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# Removal of a Reactive Dye by Adsorption Utilizing Waste Aluminium Hydroxide Sludge as an Adsorbent

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***Abstract*—**Removal of a reactive dye (Reactive blue 4) by adsorption utilizing waste aluminium hydroxide sludge as an adsorbent was investigated. The removal of the dye was optimized using response surface methodology (RSM). In the RSM experiments; initial dye concentration, adsorbent concentration and contact time were critical parameters. RSM experiments were performed at the range of initial dye concentration 31.82-368.18 mg/L, adsorbent concentration 3.18-36.82 g/L, contact time 15.82-56.18 h. Optimum initial dye concentration, adsorbent concentration and contact time were obtained as 108.83 mg/L, 29.36 g/L and 33.57 h respectively. At these conditions, maximum removal of the dye was obtained as 95%. The experiments were performed at the optimum conditions to verify these results and the same results were obtained.

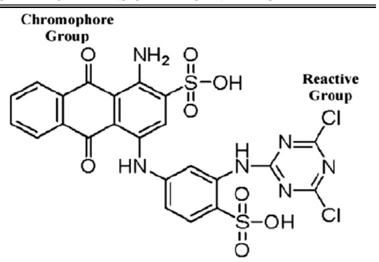
***Keywords*—**Adsorption, Reactive blue 4, Response surface methodology (RSM), Waste aluminium hydroxide sludge

## I. INTRODUCTION

DYES are used in large quantities in many industries including textile, leather, cosmetics, paper, printing, photographic, plastic, pharmaceuticals, food, etc. to colour their products [1], [2]. They generate a considerable amount of coloured wastewater. lt is estimated that more than 100000 commercially available dyes with over $7x10^5$ tonnes of dyestuff produced annually. lt is recognized that public perception of water quality is greatly influenced by the colour. The colour is the first contaminant to be recognized in wastewater. The presence of even very small amounts of dyes in water - less than 1 ppm for some dyes – is highly visible and undesirable [3]. Presently more than 9000 dyes are incorporated in colour index belonging to various chemical application classes. The textile industry alone accounts for two thirds of the total dye stuff production, about 10-15% of the dyes used come out through the effluent [1]. The dyes are used in the textile industries include several structural varieties such as acidic, reactive, basic, disperse, azo, diazo, anthraquinone-based and metal complex dyes [4]. Reactive dyes are synthetically produced and are increasingly used in the textile industries because of their ease and cost effectiveness in synthesis, firmness and variety in color. The strong color of discharged dyes even at very small concentrations has a huge impact on the aquatic environment caused by its turbidity and high pollution strength. One of the often used and very important in dyeing of cellulosic fabrics and textile industry dyes is an anthraquinonebase chlorotriazine dye, known as Reactive Blue 4 (Table I) [5].

The dye effluents may exhibit toxic effects on microbial populations and can be toxic and/or carcinogenic to mammalian animal [6]. Over 90% of some 4000 dyes tested in ETDA (Ecological and Toxicological Association of the dyestuff) survey had $LD_{50}$ values greater than 200 mg/kg [1]. The removal of synthetic dyes from wastewaters is especially difficult when reactive dyes are present, for which conventional wastewater treatment plants give a low removal efficiency [7]. Textile dyeing effluents are composed of complex mixtures of dyes, auxiliary chemicals, salts, acids, bases, organochlorinated compounds, and occasionally heavy metals. Colour removal is, however, one of the main problems in the treatment of this kind of effluent, due to dye resistance to biodegradability, light, heat, and oxidizing agents. Considerable research has been done on colour removal from industrial effluents to decrease their impact on the environment. These technologies include adsorption onto inorganic or organic matrices, decolourization by photocatalysis or photo-oxidation processes, microbiological

TABLE I
PHYSICAL AND CHEMICAL PROPERTIES OF REACTIVE BLUE 4

| | |
|---|---|
| Chemical structure |   |
| Molecular formula | $C_{23}H_{14}Cl_2N_6O_8S_2$ |
| Molecular weight | 637.43 |
| $\lambda_{max}$ (nm) | 598.5 |
| Physical appearance | Dark blue powder |

