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ADSORPTION OF NEUTRAL RED DYE FROM AN AQUEOUS SOLUTION ONTO NATURAL SEPIOLITE USING FULL FACTORIAL DESIGN

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Abstract—The main objective of factorial design is to construct an empirical model to understand complex phenomena such as a purification process up to a given level of accuracy. The present study aimed to investigate the adsorption of Neutral Red dye (NR) from an aqueous solution onto sepiolite using 2^4 full factorial design. The combined effect of initial dye concentration, adsorbent dosage, pH, and particle size on adsorption of the dye was studied. The results were analyzed statistically using the student's t-test, analysis of variance (ANOVA), and an F-test to define important experimental factors and their relative levels of importance. A regression model which may be used to estimate the removal efficiency of NR without performing any experiments was suggested. The coefficient of determination ($R^2 = 0.9938$) indicated that <1% only of the total variations remain unexplained by the regression model. The experimental factors selected were determined to influence the adsorption process, but their relative importance varied according to the following sequence: pH > adsorbent dosage > particle size > initial concentration. The magnitude of the effects measured in this work can be used as a guide for how to adapt the adsorption process for different process conditions. The results also indicated that natural sepiolite is a suitable adsorbent for NR.

Key Words—Adsorption, Full Factorial Design, Neutral Red, Sepiolite.

INTRODUCTION

Dyes and pigments are used widely in industries such as textiles, paper, plastics, leather, food, cosmetics, *etc.*, and their discharge into water systems causes environmental problems (Köse, 2008; Lian *et al.*, 2009; Jaikumar and Ramamurthi, 2009; Luo *et al.*, 2010; Iram *et al.*, 2010; Mahmoodi *et al.*, 2011). More than 10,000 different types of dyes and pigments, with an annual production of >0.7 million tons, are commercially available and 5 to 10% of the dye stuff is lost as industrial effluent. The presence of even very low concentrations of dyes in the effluents from these industries is highly visible and undesirable. The discharge of colored waste into streams not only affects the aesthetic nature of the streams but also interferes with the transmission of sunlight, thus reducing photosynthetic action (Thinakaran *et al.*, 2006; Binpriya *et al.*, 2007; Ahlawat *et al.*, 2008).

Most of the dyes, including NR, are toxic. Neutral Red is a cationic dye used extensively for nuclear counterstaining in biological research. It is also used widely in analytical laboratories as a pH indicator. On decomposition, NR releases carbon monoxide, carbon dioxide, nitrogen oxides, and hydrogen chlorides which are toxic and can cause severe health problems for humans and animals. Many governments have established environmental controls for the quality of colored effluents and have forced dye houses to decolorize their effluents before discharging them (Özcan *et al.*, 2007; Rauf *et al.*, 2007; Saravanathamizhan *et al.*, 2007; Yi and Zhang, 2008).

The treatment of wastewaters that contain colored contaminants has been a technological challenge for many decades because most of the dyes have complex structures and are designed to resist breakdown with time, sunlight, water, soap, and oxidizing agents. Various treatment methods have been developed for decontamination purposes. Conventional physicochemical and biological treatment methods are ineffective at removing dyes because the dyes are too stable. Chemical oxidation by Fenton's reagent, ozone, UV plus H_2O_2, or NaOCl results in cleavage of the aromatic ring and may generate chemical sludge or by-products likely to be even more toxic. Conventional aerobic biological processing, *e.g.* the activated sludge process, cannot be used readily to treat wastewater from the textile industry because most commercial dyes are toxic to the organisms used in the process and result in bulking of the sludge (Binpriya *et al.*, 2007). Adsorption, oxidation, and membrane processes are used widely for wastewater treatment from the textile industry. Adsorption is recognized as one of the most effective processes for removing colors from aqueous solutions (Lee *et al.*, 2007; Qu *et al.*, 2008; Alkan *et al.*, 2008; Ozdemir *et al.*, 2009). Activated carbon, the most widely used adsorbent, has been successful, but has high costs associated

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with its replacement and regeneration. The high cost has led to the search for inexpensive and readily available adsorbents, *e.g.* natural and recycled waste materials (Santos and Boaventura, 2008; Tabak *et al.*, 2009). Natural materials (such as biomass, clay minerals, *etc.*) and certain waste materials (such as carbon slurry, bottom ash, fly ash, red mud, peat and bean wastes, deoiled soya, rice husk, and bagasse pith, *etc.*) are classified as low-cost adsorbents. Clays hold some promise as alternative adsorbents due to their low cost, abundance, ease of use, large specific surface area, and large adsorption capacity (Marcelo *et al.*, 2001; Chowdhury *et al.*, 2009; Gok *et al.*, 2010; Tong *et al.*, 2010).

