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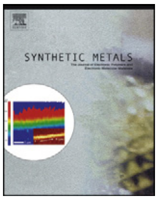

Analysis of adsorption of reactive azo dye onto $CuCl_2$ doped polyaniline using Box–Behnken design approach

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ABSTRACT

The polyaniline (PANI) doped with 8% $CuCl_2$ was investigated as adsorbent for removal of the reactive azo dye by using batch adsorption process. Effects of the major independent variables (initial dye concentration, initial pH, and PANI mass) and their interactions during reactive azo dye adsorption were determined by response surface methodology (RSM) based on three-level Box–Behnken design (BBD). The results indicated that the adsorption efficiency of dye in aqueous solution was affected by all of the three factors studied. The PANI mass was the most significant variable affecting the reactive azo dye removal. Optimized values of initial dye concentration, initial pH and PANI mass for reactive azo dye sorption were found as 60 mg/L, 6, and 0.3006 g, respectively which correspond to 99.83% adsorption efficiency.

1. Introduction

Synthetic dyes have been used widely in textile, paint, paper and printing industries. Wastewaters originated from textile industry contain various pollutants including a high content of organic matter and color problem depending on types of dyes, surface active materials and textile additives used in the process [1]. Textile dyes are structurally different. Reactive azo dyes are the most commonly applied among more than 10,000 dyes in textile processing industries [2]. Besides esthetic reasons, discharge of azo dyes is not desirable since many azo dyes and their intermediate products are toxic to aquatic lives and mutagenic to humans [3].

Biological treatment systems can be used for the color removal from wastewater by the physical/chemical methods such as flocculation/coagulation [4], adsorption [5–7], anaerobic process [8] and chemical oxidation [9]. The survey of literature reveals that adsorption is a very effective method for color removal. Adsorption capacity of adsorbent used in adsorption studies is also important. In the past two decades, there has been growing interest in the field of conducting polymers in science and industry. Because of their low cost of synthesis and easy processability, conducting polymers have a wide range of attractive applications in production of battery which can be charged, sensor productions, diode, transistors and microelectronic devices, modified electrode productions, electronic display boards, and biochemical analysis [10–16]. There are a few studies regarding the use of doped polyaniline (PANI) for the removal of dyes in literature. PANI doped with functionalized protonic acids (HCl, *p*-toluenesulfonic acid (PTSA) and camphorsulfonic acid (CSA)) has been utilized for removal of anionic dyes by Mahanta et al. [17,18]. It has been demonstrated that, the maximum dye adsorption/removal by PANI depends on the nature of the dopant (the order being CSA > PTSA > HCl). In another study, the polyaniline emaraldine salt samples has been used for the removal of indigo carmine anionic dye and Pb(II) ion from aqueous solutions [19].

Design of experiments (DOE) and response surface methodology (RSM) is widely used for modeling process parameters, especially in adsorption process [20–33]. Because RSM contains a small number of experiments, it is advantageous over conventional methods available. It is suitable for multi-factor experiments and searches the common relationship between various factors for the most favorable conditions of the processes. Response surface methodologies are central composite design (CCD), Doehlert matrix (DM) and Box–Behnken design (BBD) The objective of this study was the application of the RSM as a statistical technique in optimizing adsorption process of reactive azo dye using the PANI doped with 8% $CuCl_2$.

2. Materials and methods

2.1. Instruments

In the experimental studies, HACH Lange DR 2000 model spectrophotometer was used for determination of remaining dye concentrations. THERMO Scientific ORION 3 brand pH-meter was

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used in pH measurements and NUVE ST-402 model shaker was used for bath adsorption experiments.

