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# Removal of Diazinon from Aqueous Solutions in Batch Systems Using Cu-modified Sodalite Zeolite: an Application of Response Surface Methodology

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ABSTRACT

In this work, perlite was used as a low-cost source of Si and Al in the synthesis of sodalite zeolite using hydrothermal synthesis method. $Cu_2O$ nanoparticles were coated on a bed of sodalite zeolite and used as an adsorbent for removal of diazinon from aqueous solutions. To analyze the process, a significant variable .i.e. removal efficiency (%) of diazinon and three dependent parameters as the process responses were examined through a central composite design (CCD) under the response surface methodology (RSM). The optimum conditions included: 0.22 g adsorbent, 23.62 min contact time, at 29.28 °C. The percentage removal of diazinon in batch administrations was 97.24.

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## 1. INTRODUCTION

The presence of pesticides in soils, ground water and surface water is currently an important concern throughout the world because many of these materials are harmful to both human health and the environment. Increasing application of pesticides in agriculture fields for controlling pests is polluting water resources every day [1, 2]. Organophosphate pesticides are among insecticides with widespread application in pest control in the many agricultural areas. These pesticides originate from different sources especially from agricultural drainage [2]; wastewater treatment plants [3] and other water resources. These pesticides are mainly nonbiodegradable environmental pollution and are carcinogenic in nature. Therefore, pesticides toxicity and their post-degradation products that make serious contribution to increased levels of environmental and water contamination have become predominant all around the world [4]. Diazinon is considered as a kind of organophosphate pesticide. Diazinon is utilized as a control measure for pests in fruits, vegetables, and field crops, but excessive concentration of this insecticide has detrimental effect on organisms and blood. Hence, the amount of usage should be carefully determined in case the toxicant contaminate ground or sea water [5, 6]. At the same time, diazinon is easily absorbed into the skin and holds a synergic characteristic with other toxins such as pyrethrines [7]. A maximum allowed concentration of 0.5 µg/L was determined by the European Union for the combination of all pesticides and 0.1 µg/L for individual compounds in drinking water [8]. Several techniques were employed to remove the toxicant from water, such as treatment by adsorption processes [9, 10], advanced oxidation processes [11, 12] and electrocoagulation process [6]. Adsorption reveals one of the most effective methods for the removal of pollutants from the environment. This technique uses an equipment that is easy to use and readily available, yet not energy intensive. The treatment is also cost effective [13-15]. Various adsorbents were utilized for the elimination of diazinon from the water and wastewater such as agricultural soil [16], surfactant modified agricultural soil [17], Organo-Zeolites [18] and modified Bentonite [19]. Zeolites are one of the capable

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materials for the adsorption of organic compounds. In the case that the volume with a high concentration of organic compounds, the zeolite is used as a sorbent that can be then reused or recycled. For the low concentrations of organic compounds, the sorption can be combined with an oxidative catalyze process. Advantage of zeolite application rather than carbon bases such as activated carbon is its capability to be used for the flow which contains fewer pollutant concentration and moisture. In these cases, application of the zeolites with a high amount of silica which are hydrophobic, are so effective [20]. The nanoparticles are widely applied as catalyst in various fields and environmental issues. For an example of air pollution controlling case, Catalytic incineration of benzene on metal oxide catalysts has been studied and the results showed a complete destruction of benzene at 300°C and 5.5% (weight percent) of copper nanoparticles on TiO2. The results of a research to complete oxidation of naphthalene on metal oxide catalysts, illustrated the catalytic properties of metal oxides such as CuO in naphthalene removal [21]. Some other researches have demonstrated destruction of the volatile organic compounds by iron nanoparticles [22, 23]. Perlite is a rhyolitic glass the structure of which is made up of more than 70% silica and 13% alumina. The amounts of silica and alumina are different in various types and forms [24]. After heating, perlite changes to a light weight material and is typically light grey to white in color and is named ‘‘expanded’’ perlite. Perlite has various properties due to the differences in composition and structure. Among the countries that produce perlite, Iran is considered the largest producer [24]. Perlite is commercially low in price as a result of its abundant utilization as in ceiling tile, pipe insulation, gypsum wallboard, cryogenic insulation and filter media, etc. [25]. Zeolites were successfully utilized in the chemical industry and environmental protection over the last 35 years in accordance with their significant physical and chemical properties which include molecular sieving, adsorbing and cation exchange capability [25]. Preparation of zeolites from low-cost sources has been the main objective in many researches [26]. Many research groups were formed to prepare zeolites from perlite in laboratories that led to the formation of different types of zeolites, such as zeolite-X, gismondine, heulandite, ZSM-5, etc [27]. A natural zeolite (bentonite) was used in Bensaadi Ouznadji et al. [19] for the sorption of diazinon from aqueous solutions. The latter objective was to explain the effects of different parameters such as pH, temperature, contact time, adsorbent dosage, and initial pesticide concentration on the diazinon removal. In another study, the possibility of using MCM-41 and MCM-48 mesoporous silicas was examined for the diazinon and fenitothion removal from non-polar solvent via the batch sorption method [28]. The organ-zeolite was also employed as a low cost sorbent for the removal of atrazine, lindane and diazinon from water. In addition, the effect of different operating variables was studied on the sorption of atrazine, lindane and diazinon onto organo-zeolite and equilibrium isotherm of this sorption process [18]. The main objective in this research was to examine the synthesized sodalite zeolite obtained from perlite. Sodalite zeolite was modified by Copper oxide ($Cu_2O$) nanoparticles and utilized as an attractive adsorbent for the diazinon pesticide treatment from aqueous solution. Moreover, many statistical and experimental designs were recognized as useful tools to optimize the variables of diazinon sorption onto modified zeolite.