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decomposition, chemical oxidation, ozonation, and coagulation [8]. Removal of dye from industrial effluents using the adsorption process has been generally considered to be the most efficient method for quickly lowering the concentration of dissolved dyes in an effluent. However, activated carbon, the most widely used adsorbent, remains an expensive adsorbent and has high regeneration cost while being exhausted. For these reasons, there is growing interest in using low-cost alternatives to carbon adsorbent [6]. These low-cost alternative adsorbents may be classified in two ways either (i) on basis of their availability, i.e.,

(a) Natural materials such as wood, peat, coal, lignite etc. (b) Industrial/Agricultural/Domestic wastes or by-products such as slag, sludge, fly ash, bagasse flyash, red mud etc and (c) Synthesized products; or (ii) depending on their nature, i.e., (a) Inorganic and (b) Organic [9].

If the industrial solid wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost. In view of the low cost of such adsorbents, it would not be necessary to regenerate the spent materials. Thus, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters [10]. The effectiveness of treatment depends not only on the properties of the adsorbent and adsorbate, but also on the following environmental conditions and variables used for the adsorption process: pH, ionic strength, temperature, existence of competing organic or inorganic ligands in solution, contact time and adsorbent concentration [11].

In this study, removal of a reactive dye (Reactive Blue 4) from aqueous solutions by adsorption using waste aluminium hydroxide sludge was aimed. The study involved the determination of the optimum reaction conditions in order to reach the maximum removal of the dye, statistical investigation of the effects of operational conditions such as initial dye concentration, adsorbent concentration and the contact time.

## II. Material and Methods

Aluminium hydroxide sludge was used as an adsorbent for the removal of Reactive Blue 4 from aqueous solutions. The wastes were obtained from Fenis Aluminium Co. Inc. (Kocaeli, Turkey). Aluminium hydroxide sludge were dried in an oven at 105°C for approximately 8 hours. After drying, the industrial waste was ground using a mill (Retsch ZM 200). The waste was sieved and the part of 355-500 μm particle size was used in the experiments.

Reactive Blue 4 were purchased from Sigma-Aldrich Co. In the preparation of the dye solutions, distilled water was used.

The experiments were carried out in 250 mL screw cap glass bottles with 100 mL solution volume. Adsorption tests were performed at 30 °C and 150 rpm using an orbital shaker (Labcon 5081U). Samples were centrifuged at 4000 rpm and 25 °C for 10 minutes (Hettich Zentrifugen Rotina 35 R). After the centrifugation, the samples were analysed by using spectroscopic measurements which were carried out at 598.5 nm by using Shimadzu UV 1601. Then, the percentage of removal of dye after adsorption was calculated from:

$$\mathrm{Re}\,moval\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

In this equation, $C_0$ and $C_t$ are the initial dye concentration (mg/L) and dye concentration after desired time, respectively.

The aim of RSM is to find out the optimum operating conditions for a given system, or the way in which a particular response is affected by a set of variables. The quadratic response surface model over some specific region of interest. was fitted to the following equation:

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

where $x_1, x_2, \ldots, x_k$ the input variables, which influence on the response $Y$; $\beta_i$ ($i$=1, 2,…, $k$), $\beta_{ij}$ ($i$ = 1,2,…, $k$; $j$ = 1,2,…, $k$) the unknown parameters and $\varepsilon$ is a random error. In the regression equation, the test variables were coded according to the following equation:

$$x_i = \frac{(X_i - X_i^*)}{\Delta X_i} \qquad (3)$$

where $x_i$ is the coded value of the $i$-th independent variable, $X_i$ is the uncoded value of the $i$-th independent variable, $X_i$ * is the uncoded $i$-th independent variable at the centre point and $\Delta X_i$ is the step change value [12]. More specifically, coded values of the independent variables were calculated as follows:

$$x_1 = \frac{(X_1 - 200)}{100} \qquad (4)$$

$$x_2 = \frac{(X_2 - 20)}{10} \qquad (5)$$

$$x_3 = \frac{(X_3 - 36)}{12} \qquad (6)$$

The ‘‘Design Expert’’ software (Version 6.010, Stat-Ease, Minneapolis, USA) was used for regression and graphical analysis of the data obtained. The operational conditions were independence variables which were $X_1$ (initial dye concentration), $X_2$ (adsorbent concentration) and $X_3$ (contact time). The intervals of reaction parameters were selected as 31.82-368.18 mg/L for initial dye concentration, 3.18-36.82 g/L for adsorbent concentration and 15.82-56.18 h for the contact time. The experimental range and levels of the independent variables were indicated Table II.