2.2. Chemicals and reagents

The reactive azo dye (CIBACRON NAVY P-2R-01) with 70–80% purity, supplied by Ciba Specialty Chemicals was used as adsorbate. This reactive dye was used without further purification. The used azo dye contains of mixture of a sulfonated dye with two azo groups (sodium 4-amino-6-[[5-[(4-amino-6-chloro-1,3,5-triazinyl)amino]-2-sulphophenyl]azo]-3-[(2,5-disulphophenyl)azo]-5-hydroxyl-2,7-naphthalenedisulphonate) at ratio of 10–20% and a sulphonated dye with mono azogroups (sodium2-[[8-[[4-klor-6-(ethylphenylamino)-1,3,5-triazin-2-yl]amino]-1-hydroxyl-3,6-disulpho-2-naphthyl]azo]-1,5naphthalenedisulphonate) at ratio of 1–5%. The chemical structure of the used dye is shown in Fig. 1.

In batch experiments, 0.1 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH) were used to adjust pH.

2.3. Synthesis of polyaniline (PANI)

PANI was synthesized by chemical oxidation coupled with polymerization where ammonium persulphate [$(NH_4)_2S_2O_8$] (Merck, Germany) was used as an oxidant. 10 g of $(NH_4)_2S_2O_8$ dissolved in 20 mL deionized water was added into solution of aniline (5 mL) dissolved in 1.5 M HCl (70 mL) (Merck, Germany).

The solution mixture was stirred at 400 rpm for 5 h at a constant temperature of 25 °C. A color change from white through blue (after an induction period of approximately 90 min) to dark green was observed. After the polymerization leading to green emeraldine salt form of PANI granules, the solution was filtered, washed, and dried [34].

$CuCl_2$ (Merck, Germany) at various doping levels (0%, 2%, 4%, 6%, 8% and 10%) prepared in 5 mL deionized water were added into the solution mixture as described earlier prior to the stirring. The solution was then stirred at 400 rpm and at a constant temperature of 25 °C for 5 h. After the polymerization, the solution was filtered, washed, and dried leading to doped PANI samples [37].

2.4. Experimental procedure

The adsorption of reactive azo dye onto PANI doped with 8% $CuCl_2$ was investigated using batch experiments. In these studies 1000 mg/L stock solution was prepared by dissolving 1 g of dye in 1000 mL distilled water. Different concentrations (20–200 mg/L) of dye solutions were prepared by this stock solution. Solutions were evacuated to flasks of 100 ml. Then adsorbent in the range of dosage 0.05–0.5 g was added and placed in the water bath shaker after pH adjustments made in the range of 2–10. The suspensions were shaken at 200 rpm for 120 min at room temperature. Samples from shaker were filtered with filter paper, and then remaining dye levels were measured spectrophotometrically at absorption maxima of reactive dye at 622 nm. Finally adsorption efficiency (E, %) is calculated by the following formula as follows,

$$E = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{3}$$

where C_0 is initial dye concentration (mg/L); C_e is the residual concentration of the dye after the treatment (mg/L) and E is adsorption efficiency (%).

Table 1
Design matrix and levels based on the Box–Behnken design.

Experiment Number	Actual level of factors C_0 (X_1)	 pH (X_2)	 m (X_3)	Adsorption efficiency, E (%)
1	20 (−1)	2 (−1)	0.275 (0)	94.16
2	200 (+1)	2 (−1)	0.275 (0)	40.02
3	20 (−1)	10 (+1)	0.275 (0)	98.98
4	200 (+1)	10 (+1)	0.275 (0)	49.83
5	20 (−1)	6 (0)	0.050 (−1)	88.70
6	200 (+1)	6 (0)	0.050 (−1)	17.05
7	20 (−1)	6 (0)	0.500 (+1)	96.01
8	200 (+1)	6 (0)	0.500 (+1)	35.70
9	110 (0)	2 (−1)	0.050 (−1)	16.66
10	110 (0)	10 (+1)	0.050 (−1)	17.75
11	110 (0)	2 (−1)	0.500 (+1)	58.04
12	110 (0)	10 (+1)	0.500 (+1)	85.02
13	110 (0)	6 (0)	0.275 (0)	80.13
14	110 (0)	6 (0)	0.275 (0)	80.14
15	110 (0)	6 (0)	0.275 (0)	80.13