## 2. MATHEMATICAL MODEL

**2. 1. Reagents and Chemicals** In this experiment, the diazinon (95–96% active substance) was provided by Merck. Diazinon solution of 50 mg/L was prepared in deionized water and kept in a refrigerator at 3 $^oC$ until use. Table 1 shows the chemical and physical properties of diazinon. Using $H_2SO_4$ (1 M) and NaOH (1M), the solution pH was adjusted. Diazinon concentration of the aqueous solution was determined using the Uv-vis spectrophotometry technique. Spectra were recorded at maximum wavelength ($\lambda_{max}$) 247 nm [6, 28]. Uv-vis of diazinon are presented in Figure 1. The adsorbent, namely perlite, was provided by Afrazand Company, Iran. The source of this perlite was Meyaneh, Iran. Copper oxide ($Cu_2O$) with a 30-60 nm particle size was purchased from Merck.

**2. 2. Synthesis of Sodalite Zeolite** A starting material such as raw perlite was employed with a grain size of <75 μm (72.68 wt.% $SiO_2$; 11.74 wt.% $Al_2O_3$).

**TABLE 1.** Chemical and physical properties of diazinon.

| Property | Information |
|---|---|
| Chemical class | Organophosphate |
| Chemical fomula | $C_{12}H_{21}N_2O_3PS$ |
| Molecular weight | 304.345502 g/mol |
| Color | Clear colorless liquid |
| Physical state | Liquid |
| Boiling point | 83–84 °C at 2x10$^{-3}$ mm Hg; decomposes at **> 120 $^o$C** |
| Specific Denisty | 1.11 (20 °C) |
| Melting Point | Decomposes at >120°C |

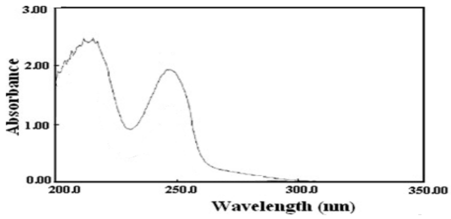


**Figure 1.** UV–vis spectrum of a diazinon solution.

First, the aluminate solution was prepared after 0.873 g Al-foil added to 15 mL of 2.7 N NaOH solution was dissolved. Then, the silicate solution was prepared by mixing 3.651 g of perlite which was later transferred to a polypropylene bottle containing 31 mL of 2.7N NaOH solution. Through magnetic stirring, the mixture was heated for 2h at a constant temperature of 70 °C. Then, the suspension was filtered. Next, the silica source was added slowly to the alumina source. The resulting mixture was stirred for 60 min to obtain a homogenous and clear solution. Afterwards, the mixture was transferred into a stainless steel autoclave with teflon tube and heated in an oven at 110 °C for 25 h. After the finalization of the hydrothermal treatment, the products were collected by means of filtration, washed with deionized water and dried at 80 °C overnight.

**2. 3. Synthesis of Cu Modified Sodalite** Through the grains draining in a dispersed suspension of nanoparticles, coating of nanoparticles on zeolite grains was carried out. Typically, 0.1gr Copper oxide ($Cu_2O$) with a particle size of 30-60 nm was spilled into an Erlenmeyer flask containing 10 mL distilled water and later sonicated a few minutes to make a uniform suspension. Then, 2 gr sodalite zeolite was added to the flasks and shook moderately for 2h. Ultimately, the contents of the flasks were dried slowly at 80°C for 10h. The added value of nanoparticles was 4.5 wt% of zeolite [29, 30].

**2. 4. Instrumentation** In the present study, X-ray diffraction (XRD) patterns were examined by a GBC MMA diffractometer (MMA, GBC Scientific Equipment LLC, USA) through CuKα radiation. Scans were recorded in an angular range from 5° to 70°. To study the surface of the sodalite zeolite, Scanning Electron Microscope (SEM) model S3400, Hitachi, Japan was employed. Gold and palladium were used to coat the sample using a sputter coater with conductive materials in order to improve the image quality. The thickness and density of coating were 30.00 nm and 19.32 g/cm$^3$, respectively. Energy dispersive X-ray (EDX) spectra were recorded on an EDX Genesis XM2 attached to SEM. The sodalite infrared spectra (IR) were obtained by FTIR Spectrometer (Shimadzu 4100) to determine the sodalite functional groups. Using KBr pellets, spectra were collected with a spectrometer. In each case, the homogenization of 1.0 mg of dried sodalite and 100 mg of KBr was done using mortar and pestle. Subsequently, they were pressed onto a transparent tablet at 200 kgf/cm$^2$ for 5 min. The pellets are characterized by a FTIR spectrometer in the transmittance (%) mode with a scan resolution of 4 cm$^{-1}$ in the range 4200–500 cm$^{-1}$.

