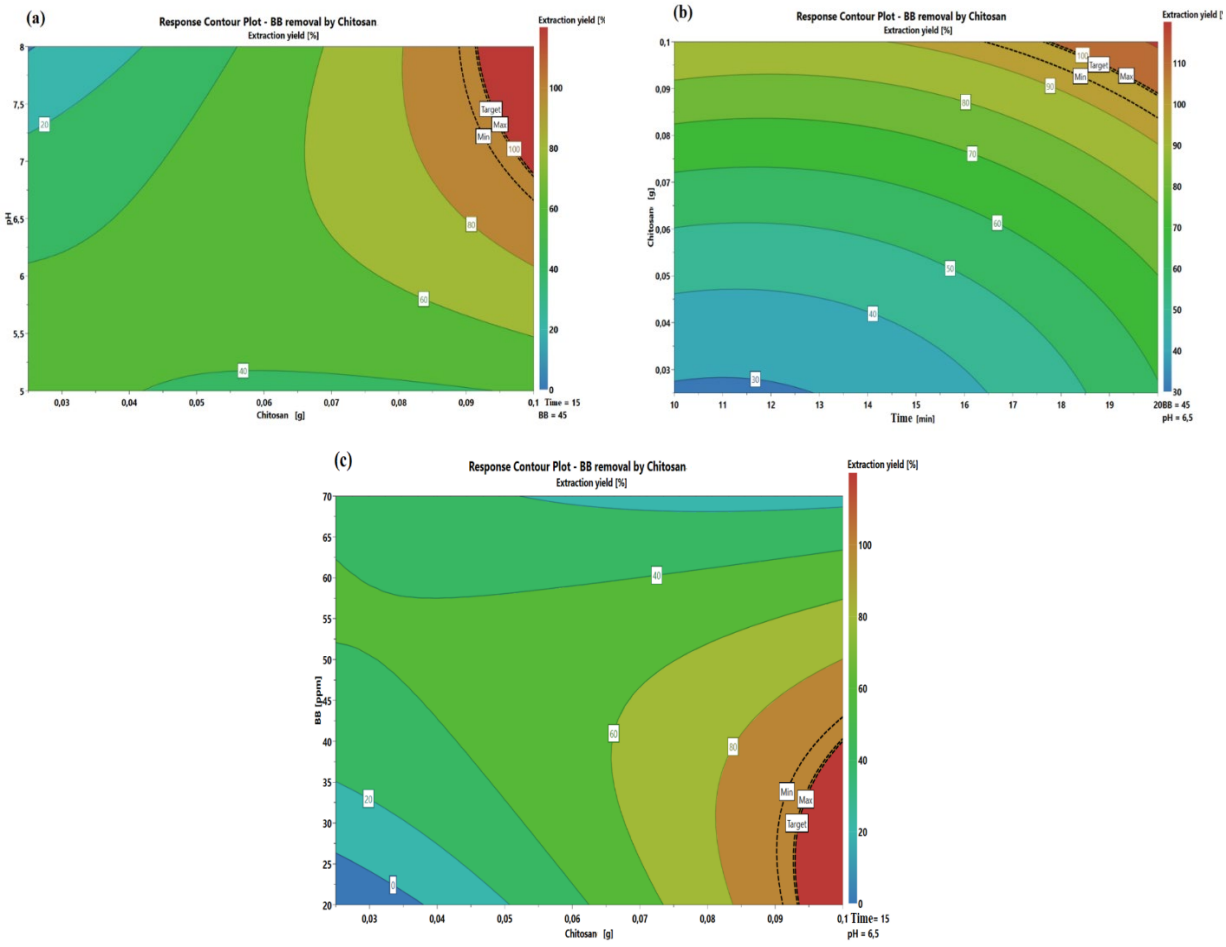

Figure 6: Contour plots and response surface of the effects: (a) pH and chitosan; (b) chitosan and time; (c) BB and chitosan, for the removal of Bezathren blue by chitosan

Table 4
Optimization of BB extraction yield

Parameter	Optimum value
Time (min)	17.5
Mass of chitosan (g)	0.095
[BB] (ppm)	45
pH	6.5

The chitosan had a mass of 0.095 g in contact with the BB solution with an initial concentration of 45 ppm. The initial pH of the solution was 6.5 (natural pH of solution) for 17.5 minutes under agitation (250 rpm) at room temperature.

Density functional theory (DFT)

The frontier molecular orbitals (FMOs), specifically the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are crucial characteristics in quantum chemistry. They have a vital role in maintaining the chemical stability of the molecule.[43-45] They are referred to as frontier orbitals because they engage in interactions with other species. Gauss View 6.0 in the Gaussian 09 software package was utilized to compute the group contributions to the molecular orbitals (HOMO and LUMO) and generate the density of states (DOS), as depicted in Figure 7. Thus, we can ascertain the molecular configuration.