Sepiolite ($Si_{12}O_{30}Mg_8(OH)_4(H_2O)_48H_2O$) is a naturally occurring clay mineral and an efficient natural adsorbent. Most of the world's sepiolite reserves are found in Turkey, mainly in Eskişehir and Konya (Aydoğan and Kadir, 2003; Önal *et al.*, 2008; Tabak *et al.*, 2009; Eren *et al.*, 2010a, 2010b; Işık *et al.*, 2010). Sepiolite is used widely to remove undesirable components from household wastewaters (Eren *et al.*, 2010a, 2010b; Tarlan-Yel and Önen, 2010) and is also used in various industrial manufacturing processes, *e.g.* in the removal of organic matter, heavy metals, ammonium and phosphate dyes, phenol, and lignin from wastewater. Adsorption occurs because of the presence of active adsorption centers on sepiolite surfaces (oxygen atoms in the tetrahedral sheet, water molecules coordinated with the Mg^{2+} ions at the edge of the structure, and silanol groups caused by the break-up of Si–O–Si bonds) (Balci, 2004; Karakaya *et al.*, 2004; Kocaoba and Akyüz, 2005; Lazarevic, 2007; Öztürk and Köse, 2008). Organic cations may bind to a sepiolite mineral surface in three possible ways: (1) an electrostatic interaction between the organic cation and a monovalent negative site on the silicate blocks, resulting in a neutral complex; (2) a second organic cation may bind to a neutral sepiolite–organic complex by non-coulombic interactions, forming a single, positively charged complex with two organic cations and one charged site; and (3) where neutral sites occur at external surfaces of sepiolite, a monovalently charged complex may form by the binding of one organic cation and a neutral site (Santos and Boaventura, 2008). Adsorption depends on various factors such as adsorbent dosage, initial adsorbate concentration, contact time, temperature, pH, and particle size. In order to determine the influence of each of these factors, conventional experiments were carried out by varying systematically the factors studied and keeping the others constant. Such an approach requires a large number of experiments, and optimum conditions may not be established if interactions between the different factors occur. A factorial design approach has been used here to investigate the effects of experimental factors and the interactions between those factors in a response. The advantages of factorial experiments include relatively low cost, a reduced number of experiments, and more opportunities to evaluate possible interactions between the variables (Tekbaş and Bektaş, 2009; Uğurlu, 2009; Bingöl *et al.*, 2010).

Despite the fact that sepiolite has been used extensively in the removal of dye and metal ions from wastewater, relatively few studies of the adsorption of dye ions on sepiolite using full factorial design have been published in the literature. The aim of the present study was to investigate whether or to what extent initial dye concentration, adsorbent dosage, pH, and particle size have an effect, either individually and/or jointly, on the adsorption of NR from an aqueous solution. The main effects and the interactions of these factors were studied at two levels using a 2^4 factorial design, which provides a mathematical model in the form of $y = f(x)$.

MATERIALS AND METHODS

Materials

A natural sepiolite sample with known chemical composition (Table 1) was obtained from Aktaş Lületaşı Co. in Eskişehir, Turkey. Prior to batch adsorption experiments, the sepiolite was washed with distilled water in order to remove surface dust and dried at 103ºC. The surface area of the sepiolite, measured using the BET method (Brunauer *et al.*, 1938), was 82.35 m^2/g. All the chemicals and reagents used were of reagent grade. The basic dye, Neutral Red (NR, $C_{15}H_{17}ClN_4$) (Table 2), was selected for adsorption studies. A stock solution of 1000 mg/L was prepared by dissolving an accurately weighed amount of NR in distilled water then diluting to 1000 mL. The initial pH of solutions was adjusted to the required value using NaOH or HCl solutions. All experiments were conducted in duplicate and the average values were used for data analysis.