**2. 5. Experimental Design** The percent removal of diazinon from aqueous solution in batch system was designed by RSM (response surface methodology) package using the Design-Expert software 7.01 (Stat-Ease Inc., Minneapolis, MN, USA) [31]. The statistical method of factorial design of experiments (DOE) removes systematic errors together with an estimation of the experimental error and minimization of the number of experiments [32, 33]. The central composite design (CCD) is mostly used under the RSM design. RSM was employed to evaluate the relationship between responses and independent variables and to optimize the relevant conditions of variables with the aim of predicting the best value of responses. By solving the regression equation at the desired values of the process responses as the optimization criteria, the optimum values of the selected variables were obtained [34]. Each independent factor was coded at five levels: −α, −1, 0, +1 and +α. The variable range and level are given in Table 2 in coded units resulting from RSM studies [35]. The design was composed of 2k factorial points augmented by 2k axial points and a center point where k is the number of variables. Thus, 20 experiments (2k +2k+6=20) were performed with 15 experiments.

Three dependent parameters of the experiments conducted in batch conditions were measured directly or calculated as response. After analyzing the variances (ANOVA), the regression equation yielded the level of diazinon removal efficiency (%) as a function of contact time (A), amount of adsorbent (B) and temperature (°C). This table presents the result of the CCD experiments that are obtained through studying the effect of three independent variables together with the predicted mean and observed responses. The results are calculated using the Design Expert software (Table 3).

**TABLE 2.** Experimental ranges and levels of the independent variables.

| Type of variable | Name of variables | Range and Level | | |
|---|---|---|---|---|
| | | -1 | 0 | +1 |
| Numerica | Contact time(min) | 2 | 16 | 30 |
| | Amount of adsorbent(g) | 0.05 | 0.17 | 0.3 |
| | Temperature (°C) | 20 | 35 | 50 |

**TABLE 3.** Full factorial central composite design matrix of orthogonal and real values along with observed .

| Run | Variable with coded levels | | | Response diazinon removal (%) | |
|---|---|---|---|---|---|
| | Contact time (min) | Amount of adsorbent (g) | Temperature ($^{o}$C) | Experimental | Predicted |
| 1 | 0 | 0 | 0 | 83.24 | 85.58 |
| 2 | -1 | 1 | -1 | 38.91 | 41.09 |
| 3 | -1 | -1 | -1 | 29.35 | 29.19 |
| 4 | -1 | 0 | 0 | 53.21 | 49.42 |
| 5 | 0 | 0 | 1 | 71.68 | 72.51 |
| 6 | 1 | 1 | -1 | 96.71 | 97.86 |
| 7 | 0 | -1 | 0 | 53.91 | 58.24 |
| 8 | 1 | -1 | -1 | 60.07 | 59 |
| 9 | 1 | 1 | 1 | 73.47 | 74.15 |
| 10 | 0 | 0 | 0 | 83.52 | 85.58 |
| 11 | 0 | 0 | 0 | 84.35 | 85.58 |
| 12 | 0 | 0 | 0 | 84.25 | 85.58 |
| 13 | 0 | 1 | 0 | 90.12 | 83.7 |
| 14 | 0 | 0 | 0 | 89.21 | 85.58 |
| 15 | 1 | -1 | 1 | 38.41 | 35.94 |
| 16 | 1 | 0 | 0 | 84.21 | 85.91 |
| 17 | 0 | 0 | 0 | 84.71 | 85.58 |
| 18 | -1 | -1 | 1 | 19.54 | 18.91 |
| 19 | 0 | 0 | -1 | 92.43 | 89.51 |
| 20 | -1 | 1 | 1 | 29.39 | 30.98 |

**2. 6. Mathematical Modeling** The experimental data were subjected to multiple regression analyses and the CCD design experimental results matched a full second-order polynomial equation [36]. The experiments revealed that each parameter could only come in three levels and the appropriate model was the quadratic equation (Equation (1)):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

where Y is the response, Xi, Xj ... Xkj are the factors, $X^2i$ , $X^2j$ , …, $X^2k$ the square effects, XiXj, XiXk and XjXk the interaction effects, β0 the intercept term, βi (i=1, 2, ..., k) the linear effect, βii (i=1, 2, ..., k) the squared effect, βij (i=1, 2, ..., k; j=1, 2, ..., k) the interaction effect, ε a random error and k the number of studied factors. The model terms were confirmed or declined in terms of the probability (P) value with a 95% confidence level. Using the Design Expert software, the results were completely analyzed via the analysis of variance (ANOVA). Dimensional plots and their related contour plots were obtained based on the effect of the two factors levels. The simultaneous interaction of the two factors on the responses was studied in terms of the three dimensional plots [37].