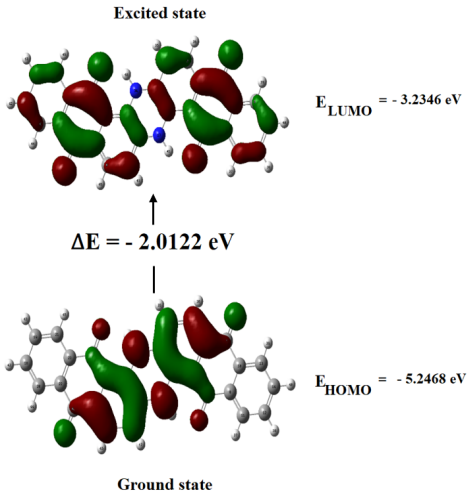

Figure 7: Frontier molecular orbitals of Bezathren blue dye

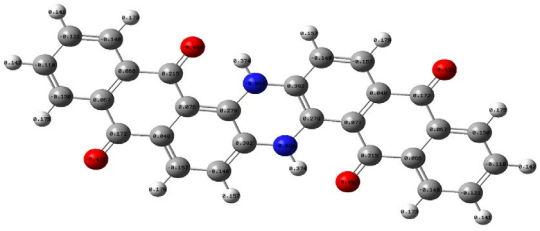

Figure 8: Mulliken distribution charges of Bezathren blue dye

The HOMO, or the highest occupied molecular orbital, is the orbital that mainly functions as an electron donor. On the other hand, the LUMO, or the lowest unoccupied molecular orbital, is the orbital that predominantly operates as the electron acceptor. The difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) describes the molecule chemical stability.[45] The frontier orbital gap is a useful indicator for determining the chemical reactivity and kinetic stability of a molecule.

Figure 7 represents the electronic structure and energy transition of a molecule from its ground state to its excited state. The molecular orbitals' electron density distribution is visualized in both states. The energy levels of HOMO and LUMO are specified, with the energy gap between these orbitals being highlighted. It is also observed that the HOMO density distribution of the BB dye is concentrated on the heterocyclic atom rings, including the nitrogen and oxygen atoms. The LUMO density distribution of the BB dye is found in the C=C and C–C=C functional groups, as well as on the oxygen and nitrogen atoms, which may play a crucial role in adsorption.

Mulliken charges of Bezathren blue dye

It has been stated in related scientific literature[46,47] that the greater the negative charge on the heteroatom, the higher its ability to be adsorbed by the adsorbent and engage in a significant donor-acceptor reaction. The Mulliken charges for the molecules of BB are presented in Figure 8. Analysis of these findings reveals that all heteroatoms possess negative charges characterized by a high electron density.

These atoms operate as nucleophilic centers when they interact with the adsorbent. By examining the numbers in Figure 8, it becomes evident that all nitrogen and oxygen atoms possess a significant surplus of negative charge, and certain carbon atoms carry a negative charge, making them adsorbent active atoms.

Molecular electrostatic potential and electrostatic potential surface of BB dye

Molecular electrostatic potential provides significant insights into the electronic characteristics of molecules. It plays a crucial role in understanding and predicting the behavior of molecules in a variety of chemical reactions, including hydrogen bonding, nucleophilic, and electrophilic interactions. The different values of the electrostatic potential at the molecular surface are depicted using a color gradient. This gradient allows for a visual representation of areas of varying electrostatic potential. The potential values increase in the following order: red < orange < yellow < green < blue. This color scheme helps in identifying regions with distinct electronic characteristics within the molecule.

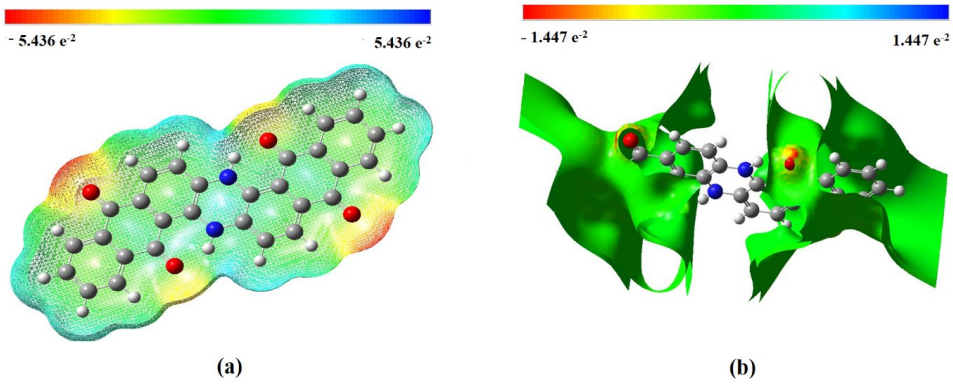

Figure 9: MEP and ESP of BB dye

As indicated by the ESP (Fig. 9), the negative ESP is primarily concentrated around the oxygen atom. The crimson glob represents the negative ESP, whilst the positive ESP is concentrated on the remaining molecules. F. Akman[48] identified the reactivity of chitosan: the dominance of negative charge around hydroxyl groups, contrasted with the positive regions, underscores the dual reactivity of these groups. Hydroxyl groups in chitosan are thus identified as reactive sites for both nucleophilic and electrophilic attacks, making them crucial for the chemical behavior of these molecules. The results indicate possible formation of H-bond interactions between Bezathren blue dye and chitosan.

CONCLUSION

The objective of this study has been to enhance the efficiency of removing BB dye from its aqueous solutions by utilizing chitosan as an adsorbent. The RSM approach, based on the DED, was used to examine the impact of contact duration, adsorbent dosage, dye concentration, and solution pH on the effectiveness of dye removal. The ANOVA findings indicated that the model had a high level of dependability in

predicting the response across different variables. The response surface methodology employed in this study indicates that the period of contact and chitosan dose had a more pronounced impact on the removal of BB dye compared to other parameters. The maximum adsorption capacity achieved was 5.9 mg/g. Utilizing density functional theory simulations, we sought to enhance our understanding of the interactions between the adsorbent and dye at the molecular level. The DFT data indicated that the primary forces between the dye and chitosan are hydrogen bonding interactions.

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