TABLE II
THE EXPERIMENTAL RANGE AND LEVELS OF THE INDEPENDENT VARIABLES

| Variables | Range and levels | | | | |
|---|---|---|---|---|---|
| | -1.68 | -1 | 0 | 1 | 1.68 |
| Initial dye concentration, mg/L ($X_1$) | 31.82 | 100 | 200 | 300 | 368.18 |
| Adsorbent concentration, g/L ($X_2$) | 3.18 | 10 | 20 | 30 | 36.82 |
| Contact time, h ($X_3$) | 15.82 | 24 | 36 | 48 | 56.18 |

## III. RESULTS AND DISCUSSION

On the basis of preliminary experiments [8], the effect of initial dye concentration, absorbent concentration and contact time on the removal of the dye was studied using RSM. A second-order polynomial model fitted to determine the optimum reaction conditions in order to reach the maximum removal of the dye. The experiments performed and the results obtained under the operational conditions employed. Full Factorial Central composite design matrix of three variables and obtained responses were indicated Table III.

The application of RSM yielded the followed regression equation, which is an empirical relationship between the removal of the dye and the test variables in coded units.

TABLE III
FULL FACTORIAL CENTRAL COMPOSITE DESIGN MATRIX OF THREE VARIABLES AND OBSERVED RESPONSES

| $X_1$ | $X_2$ | $X_3$ | Removal % |
|---|---|---|---|
| 100.00 | 10.00 | 24.00 | 51.10 |
| 300.00 | 10.00 | 24.00 | 30.80 |
| 100.00 | 30.00 | 24.00 | 94.30 |
| 300.00 | 30.00 | 24.00 | 74.70 |
| 100.00 | 10.00 | 48.00 | 68.40 |
| 300.00 | 10.00 | 48.00 | 36.20 |
| 100.00 | 30.00 | 48.00 | 92.70 |
| 300.00 | 30.00 | 48.00 | 67.40 |
| 31.82 | 20.00 | 36.00 | 93.00 |
| 368.18 | 20.00 | 36.00 | 62.70 |
| 200.00 | 3.18 | 36.00 | 19.70 |
| 200.00 | 36.82 | 36.00 | 86.90 |
| 200.00 | 20.00 | 15.82 | 51.20 |
| 200.00 | 20.00 | 56.18 | 71.40 |
| 200.00 | 20.00 | 36.00 | 67.70 |
| 200.00 | 20.00 | 36.00 | 67.20 |
| 200.00 | 20.00 | 36.00 | 76.80 |
| 200.00 | 20.00 | 36.00 | 87.50 |
| 200.00 | 20.00 | 36.00 | 88.70 |
| 200.00 | 20.00 | 36.00 | 68.00 |

$$y=75.95-10.86x_1+18.72x_2+3.50x_3+0.87x_1^2-7.80x_2^2-4.98x_3^2+0.95x_1x_2-2.20x_1x_3-3.95x_2x_3 \quad (7)$$

where y is the response, that is removal of the dye and $x_1$, $x_2$ and $x_3$ are the coded values of the independent variables initial dye concentration, absorbent concentration and contact time, respectively.

ANOVA results of these quadratic model presented in Table IV. The Model F-value of 14.17 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case $x_1$, $x_2$, $x_2^2$, $x_3^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The first-order main effect absorbent concentration, $x_2$ ($P$<0.0001) was the most significant. Then the quadratic main effect of initial dye concentration, $x_1$ (0.0003) was the second degree significant. In addition the quadratic main affect of absorbent concentration, $x_2^2$ (0.0037) and contact time, $x_3^2$ (0.0376) were also more significant than the others.

Removal of the dye for different variables can also be predicted by the contour plots (Figs. 1–3). Each contour curve represents an infinite number of combinations of two test variables with the other one maintained at its respective zero level.

The effect of one factor solely depends on the value of the other. The interaction between initial dye concentration and absorbent concentration is represented in Fig. 1. Removal of the dye increased with increasing absorbent concentration and removal of the dye increased with decreasing initial dye concentration at high adsorbent concentration.