Adsorption procedure

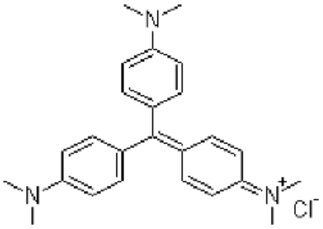
In order to determine the effect of initial metal concentration, adsorbent dosage, pH, and particle size on the efficiency of removal of NR, batch experiments were conducted. Aliquots from the stock solution of 1000 mg/L NR were diluted to various working

Table 1. Chemical composition (wt.%) of the sepiolite sample.

SiO_2	53.47
MgO	23.55
Al_2O_3	0.19
Fe_2O_3	0.16
CaO	0.71
LOI	21.49
Si/Al*	2.04

* Mass ratio

Table 2. Neutral Red dye properties.

C.I. No	50040
CAS No	55-32-42
Chemical formula	$C_{15}H_{17}ClN_4$
Molecular weight	288.78
Melting point	290ºC
C.I. name	Basic Red 5
Molecular structure	

concentrations. Dye concentration was measured using a UV-Vis Spectrophotometer at λ_{max} of 530 nm. The dye solution (100 mL in 250 mL Erlenmeyer flasks) at the desired concentration (10 and 100 mg/L) and pH (3 and 9) and the adsorbent at the desired dose (1 and 10 g/L) and particle size (16 mesh = 1190 μm and 45 mesh = 350 μm) were used. The adsorption reaction proceeded with agitation using a rotating shaker at 150 rpm for 2 h and results showed that the adsorption of NR increased rapidly with time (in the first 30 min) and reached saturation after ~120 min. The efficiency of NR removal (E) by the sepiolite was calculated using the following formula:

$$E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_o and C were the initial and final concentrations of the dye solution, respectively.

Factorial experimental design

A designed experiment consists of planned trials, where factors are set to predefined levels and one or more response variables are measured. When observations are taken on every possible treatment, the design is called a full factorial design. The number of experimental runs at b levels is b^k, where k is the number of factors (Navidi, 2008). A 'factor' is any variable that is associated with the product or process under experimental control. Two different types of variables are used in experimental design: categorical and continuous. A categorical variable is a factor that has only a discrete number of settings that have no intrinsic order, while a continuous variable can be assigned a numeric value. A 'level' is defined as a factor's specific value or setting.

In the present study, four continuous experimental factors (*i.e.* initial concentration, pH, adsorbent dosage, and particle size) were examined at two levels, high (+) and low (−), resulting in a 2^4 full factorial design. The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the factors. The resulting outcome measures the percentage of NR removed, or its removal efficiency.

RESULTS AND DISCUSSION

In order to examine the main factors and their interactions for removal of NR by adsorption, experimental parameters were selected as independent variables. The response variable was the removal efficiency of the sepiolite for the dye. The simultaneous effects of these factors on the removal efficiency for NR do not appear to have been investigated previously using factorial designs. The high (+) and low (−) levels (Table 3) were defined for experimental parameters. The level selection for each factor was carried out on the basis of the preliminary trials and previously published results. Experiments were executed in random order to evaluate experimental errors. Two measurements were made for each combination of factors (Table 4).

The null hypothesis stating that the main effects and the 2-way, 3-way, and 4-way interactions are equal to zero was tested using an F-test (Table 5) (Montgomery *et al.*, 2001). The small P values (<0.05) meant that not all the main effects and interactions are zero at the 5% significance level. In other words, reasonably strong evidence existed that at least some of the main effects and interactions were not equal to zero. A 'sum of squares' (SS) of each source quantified its importance in the adsorption process and as the value of the SS increased, the significance of the corresponding source in the undergoing process increased also. Thus, the importance of 3- and 4-way interactions was less than the others.

The effect of a factor is its change in response. The change is produced by the level of the factor. When the effect of a factor depends on the level of another factor,

Table 3. The experimental factor levels.

Factor	Coded symbol	Low level (−1)	High Level (+1)
Initial concentration (mg/L)	A	10	100
pH	B	3	9
Adsorbent dosage (g/L)	C	1	10
Particle size (mesh, (μm))	D	16 (1190)	45 (350)

Table 4. Experimental design matrix of dye-removal efficiency for NR.