2.5. Response surface methodology

The BBD has proposed as rotatable or nearly rotatable three-level designs for fitting response surfaces by Box and Behnken. These designs are formed by combining 2^k factorials with incomplete block designs, and are usually very useful in terms of the number of required experiments. In addition, these designs are more efficient and economical than their corresponding 3^k designs, mainly for a large number of variables. The BBD is a spherical design, and does not also contain any points at the vertices of the cubic region created by the upper and lower limits for each variable. This is regarded as a significant advantage. The number of experimental runs (N) is given by $N = 2k\,(k-1) + C_0$, where k is the number of variables and C_0 is the number of center points. According to RSM, a second-order polynomial model is usually given to describe the effects of various factors on a response based on experimental results as follows,

$$y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum_{1\le i\le j}^{k}\beta_{ij} x_i x_j + \varepsilon \tag{1}$$

where y is the predicted response; x_i and x_j are coded variables; and the β_0 is the constant, the β_i is the linear coefficient, the β_{ii} is the quadratic coefficient, and the β_{ij} is the interactive coefficient, ε is a random error. Commonly the following equation is used for coding:

$$x = \frac{X - \left|X_{\max} + X_{\min}\right|/2}{\left|X_{\max} - X_{\min}\right|/2} \tag{2}$$

where X is natural variable, x is the coded variable and $X_{\max}$ and $X_{\min}$ are the maximum and minimum values of the natural variable [35–37]. The first step in RSM is to find a suitable approximation for the true functional relationship between response and the set of independent variables. A statistical program package Minitab-16, was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation.

For the adsorption efficiency of dye in an aqueous solution by $CuCl_2$ doped PANI, a total of 15 experimental runs with the factors (i.e. the initial dye concentration (C_0, mg/L), the initial pH, and the PANI mass (m, g) and their levels (−1, 0, +1)) used in factorial design were set in Table 1. The experiments were done with two replicate and at random order. The quantitative relationship between the adsorption efficiency and different levels of factors was used to find out optimized levels of these parameters by Box–Behnken design.

3. Results and discussion

Adsorption efficiency of doped PANI for various doping levels (0%, 2%, 4%, 6%, 8% and 10%) of $CuCl_2$ was investigated and found to