**2. 7. Batch Adsorption Experiments** The effect of various parameters (contact time, adsorbent dosage and temperature) had considered and the conditions of maximum amount of diazinon removal in the batch method had determined.

In the adsorption tests, 100 mL of the diazinon solution was prepared from the dilution of 1 g/L stock solutions. Batch sorption experiments were performed at a constant temperature of 20 °C on a magnetic mixer at 400 rpm. At the end of the predetermined time intervals, the mixture was filtered and the filtrate was analyzed for any residual diazinon. Each experiment was performed in duplicate so that we could observe the reproducibility and the mean value used for each set of values. The experimental error was below 4%. The efficiency of diazinon, % removal was calculated as:

$$\%Removal = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

where $C_i$ is the initial concentration (mg/ L) and $C_f$ is the final concentration (mg/ L).

## 3. RESULTS AND DISCUSSION

**3. 1. Characterization of Sodalite Zeolite** The XRD, SEM, Energy dispersive X-ray (EDX) and FTIR contributed in the synthesized sodalite zeolites characterization. Figure 2 (a-b) shows the XRD powder pattern of synthesized sodalite and Cu modified sodalite. At 2θ values of 14.1°, 20.1°, 22.4°, 24.5°, 27.7°, 31.9°, 34.9°, 37.9°, 43.1°, 45.7° and 48.1°, the crystallization products matched sodalite characteristic peaks which were all given by Treacy and Higgins [38], indicating a successful synthesis of sodalite nanozeolite with good crystallinity and Cu modified sodalite exhibits a $Cu_2O$ phase which can be assigned at $2\theta=38.5^o$. This result is in agreement with previous works [39-41]. The SEM image of crystalline phase yields a useful technique to determine the size and morphology of the obtained crystals. SEM image of modified sodalite is shown in Figure 3, suggesting that formation of the spherical nano sized particle with an average diameter of 60-80 nm can be observed. Figure 4 presents the elemental analysis of Cu modified analcime by means of energy dispersive X-ray (EDX). The presence of Cu peaks in EDX spectrum is explained in detail and the amounts of elements are given in Table 4. To obtain the vibrational information on the species in materials, the FT-IR spectroscopy is a very useful technique. Thus, Figure 5(a-b) depicts the FT-IR analysis of modified sodalite in the 600–4200 $cm^{-1}$ range for products in before and after sorption. The FTIR spectrum of modified zeolite before diazinon adsorption shows a wide band located at 736.7 $cm^{-1}$ corresponding to the vibration of Al–O fragment. Also, the strong broad band at 985.4 $cm^{-1}$ is connected to the T–O band (T = silica or aluminum) and its sharpness suggest fine crystallization of the zeolitic product [42]. The peak at 1658.5 $cm^{-1}$ is attributed to the free water bending vibration. The strong broad band at 3400-3700 $cm^{-1}$ (centered at 3459.7 $cm^{-1}$) is symbolized by the stretching of water molecules adsorbed on OH groups [43-46]. It is observed from the Figure 5 (a-b) that after adsorbing diazinon in modified zeolite, there are slight changes in the absorption peak frequencies, suggesting that a diazinon binding process is taking place on the surface of the zeolite.

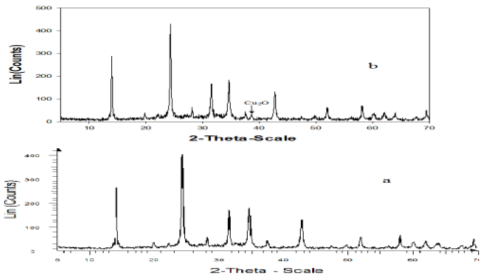


**Figure 2.** X-ray diffraction of synthesized sodalite zeolite (a) sodalite (b) Cu modified sodalite.

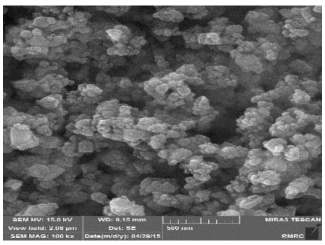

**Figure 3.** Scanning electron micrographs of modified sodalite zeolite.

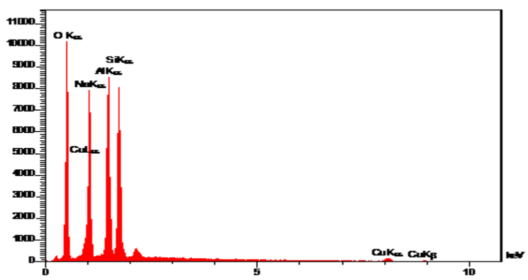


**Figure 4.** The EDX spectrum for Copper modified sodalite.

**TABLE 4.** Amounts of the elements obtained by EDX analysis.

| Element | Wt.% |
|---|---|
| O | 49.13 |
| Na | 17.07 |
| Al | 14.55 |
| `Si | 14.75 |
| Cu | 4.5 |