	— Factor —				— Efficiency (%) —		
	A	B	C	D	– Replicate –		Average
Run no.					I	II	
1	−1	−1	−1	−1	53.40	56.56	54.98
2	+1	−1	−1	−1	35.55	37.44	36.50
3	−1	+1	−1	−1	98.20	99.15	98.68
4	+1	+1	−1	−1	93.69	94.56	94.13
5	−1	−1	+1	−1	93.77	97.88	95.83
6	+1	−1	+1	−1	88.67	90.56	89.62
7	−1	+1	+1	−1	99.44	99.12	99.28
8	+1	+1	+1	−1	97.54	99.34	98.44
9	−1	−1	−1	+1	92.70	89.68	91.19
10	+1	−1	−1	+1	64.24	68.20	66.22
11	−1	+1	−1	+1	99.66	98.86	99.26
12	+1	+1	−1	+1	94.50	97.41	95.95
13	−1	−1	+1	+1	98.85	99.20	99.03
14	+1	−1	+1	+1	96.98	98.70	97.84
15	−1	+1	+1	+1	99.20	99.90	99.55
16	+1	+1	+1	+1	98.82	98.70	98.76

the two factors are said to interact. Estimates of all the effects and interactions for NR are shown (Table 6). In order to determine which main and 2- and 3-way interaction effects were significant, the student's t-test was used (Montgomery *et al*., 2001). The null hypothesis that the effects are equal to zero was rejected except for *AD* and *ABD* interactions with *P* values >0.05, *i.e.* the removal efficiency for NR depends on the effects of *A*, *B*, *C*, and *D*, and the interactions of *AB*, *AC*, *BC*, *BD*, *CD*, *ABC*, *ACD*, *BCD*, and *ABCD*,

A normal probability plot of the standardized effects determines the statistical significance of both the main and interaction effects. The effects that are not significant will fall along a line; significant effects stray from that line. Thus, all the main effects and interactions except *AD* and *ABD* are clearly statistically significant (Figure 1). Because *BC*, *BD*, *A*, *CD*, *ABC*, and *ABCD* lie to the left of the line, their contributions have negative effects on the model. The reverse is true for the rest of the significant effects, which lie to the right. The factor pH (*B*) appears to have the largest effect because it lies furthest from the line.

In order to see the effects of interactions between the experimental factors, a 'multi-vari chart' was generated (Figure 2) from which the effect of increasing the pH level is clearly observed for particle size (−1) and adsorbent dosage (−1). When particle size and adsorbent dosage are held at their lower levels, a removal efficiency of >90% can be reached by increasing the pH. The effect of initial concentration is evident for low levels of adsorbent dosage and pH. On the other hand, the effects of particle size and pH on removal efficiency of NR are rather small where the adsorbent dosage is kept at its high level. Therefore, similar results can be reached for particle size at low level (16 mesh, 1190 μm) and pH at high level (9). In conventional experiments, such interactions would not be revealed.

In any designed experiment, examining the model for predicting responses is important. The linear model associated with a two-level statistical design in the case

Table 5. Analysis of variance.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main effects	4	6691.8	6691.78	1672.95	777.22	0.000
2-way interactions	6	3518.3	3518.30	586.38	272.42	0.000
3-way interactions	4	465.4	465.38	116.34	54.05	0.000
4-way interactions	1	23.5	23.48	23.48	10.91	0.004
Residual error	16	34.4	2.15	2.15		
Pure error	16	34.4	34.44	2.15		
Total	31	10733.4	34.44			

DF: degree of freedom, Seq SS: sequential sum of squares, Adj SS: adjusted sum of squares, Adj MS: adjusted mean squares, F: F test, P: probability

Table 6. Estimated effects and coefficients.

Term	Effect	Coef	SE Coef	T	*P*
Constant		88.515	0.2594	341.29	0.000
A	−7.417	−3.708	0.2594	−14.30	0.000
B	19.232	9.616	0.2594	37.08	0.000
C	17.554	8.777	0.2594	33.84	0.000
D	10.171	5.085	0.2594	19.61	0.000
A*B	5.296	2.648	0.2594	10.21	0.000
A*C	5.161	2.580	0.2594	9.95	0.000
A*D	0.104	0.052	0.2594	0.20	0.843
B*C	−15.801	−7.900	0.2594	−30.46	0.000
B*D	−9.169	−4.585	0.2594	−17.68	0.000
C*D	−7.167	−3.583	0.2594	−13.82	0.000
A*B*C	−3.854	−1.927	0.2594	−7.43	0.000
A*B*D	0.469	0.235	0.2594	0.90	0.379
A*C*D	1.164	0.582	0.2594	2.24	0.039
B*C*D	6.461	3.230	0.2594	12.46	0.000
A*B*C*D	−1.713	−0.857	0.2594	−3.30	0.004