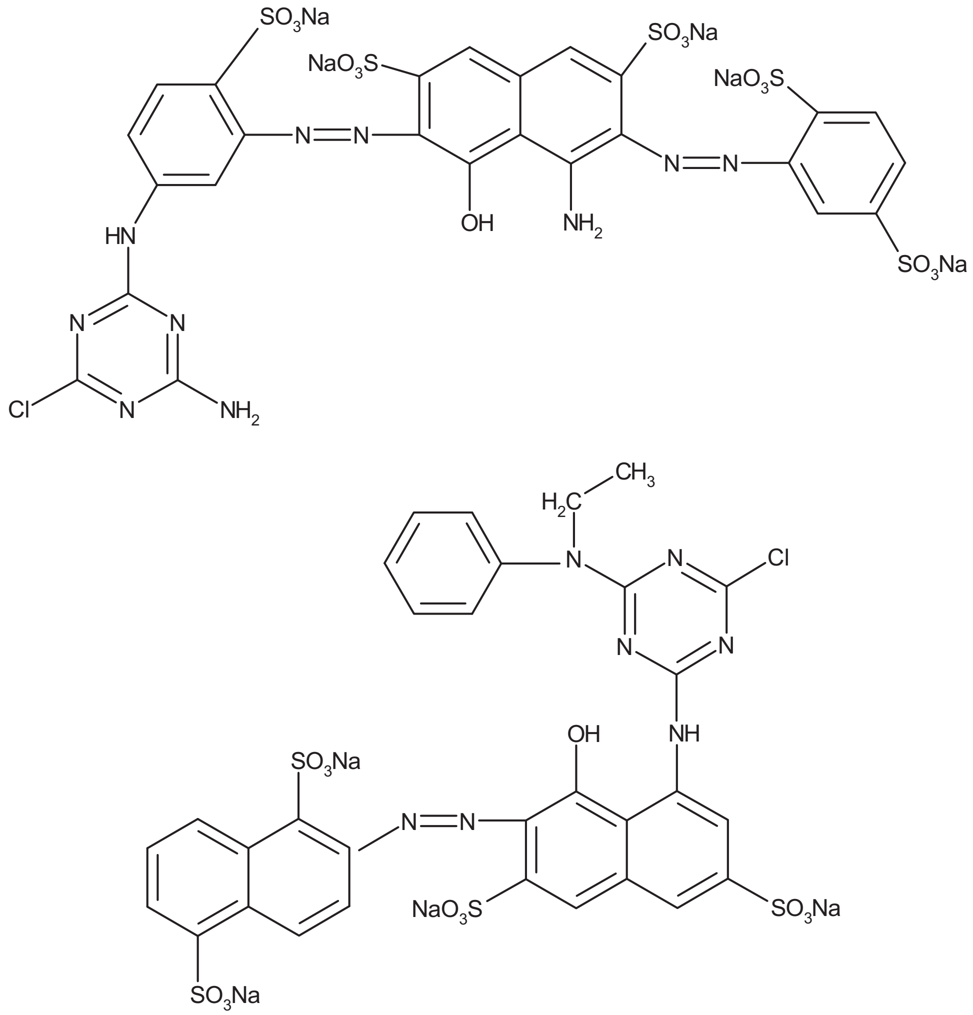

Fig. 1. The chemical structure of the dye used.

be 81.13%, 92.35%, 66.68%, 90.95%, 96.34% and 87.68%, respectively. Accordingly, adsorption efficiency of 8% $CuCl_2$ doped PANI was higher than others. So, 8% $CuCl_2$ doped PANI were used as adsorbent in the experiments. The optimum conditions for adsorption of reactive azo dye onto surface of 8% $CuCl_2$ doped PANI were determined by means of the BBD under RSM. Based on the analysis of variance (ANOVA) of the estimated model, terms which have significant effects on the adsorption efficiency can be determined. Model adequacy for the Box–Behnken design was checked by *t*-test with 95% probability and ANOVA (Table 2), residuals distribution (Fig. 2), and

Table 2

Estimated effects, coefficients and analysis of variance with uncoded units for suggested quadratic model.

Terms	Coeff.	SE	*T*	*P*
Constant	47.15	14.64	3.221	0.004
Initial dye concentration (X_1)	−0.46	0.13	−3.666	0.002
pH (X_2)	8.21	3.16	2.598	0.017
PANI mass (X_3)	272.92	50.58	5.396	0.000
Initial dye concentration–initial dye concentration (X_1^2)	0.00	0.00	0.810	0.428
pH–pH (X_2^2)	−0.77	0.23	−3.405	0.003
PANI mass–PANI mass (X_3^2)	−463.25	71.47	−6.482	0.000
Initial dye concentration–pH (X_1X_2)	0.00	0.01	0.359	0.723
Initial dye concentration–PANI mass (X_1X_3)	0.13	0.17	0.744	0.466
pH–PANI mass (X_2X_3)	7.19	3.86	1.863	0.077

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Analysis of variance used for suggested quadratic model						
Regression	5	24,051.1	24,051.1	4810.2	248.42	0.000
Residual error	24	464.7	464.7	19.4		
Total	29	24,515.8				

S = 9.832, *R*-Sq = 92.69%, *R*-Sq(pred) = 81.29%, *R*-Sq(adj) = 89.40%.

Values for the reduced model with significant coefficients, *S* = 4.400, *R*-Sq = 98.10%, *R*-Sq(pred) = 96.90%, *R*-Sq(adj) = 97.71%.

Coeff., coefficients; SE, standard errors; *T*, value *T*; *P*, probability; *DF*, degrees of freedom; Seq SS, sequential sum of squares; Adj MS, adjusted sum of squares; *F*, factor, *F*.