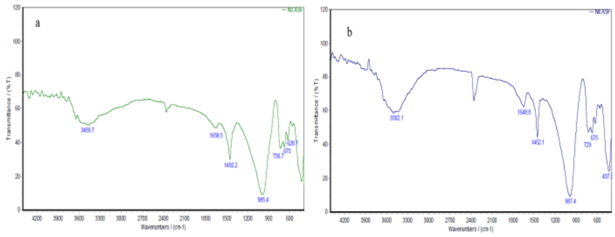


**Figure 5.** FTIR spectrum of modified sodalite zeolite a- befor sorption b- after sorption.

**3. 2. Statistical Analysis** The analysis of variance ANOVA based on the RSM approach was performed for the second-order response surface model. The results related to all responses are presented in Table 5. Based on Equation (1), the F-values and those of probability >F show the significance of each coefficient [47]. The larger the magnitude of the F-values, the smaller the p-values and the more significant the corresponding coefficients. The “prob > F” values were less than 0.05. This also indicates a high significant regression at 95% confidence level [48]. In this case, the factors first-order effects, square effects and interaction effects were specified as significant model terms. However, the F-value of the model was selected in the range of 50.82 for diazinon removal percentage and prob >F (<0.0001) values for all responses model which suggests that the model terms are significant. The prob >F value is less than 0.05. This reveals that the model terms are regarded as statistically significant. The insignificant value resulting from the lack of fit (more than 0.05) shows that the quadratic model is valid for response. The examination of the fit summary output suggests that the quadratic model is statistically significant for the response and thus was used for further analysis [35]. Through the determination of the coefficient (R2), the model goodness of fit was checked [37]. Table 6 represents the empirical relationship between responses (Y) and the three variables (factors) in coded values obtained by the application of RSM. The Prob > F values were less than 0.05. This suggests that the model terms, as presented in this table, are significant. Therefore, in this paper, Y indicates the responses; A, B and C are the coded values of the variables, i.e. contact time (min); amount of adsorbent (g) and temperature ($^oC$) respectively. For each response, the square of correlation coefficient was computed as the R square ($R^2$) that is a measure of the amount of variation around the mean explained by the model [33, 37]

The value of the coefficient of determination obtained in this case was 0.9883 for response, indicating the statistical significance of this regression and only 0-4% of the total variations are not explained by the model. The value of the predicted determination of the coefficient (Pred. $R^2$=0.9252) is in reasonable accord with the value of adjusted determination of the coefficient (Adj. $R^2$=0.9777). However, a relatively lower value of the coefficient of variance (CV=0.95%) for response suggests a good precision and reliability in the conducted experiments

**TABLE 5.** An analysis of variance (ANOVA) for the response surface quadratic model.

| Source | Sum of Squares | Df | Mean Square | F Value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Model | 11332.16 | 9 | 1259.13 | 93.77 | < 0.0001 | Significant |
| A- contact time | 3329.53 | 1 | 3329.53 | 247.95 | < 0.0001 | |
| B- amount of dosage | 1621.04 | 1 | 1621.04 | 120.72 | < 0.0001 | |
| C-Temp | 722.16 | 1 | 722.16 | 53.78 | < 0.0001 | |
| AB | 341.78 | 1 | 341.78 | 25.45 | 0.0005 | |
| AC | 81.73 | 1 | 81.73 | 6.09 | 0.0333 | |
| BC | 0.21 | 1 | 0.21 | 0.015 | 0.0034 | |
| $A^2$ | 882.25 | 1 | 882.25 | 65.70 | < 0.0001 | |
| $B^2$ | 586.70 | 1 | 586.70 | 43.69 | < 0.0001 | |
| $C^2$ | 57.34 | 1 | 57.34 | 4.27 | 0.0457 | |
| Residual | 134.28 | 10 | 13.43 | | | |
| Lack of Fit | 110.29 | 5 | 22.06 | 4.60 | 0.0598 | not significant |
| Pure Error | 23.99 | 5 | 4.80 | | | |
| Cor Total | 11466.45 | 19 | | | | |

**TABLE 6.** ANOVA results for response parameters.

| Standard deviation | 0.85 | R-Squared | 0.9883 |
|---|---|---|---|
| Mean | 67.03 | Adj R-Squared | 0.9797 |
| C.V.% | 0.95 | Pred R-Squared | 0.9511 |
| PRESS | 560.25 | Adeq Precision | 33.69 |

$$Y = +85.58 + 18.25A + 12.73B - 8.5C + 6.54AB - 3.2AC - 0.16BC - 17.91A^2 - 14.61B^2 - 4.57\,C^2$$

### 3. 3. The Effect of Operation Parameters of the Model on the Removal Efficacy of Diazinon

To study the effect of each variable on the response, the 3-D diagrams and counter were used. Moreover, the interaction diagrams were applied to illustrate the two parameters interaction effect on each other and on the removal of diazinon. Figure 6 depicts the overall effect of parameters. As shown in Figure 6, the effect of changing contact time on diazinon removal suggests that the increase in contact time leads to a rapid increase of yield. Changing the adsorbent material has some effect on the removal yield of diazinon which is indicative of the fact that increasing the adsorbent material leads to an increase in the diazinon removal yield. The effect of temperature on diazinon removal yield suggested that increasing the temperature leads to a linear decrease of the diazinon removal yield in the model.