S = 1.46713 R^2 = 99.68% R^2(adj) = 99.38%
Coef: coefficient, SE Coef: standard error of coefficient, T: Student's t-Test, *P*: probability

of four independent variables (*A, B, C*, and *D*) is expressed as follows:

$$\hat{Y} = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{14}X_1X_4 + \beta_{23}X_2X_3 + \beta_{24}X_2X_4 + \beta_{34}X_3X_4 + \beta_{123}X_1X_2X_3 + \beta_{124}X_1X_2X_4 + \beta_{123}X_1X_2X_3 + \beta_{124}X_1X_2X_4 + \beta_{134}X_1X_3X_4 + \beta_{234}X_2X_3X_4 + \beta_{1234}X_1X_2X_3X_4 \quad (2)$$

Here, each combination of the input *X* variables is prefixed with a multiplier coefficient represented by the β values. Based on the coefficients (Table 6), the regression equation ignoring the insignificant terms is as follows:

$$\hat{Y} = 88.515 - 3.708\,A + 9.616\,B + 8.777\,C + 5.085\,D + 2.648\,AB + 2.580\,AC - 7.900\,BC - 4.585\,BD - 3.583\,CD - 1.927\,ABC + 0.582\,ACD + 3.230\,BCD - 0.857\,ABCD \quad (3)$$

A negative sign for a given parameter indicates that the response decreases with the increase in the value of the variable. That is, a (+1) level of factor *A* (initial concentration) decreases the removal efficiency. The magnitude and sign of *B* indicates that the contribution of this factor to the model is 9.616% for the high level (+1). Similar explanations apply to other terms. The contribution of the 3-way and 4-way interaction terms to the model seems rather low according to their coefficients. The NR adsorption model given in equation 3 predicted a minimum removal efficiency of 36.32% (for initial concentration = 100 mg/L, pH = 3, adsorbent amount = 1 g/L, and particle size = 16 mesh, 1190 μm) and a maximum removal efficiency of 99.84% (for initial concentration = 10 mg/L, pH = 9, adsorbent amount = 10 g/L, and particle size = 45 mesh, 350 μm).

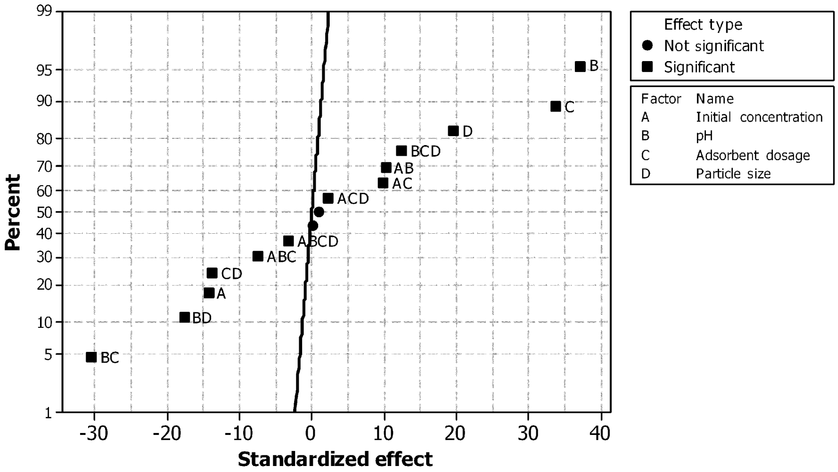


Figure 1. Normal probability plot of standardized effects (response is efficiency, α = 0.05).

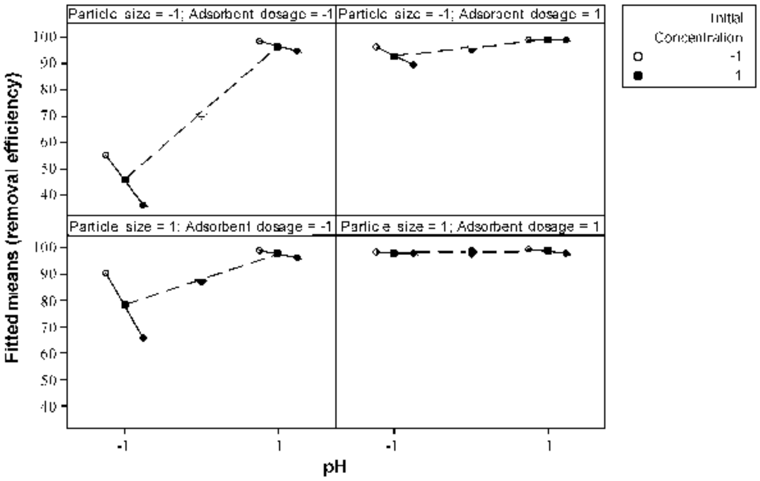


Figure 2. Multi-vari chart.