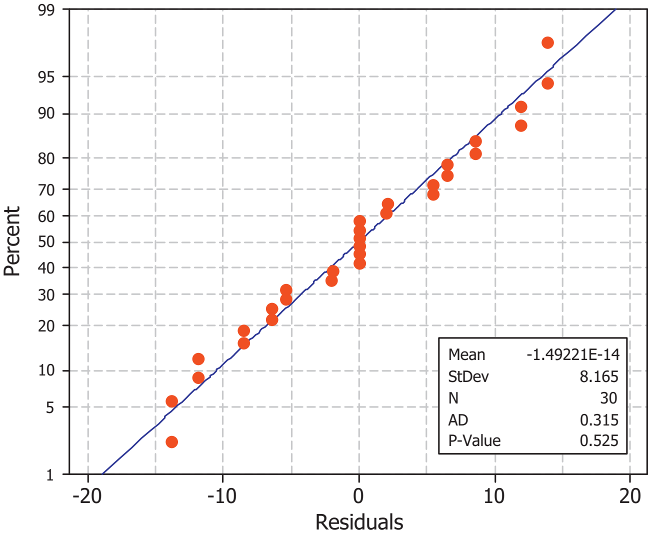

Fig. 2. The normal probability plot of residuals.

the equality of variances (Fig. 3). The method of least squares was used to estimate the parameters in the approximating polynomials. The estimated effects and coefficients for model are listed in Table 2. Model terms were evaluated by the *P*-value (probability) with 95% confidence level. The *P*-values were used to estimate whether *F* was large enough to indicate statistical significance and used to check the significance of each coefficient. The *P*-values lower than 0.05 indicated that the model and model terms were statistically significant. All the factors and their square interactions ($P < 0.05$) except for interaction of initial dye concentration–initial dye concentration (X_1^2), were significant at the 95% confidence level. PANI mass was the most significant factor that affect the removal of dye. Also, the quadratic effect of PANI mass–PANI mass (X_3^2) was found larger than effect of PANI mass, and the removal of dye significantly decreased with the quadratic effect of X_3^2.

In addition, Table 2 shows also statistical analysis of the model performed to evaluate the ANOVA. As can be seen, all of the linear, and square coefficients were highly significant ($P < 0.05$) at 5% probability level for the adsorption efficiency. A quantitative reduced model equation for the adsorption efficiency of dye can be written with coded units in terms of the statistically significant effects on the adsorption efficiency. The responses function of the determined coefficients for percent adsorption efficiency (*E*, %) is presented by Eq. (4).

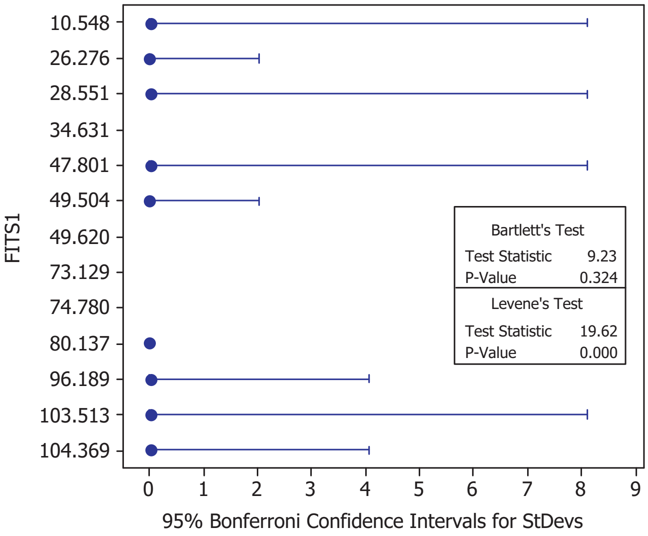

Fig. 3. Test for equal variances of residuals.

$$E = 25.71 - 0.33 \cdot X_1 + 10.74 \cdot X_2 + 332.58 \cdot X_3 - 0.78 \cdot X_2^2 - 467.70 \cdot X_3^2 \qquad (4)$$

The quality of the fitted model was expressed by the coefficient of determination, R^2. The R^2 coefficient gives the proportion of the total variation in the response predicted by the model and a high R^2 value (close to 1) is desirable. Eq. (4) demonstrated that the model is well fitted, considering the determination coefficient ($R^2(\text{adj}) = 97.71\%$) and only 2.29% of total variation was not explained by the model.