### 3. 4. Effect of Contact Time on the Response

The aim of this research is to study the effect of a variable i.e. contact time on the system response or absorption and adsorbent processes. In every batch treatment system, contact time has a meaningful effect on the final yield of the system and the overall capacity of the treatment system.

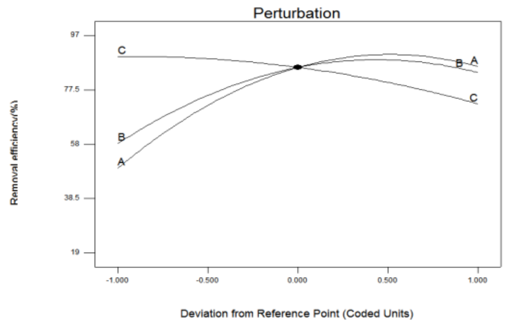


**Figure 6.** The overall diagram of the effect of parameter deviations on diazinon removal.

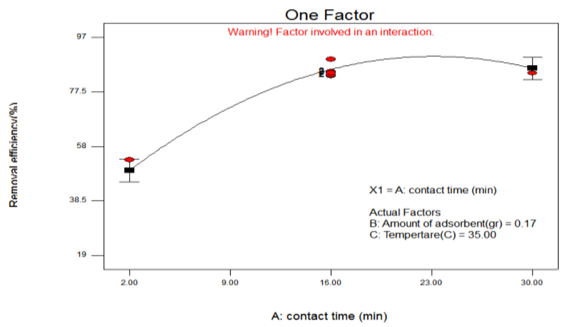


**Figure 7.** Diagram of the contact time effect on the removal yield of diazinon

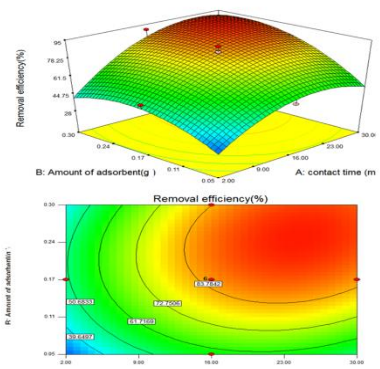


**Figure 8.** Contour and 3-D diagram of the effect of contact time and adsorbent dosage on diazinon removal efficacy.

In treatment systems related to other processes, the time or waste time in each section may have effects on the system overall capacity and efficacy. In fact, one can mention that the time of every part of the system and the respective sensitivity to deviation, have a direct and/or indirect effect on all costs and yields. It should be noted that the contact time in the absorption process is considered a parameter of equilibrium. This signifies that the variable was optimized and the subsequent increase in the point of equilibrium has no effect on the absorption process.

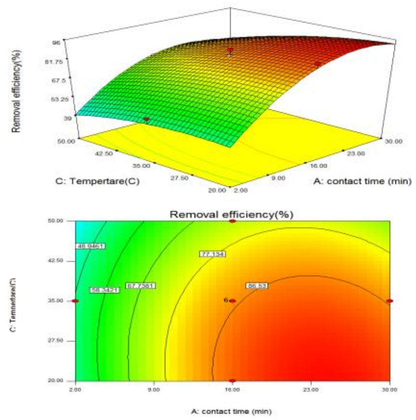


**Figure 9.** Contour and 3-D diagram of effect of Contact Time and Temperature on diazinon removal efficacy.

Therefore, future studies should be conducted on the variables that are of high importance and necessity. Figure 7 illustrates the effect of contact time on the removal yield of diazinon. As can be seen from the figure, any increase in contact time leads to an increase in the diazinon removal efficacy which has a slight slope. When the equilibrium value is reached, it stays constant and no increase or decrease occurs. Using 3-D and contour diagrams of contact time, Figure 8 depicts the existing effect on contact time and adsorbent mass in the removal of diazinon from aqueous solution by modified zeolite adsorbent. It was observed that the temperature value was constant and equaled 35 $^{o}$C and the removal yield was between 39.6497 to 83.7842. Clearly, the increase in contact time and adsorbent amount leads to an increase in the removal yield of diazinon with a 30min contact time and an adsorbent amount of 0.3. Figure 9, through 3-D diagrams and the contact time contour effect on the temperature, illustrates the removal of diazinon indices from aqueous solution by modified zeolite. It is evident whenever the amount of adsorbent is constant and equals the mean value of 0.17 (g) and the removal efficiency is between 48.9461 and 86.53, any increase in contact time leads to a simultaneous decrease in the temperature, an increase in the diazinon removal efficacy at contact time=30 min, an temperature of 20 $^{o}$C and a maximum removal yield of diazinon of 86.53.