A residual is the difference between an observation and its predicted value according to the statistical model being studied. Residuals contain information about unexplained variability. The analysis of a 2^k design assumes that the residuals are normally and independently distributed with the same variance in each treatment or factor level (Montgomery *et al.*, 2001). The normality assumption was checked by constructing a normal probability plot of the residuals (Figure 3). Because the residuals lie approximately along a straight line, no problems with normality in the data were suspected. The independence assumption was checked by plotting the residuals against the run order in which the experiment was performed (Figure 4). No problem with the independence of the data was detected because no patterns such as sequences of positive and negative residuals were observed.

The surface plot was used to create a graphical representation of how two factors together at one time affect the output (removal efficiency). Because more than two factors are possible, the factors not displayed in graphs are held constant. The maximum removal was found to occur at the (-1) level of the initial concentration (*A*) and the (+1) level of the other factors (Figure 5). The smallest removal efficiencies were found where the initial concentration was at a high setting and the other factors were at low settings. As pH, adsorbent dosage, and particle size move toward their high settings, the values for removal efficiency increased steadily. However, compared to pH and adsorbent dosage, the increase in removal efficiency was relatively small, all the way from a low level to a high level of particle size. The surface plots also illustrate that the increase in response from the low to the high levels of pH, adsorbent dosage, and particle size is greater at the high level of initial concentration. At lower concentrations, NR ions present in the adsorption medium can interact with the binding sites. At higher concentrations, because of the saturation of the adsorption sites, the rate constant of dye adsorption onto the sepiolite showed a decreasing trend.

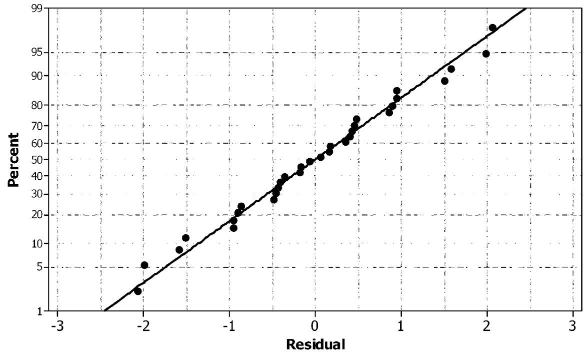


Figure 3. Normal probability plot of the residuals.

A plot of removal efficiency *vs.* pH and initial concentration (Figure 5a) showed that the removal efficiency depended on pH and initial concentration for constant adsorbent dosage and particle size. For NR removal at an initial concentration of 100 mg/L, a significant increase in the removal efficiency was observed with increasing initial solution pH from 3 to 9. This increase is a result of the increase in the negative surface charge on the adsorbent as the pH increased, leading to a greater degree of adsorption of cationic species. With decreasing pH, the negatively charged surface of sepiolite tended to be saturated by protons, and the NR cations had to compete with hydrogen ions for the adsorption sites, so the adsorption capacity decreased. At pH 3, the surface of sepiolite was positively charged and the adsorption became unfavorable. Studies of other basic dyes and adsorbents have reported an increase in adsorption capacity with pH (Balci, 2004; Öztürk and Köse, 2008). The removal