The ANOVA analysis assumes that the residuals are normally and independently distributed with the same variance in each treatment or factor level. The residuals are the difference between the actual values and the predicted values, and are not explained by the model. Residual plots given in Fig. 2 were used to check the assumption. A residuals distribution was evaluated for normality according to the Anderson–Darling test (*P*-value > 0.05). It could be seen that the residuals lie approximately along a straight line.

To check the equality of variances (the independence assumption), the residuals were plotted against the run order in which the experiment was performed (Fig. 3). The *P*-value (0.324 > 0.05) of residuals for Bartlett's test (due to normal distribution) shows that the residuals in different fit values are equal variances.

The response surface analysis is then performed using the fitted model, if the fitted model will be approximately equivalent to analysis of the actual system. 3D plots demonstrate relationships between the adsorption efficiency with the two factors (when other factor was kept at the center level), describing the behavior of sorption system in a batch process. Fig. 4 shows the 3D response surface relation between pH and dye concentration on adsorption efficiency at center level of PANI mass. Due to electrostatic interactions between the sulphonate groups ($-SO_3^-$) of dye molecule and copper ions of dopped PANI molecules, the adsorption efficiency increased at low pH values. In addition, the adsorption efficiency decreased as a result of the copper hydroxyl complexes formed between copper ions with $-OH^-$ ions, which are more active than the $-SO_3^-$ groups at high pH values [38–40].

In addition, Fig. 4 shows the 3D response surface relation between PANI mass to initial dye concentration, pH to initial dye concentration and PANI mass to pH on adsorption efficiency at center level of pH, PANI mass and dye concentration, respectively. As shown in these figures, the adsorption efficiency decreased with increasing the initial dye concentration, and the high adsorption efficiency was achieved at the center level of pH and PANI mass. The adsorption efficiency increased with increase of initial solution pH ranging from 2 to 7 Nevertheless, pH values higher than 7 reduced the adsorption efficiency. Therefore, the removal of dye in aqueous solution was affected by pH 7. In the other hand, the adsorption efficiency increased with increasing PANI mass ranging from 0.05 to 0.35 g and decreased with increasing initial dye concentration depending on the saturation of the adsorbent. This means that the higher adsorption efficiency values obtained by increase in pH and PANI mass simultaneously up to center levels.

Another way to predict the relationships between responses and factors and interactions is to analyze the contour plots. Each contour plot represents a number of combinations of two test variables with the other variable maintained at different levels. The contours of the response surface were plotted versus the levels of pH and initial dye concentration, PANI mass and initial dye concentration and PANI mass and pH as shown in Fig. 5. The shapes of contour plots indicate the presence of quadratic effects (X_2^2 and X_3^2)

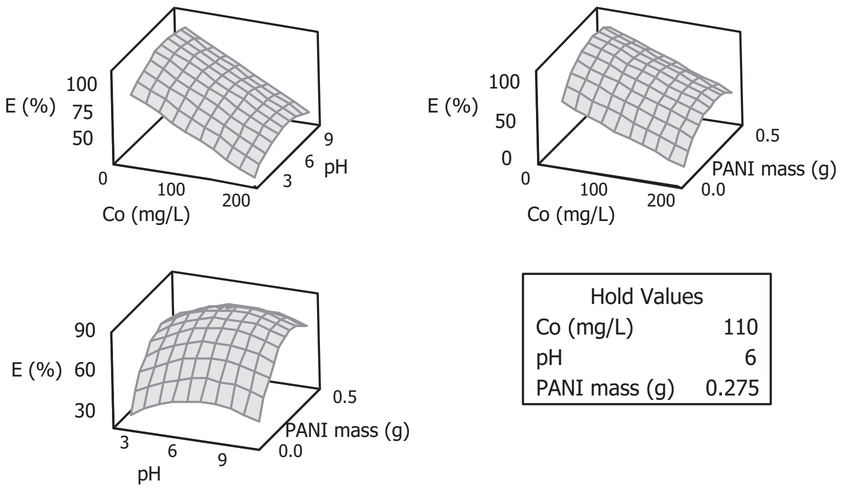

Fig. 4. The response surface plots.