### 3. 5. The Effect of the Adsorbent Amount of the Model on the Responses

The next operational parameter or system variable which was studied is the amount of adsorbent in waste samples. The adsorption process taking place on molecules and adsorbent surfaces and the availability of absorbable surface have meaningful effect on removal yield. In addition, this parameter, like other operational parameters, has both direct and indirect effect on the processes and costs and other related problems of the treatment system. In fact, the quantity of adsorbent is the main factor in selecting or not selecting the material in a system based on the absorption because the overall cost of preparation and use of the material, and if necessary washing or excretion, could bring economic benefits and/or be unaffordable. Consequently, these parameters must be studied carefully. Figure 10 illustrates the effect of increase in the quantity of adsorbent on the removal yield of diazinon. As can be seen, increasing the amount of absorbent leads to a linear increase in the removal yield of diazinon in the model. It is readily understood that the availability of larger surface area and more adsorption sites increase upon every increase in the adsorbent dose.

At higher concentrations of sorbate, the equilibrium uptake did not increase significantly with the increase in zeolite. Another reason may be the particle interaction such as aggregation which results from high adsorbent dose. Such aggregation would lead to a decrease in the total surface area of the adsorbent and an increase in diffusional path length [49]. Figure 11 illustrates 3-D and contour diagrams of the effect of amount of adsorbent and temperature on removal efficiency of diazinon which occurs when the contact time reaches 16 min. It can be seen that with the increase in amount of adsorbent and decrease in temperature, the diazinon sorption increases and the maximum diazinon removal, i.e. 84.53 is achieved.

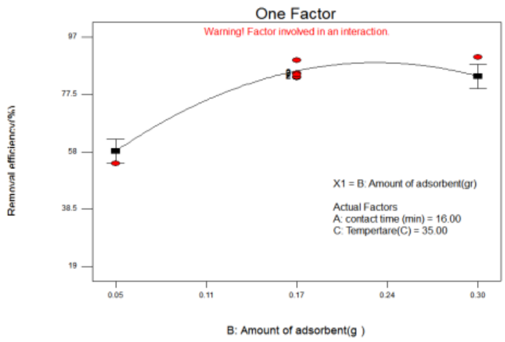


**Figure 10.** Diagram of effect of absorbent amount on diazinon removal yield.

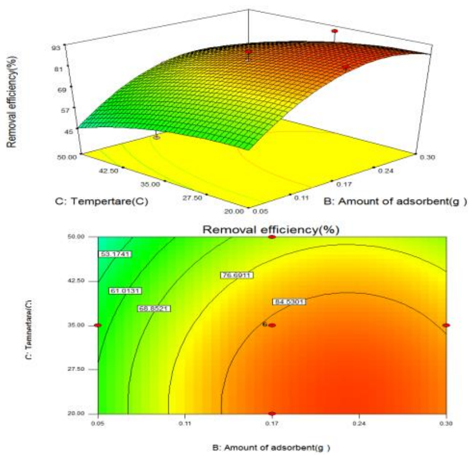


**Figure 11.** Contour and 3-D diagrams of effect of absorbent amount and temperature on diazinon sorption.

### 3. 6. Effect of Temperature on the Responses

Solution temperature exerts a significant influence on the rate of adsorption. The temperature has two major effects on the sorption process. Increasing the temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbent particles because liquid viscosity decreases as temperature increases.

In addition, temperature affects the equilibrium capacity of the adsorbent depending on weather the interaction between the adsorbent and the adsorbate is exothermic or endothermic. The results indicate that the adsorption capacity of modified zeolite with respect to diazinon decreases with increase in temperature, indicating that the adsorption process is exothermic in nature. Figure 12 shows the changing parameter of temperature merely on diazinon removal yield. It is clear that the increase in temperature leads to a decrease in sorption.

### 3. 7. Process Optimization

The last target of the response surface methodology is to find the optimum operating condition for the process. The purpose of this optimization is to achieve maximum diazinon removal efficiency alongside the best conditions of variables.

The optimized condition preset at high and low level or in the ranges of the process variables. Table 7 depicts the optimization criteria used to obtain the optimal region for the response. To carry out the optimization phase, the desirability function procedure was used. The desirability function procedure is one of the widely used multi-response optimization methods in practice that locates one or more points that maximize this function. The desirability lies between 0 and 1 and it is indicative of the proximity of a response to its ideal value [50, 51].

Table 8 shows the results of the optimum conditions. In Table 8, the best optimum condition of process variables is number 1 which has the highest value of desirability. Figure 13 shows the desirability for each parameter and response solely for the best optimal conditions. As discussed earlier, for optimizing response, simultaneous objective function is a geometric mean of all transformed responses.

The highest desirability was observed for efficiency. That means that efficiency is closer to its target value. Additional experiments were performed at 5 optimum conditions to verify the accuracy optimal conditions produced by the design expert software. The comparison of the experimental values and the software-predicted ones is presented in Table 9. Results suggest there is a mean error of 1.246%.