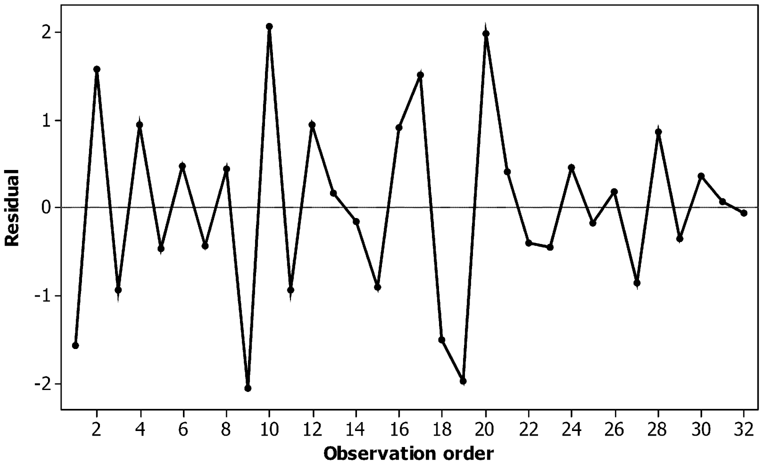


Figure 4. Residuals *vs.* the order of the data.

efficiency was observed to increase from 53.40% to 93.77% with an increase in adsorbent dosage from 1 to 10 g/L, attributable to the increase in the specific surface area of the adsorbent and the availability of more adsorption sites. The results show that dye-concentration/sepiolite ratios are inversely proportional to removal rates, *i.e.* low concentration, low pH, and large sepiolite dosage (Figure 5b)[sd1] A plot of the removal efficiency *vs.* pH and initial concentration (Figure 5c) indicated that the effects of particle size and initial concentration from low level to high level was rather small when pH and adsorbent dosage were held at their high level.

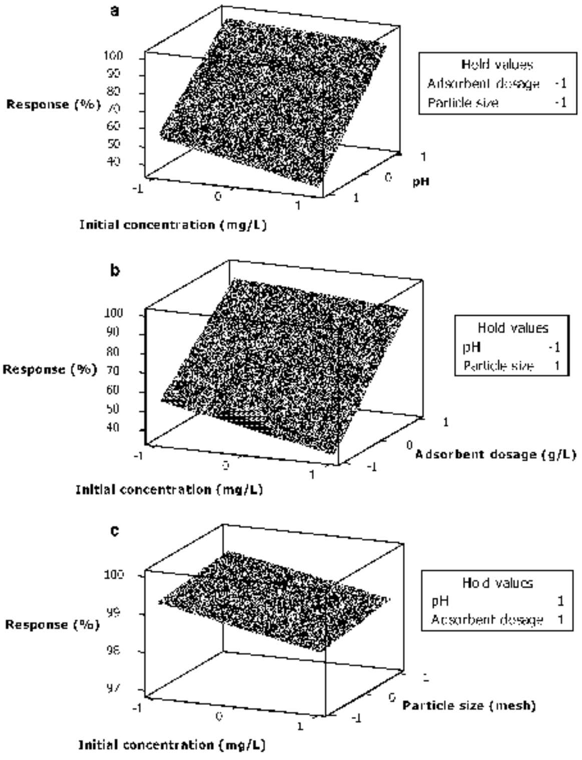


Figure 5. Surface plots of the removal of NR by sepiolite: (a) removal efficiency *vs.* pH and initial concentration; (b) removal efficiency *vs.* adsorbent dosage and initial concentration; and (c) removal efficiency *vs.* particle size and initial concentration.

CONCLUSIONS

In the present study, the concentration of dye ions, adsorbent dosage, pH, and particle size which affect the adsorption process were studied using 2^4 full factorial design experiments. Emphasis was placed on ascertaining the effects of two-way and higher-order interactions on the adsorption process. Such information is impossible to obtain with the more familiar 'one-at-a-time' approach used frequently in traditional studies.

The experimental results indicated that the most important factor affecting the removal of NR by sepiolite is the pH of the solution, followed by adsorbent dosage, particle size, and initial concentration. An adsorption capacity for NR of 36.32 mg/g was obtained for an initial concentration of 100 mg/L, pH = 3, adsorbent amount = 1 g/L, and particle size = 16 mesh (1190 μm).

The NR adsorption model predicted a minimum removal efficiency of 36.32% (for initial concentration = 100 mg/L, pH = 3, adsorbent amount = 1 g/L, and particle size = 16 mesh (1190 μm)) and a maximum removal efficiency of 99.84% (for initial concentration = 10 mg/L, pH 9, adsorbent amount = 10 g/L, and particle size = 45 mesh (350 μm)). The observed interactions between experimental factors gave a better explanation of the adsorption process of sepiolite which could not be obtained from 'one-at-a-time' studies. Based on the present findings, adjustment of factor levels in order to achieve a required level of removal is possible.

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