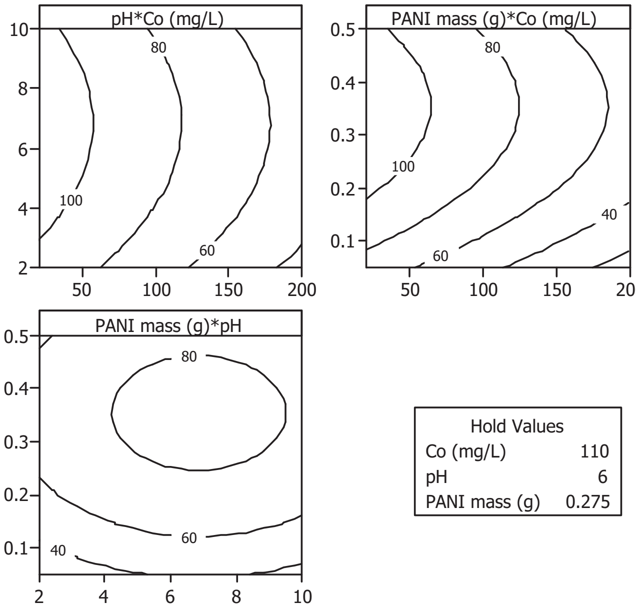

Fig. 5. The contour plots.

found larger than main effects (Eq. (4)). It has been noted that the main objective of this work was to maximize the adsorption efficiency together with finding the optimum conditions of adsorption process from the statistically developed model. In that case, the adsorption efficiency was predicted to be 99.83%.

4. Conclusions

The optimum conditions for adsorption of reactive azo dye on the PANI doped with 8% $CuCl_2$ were determined by means of the BBD and RSM. The ANOVA of the quadratic model demonstrates that the model was highly significant. The optimized conditions of initial dye concentration, initial pH and PANI mass for reactive azo dye sorption were found as 60 mg/L, 6, and 0.3006 g, respectively which correspond to 99.83% adsorption efficiency. PANI mass was the most significant factor affecting dye removal. Therefore, it is apparent that the response surface methodology not only gives valuable information on interactions between the factors but also helps to the recognition of possible optimum values of the studied factors.