**TABLE 7.** Parameters of the Response Optimization

| Criteria | Target | Lower limit | Upper limit |
|---|---|---|---|
| Contact time(min) | Is in range | 16 | 30 |
| Amount of adsorbent(g) | Is in range | 017 | 0.3 |
| Temperature(°C) | Is in range | 20 | 35 |
| Diazinon removal, % | Maximize | 19.54 | 96.71 |

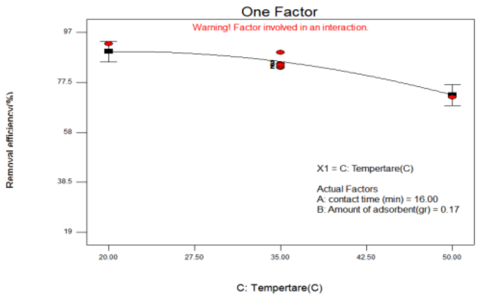


**Figure 12.** Diagram of the effect of the temperature on the removal yield of diazinon.

**TABLE 8.** Optimum diazinon removal condition

| No. | Contact time (min) | Amount of adsorbent (g) | Temperature (°C) | Diazinon removal | Desirability |
|---|---|---|---|---|---|
| 1 | 23.62 | 0.22 | 29.28 | 97.24 | 1 |
| 2 | 22.89 | 0.23 | 21.68 | 99.74 | 1 |
| 3 | 25.01 | 0.19 | 21.15 | 97.54 | 1 |
| 4 | 29.35 | 0.24 | 27.72 | 97.17 | 1 |
| 5 | 21.84 | 0.25 | 22.98 | 99.06 | 1 |
| 6 | 25.54 | 0.27 | 29.19 | 97.56 | 1 |
| 7 | 24.98 | 0.27 | 30.19 | 97.33 | 1 |
| 8 | 24.36 | 0.23 | 30.56 | 97.18 | 1 |
| 9 | 26.42 | 0.26 | 31.43 | 96.74 | 1 |
| 10 | 21.19 | 0.27 | 26.86 | 96.73 | 1 |

**TABLE 9.** Verification Experiments at Optimum Condition

| Run | Diazinon removal (%) | | |
|---|---|---|---|
| | Experimental | Predicted (DoE) | Error% |
| 1 | 96.34 | 97.24 | 0.93 |
| 2 | 97.45 | 99.74 | 2.3 |
| 3 | 96.14 | 97.54 | 1.46 |
| 4 | 97.53 | 97.17 | 0.37 |
| 5 | 97.91 | 99.06 | 1.17 |
| | Mean error% | | 1.246 |

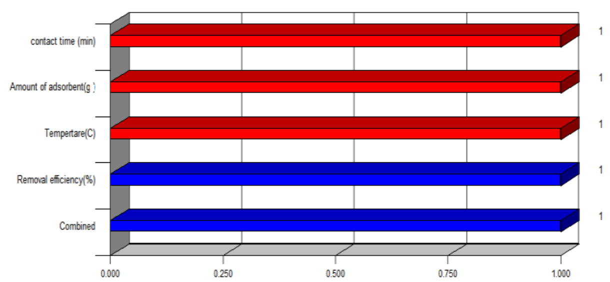


**Figure 13.** Desirability of the optimum condition for the best optimal conditions.

## 4. CONCLUSION

Sodalite zeolite crystals can be successfully synthesized from perlite in an alkaline solution. Results suggested that the modified zeolite have considerable potential for the removal of diazinon from aqueous solutions. The studies carried out on the adsorption onto modified zeolite with $Cu_2O$ nanoparticles proved to be highly effective in the sorption of diazinon. To obtain the operational conditions for the maximum removal rates of this substance, the RSM experimental design was used. The employed variables for wastewater treatment process were contact time (min), amount of adsorbent (g) and temperature (°C). These variables were studied in laboratory and the optimum value of each variable was determined to reach the maximum value of responses. Results suggested that the optimum conditions were 97.86 % diazinon removal in batch runs. The results of the analysis using the Design Expert showed that the obtained approximation models for diazinon were satisfactorily fitted with $R^2$ of 0.9883.

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# Removal of Diazinon from Aqueous Solutions in Batch Systems Using Cu-modified Sodalite zeolite: an Application of Response Surface Methodology

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**چکیده**

در این پژوهش از پرلیت به عنوان منبع کم ارزش سیلیس و آلومینیوم در سنتز زئولیت سودالیت با روش هیدروترمال استفاده شده است. نانو ذرات اکسید مس ($Cu_2O$) بر روی سطح زئولیت قرار گرفته و سپس از زئولیت اصلاح شده به عنوان جاذب در حذف دیازینون از محلول آبی استفاده شد. به منظور بررسی فرآیند تصفیه سه فاکتور مهم زمان تماس، جرم جاذب و دما موردنظر بودند. تاثیر فاکتورهای ذکر شده با روش جذب سطحی (RSM) با استفاده از نقاط مرکزی (CCD) طراحی و در آزمایشات استفاده شدند. شرایط بهینه شامل زمان تماس ۲۳/۶۲ دقیقه، جرم جاذب ۰/۲۲ گرم و دما ۲۹/۲۸ درجه سانتی‌گراد بوده است و درصد راندمان حذف دیازینون در سیستم ناپیوسته ۹۷/۲۴٪ به دست آمده است.

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