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References

[1] P. Grau, Water Science and Technology 24 (1991) 97–103.
[2] F.P. Van der zee, G. Lettinga, J.A. Field, Chemosphere 44 (2001) 1169–1176.
[3] S. Meriç, D. Kaptan, T. Olmez, Chemosphere 54 (2004) 435–441.
[4] R.J. Stephenson, S.J.B. Duff, Water Research 30 (1996) 781–792.
[5] E.V. Veliev, T. Öztürk, S. Veli, A.G. Fatullayev, Polish Journal of Environmental Studies 15 (2006) 347–353.
[6] V.K. Gupta, Suhas, Journal of Environmental Management 90 (2009) 2313–2342.
[7] J. Zolgharnein, N. Asanjarani, S.N. Mousavi, CLEAN – Soil, Air, Water 39 (3) (2010) 250–258.
[8] Z. Khalili, B. Bonakdarpour, CLEAN – Soil, Air, Water 38 (10) (2010) 942–950.
[9] M. Trojanowicz, Microchimica Acta 143 (2003) 75–91.
[10] M.S. Rahmanifar, M.S. Mousavi, M. Shamsipur, M. Ghaemi, Journal of Power Sources 132 (2004) 296–301.
[11] K. Luo, X. Guo, N. Shi, C. Sun, Synthetic Metals 51 (2005) 293–296.
[12] W. Pan, S.L. Yang, G. Li, J.M. Jiang, European Polymer Journal 41 (2005) 2127–2133.
[13] A.S. Chen, K.R. Chuang, C.I. Chao, H.T. Lee, Synthetic Metals 82 (1996) 207–210.
[14] R.K. Gupta, R.A. Singh, Journal of Non-Crystalline Solids 351 (2005) 2022–2028.
[15] A.A. Athawale, S.V. Bhagwat, P.P. Katre, Sensors and Actuators B 114 (2006) 263–267.
[16] M.M. Ayad, N. Salahuddin, M.A. Shenashin, Synthetic Metals 142 (2003) 101–106.
[17] D. Mahanta, G. Madras, S. Radhakrishnan, S. Patil, Journal of Physical Chemistry B 112 (2008) 10153–10157.
[18] D. Mahanta, G. Madras, S. Radhakrishnan, S. Patil, Journal of Physical Chemistry B 113 (2009) 2293–2299.
[19] M. Yaşar, H. Deligöz, G. Güçlü, Polymer – Plastics Technology and Engineering 50 (2011) 882–892.
[20] P. Kaushik, A. Malik, Journal of Hazardous Materials 185 (2011) 837–843.
[21] F. Ghorbani, H. Younesi, S.M. Ghasempouri, A.A. Zinatizadeh, M. Amini, A. Daneshi, Chemical Engineering Journal 145 (2008) 267–275.
[22] N.T. Abdel-Ghani, A.K. Hegazy, G.A. El-Chaghaby, E.C. Lima, Desalination 249 (2009) 343–347.
[23] A.R. Cestari, E.F.S. Vieira, I.A. Oliveira, R.E. Bruns, Journal of Hazardous Materials 143 (2007) 8–16.
[24] S.H. Hasan, P. Srivastava, M. Talat, Journal of Hazardous Materials 168 (2009) 1155–1162.
[25] G. Annadurai, R.S. Juang, D.J. Lee, Advances in Environmental Research 6 (2002) 191–198.
[26] K. Ravikumar, S. Krishnan, S. Ramalingam, K. Balu, Dyes Pigments 72 (2007) 66–74.
[27] A.R. Cestari, E.F.S. Vieira, J.A. Mota, Journal of Hazardous Materials 160 (2008) 337–343.
[28] D. Bingol, N. Tekin, M. Alkan, Applied Clay Science 50 (2010) 315–321.
[29] S.A. Jabasingh, G. Pavithra, CLEAN – Soil, Air, Water 38 (5–6) (2010) 492–499.
[30] J. Zolgharnein, A. Shahmoradi, M.R. Sangi, Talanta 76 (2008) 528–532.
[31] J. Zolgharnein, Z. Adhami, A. Shahmoradi, S.N. Mousavi, M.R. Sangi, Toxicological and Environmental Chemistry 92 (8) (2010) 1461–1470.
[32] D. Bingöl, Fresenius Environmental Bulletin 20 (10a) (2011) 2704–2709.

[33] D. Das, N. Das, CLEAN – Soil, Air, Water 39 (2) (2011) 157–161.
[34] E. Ozkazanc, S. Zor, H. Ozkazanc, Polymer Composites 31 (2010) 1862–1868.
[35] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandão, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Analytica Chimica Acta 597 (2007) 179–186.
[36] D.C. Montgomery, Design and Analysis of Experiments, seventh ed., John Wiley & Sons, New York, 2008.
[37] R. Saravanathamizhan, N. Mohan, N. Balasubramanian, V. Ramamurthi, C. Ahmed Basha, CLEAN – Soil, Air, Water 35 (4) (2007) 355–361.
[38] S. Veli, T. Öztürk, Fresenius Environmental Bulletin 14 (2005) 212–218.
[39] S. Zor, Journal of the Serbian Chemical Society 69 (2004) 25–32.
[40] S. Veli, B. Alyüz, Journal of Hazardous Materials 149 (2007) 226–233.