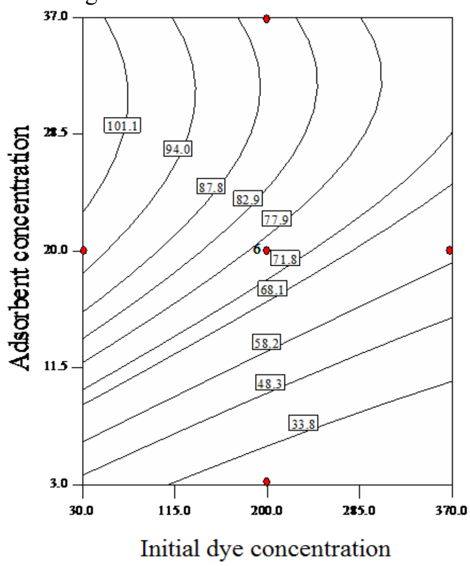


Fig. 1 Contour plot of removal of the dye concentration. The effect of initial dye concentration, adsorbent concentration and their mutual interaction on removal of Reactive Blue 4 for 36 h contact time

TABLE IV
ANALYSIS OF VARIANCE (ANOVA) FOR THE QUADRATIC MODEL
$R^2$=0.9273

| Source | Coefficient estimate | Sum of squares | DF | Mean square | F-value | Prob>F |
|---|---|---|---|---|---|---|
| Intercept | 75.95 | | 1 | | | |
| $x_1$ | -10.86 | 1611.66 | 1 | 1611.66 | 25.91 | 0.0005 |
| $x_2$ | 18.72 | 4784.39 | 1 | 4784.39 | 76.93 | <0.0001 |
| $x_3$ | 3.50 | 167.11 | 1 | 167.11 | 2.69 | 0.1322 |
| $x_1^2$ | 0.87 | 11.03 | 1 | 11.03 | 0.18 | 0.6826 |
| $x_2^2$ | -7.80 | 877.90 | 1 | 877.90 | 14.12 | 0.0037 |
| $x_3^2$ | -4.98 | 356.91 | 1 | 356.91 | 5.74 | 0.0376 |
| $x_1x_2$ | 0.95 | 7.22 | 1 | 7.22 | 0.12 | 0.7404 |
| $x_1x_3$ | -2.20 | 38.72 | 1 | 38.72 | 0.62 | 0.4484 |
| $x_2x_3$ | -3.95 | 124.82 | 1 | 124.82 | 2.01 | 0.1870 |
| Model | | 7929.19 | 9 | 881.02 | 14.17 | 0.0001 |
| Residual | | 621.94 | 10 | 62.19 | | |
| Lack of Fit | | 117.43 | 5 | 23.49 | 0.23 | 0.9322 |
| Cor Total | | 8551.13 | 19 | | | |

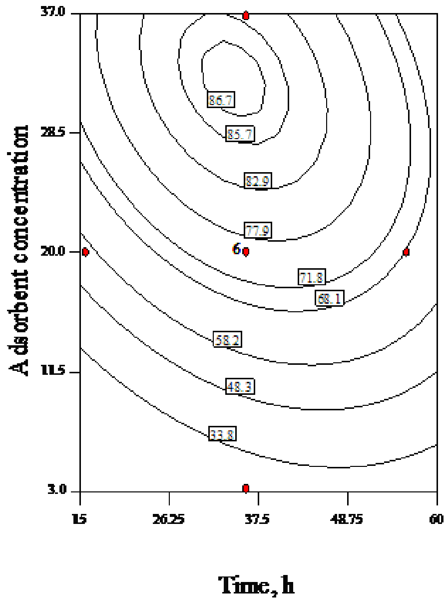


Fig. 2 Contour plot of removal of the dye concentration. The effect of contact time, adsorbent concentration and their mutual interaction on removal of Reactive Blue 4 for 200 mg/L initial dye concentration

The maximum predicted yield is indicated by the surface confined in the smallest ellipse in the contour diagram. Fig. 2 represents that interaction between contact time and the adsorbent concentration. This contour plot shows that optimal contact time is around 30–40 h and optimal adsorbent concentration is around 30-35 g/L. Removal of the dye increased with increasing absorbent concentration. Although contact time was the least significant factor, its effect on removal of the dye was still apparent from this contour. Maximum removal of the dye was obtained at around 30-40 h.

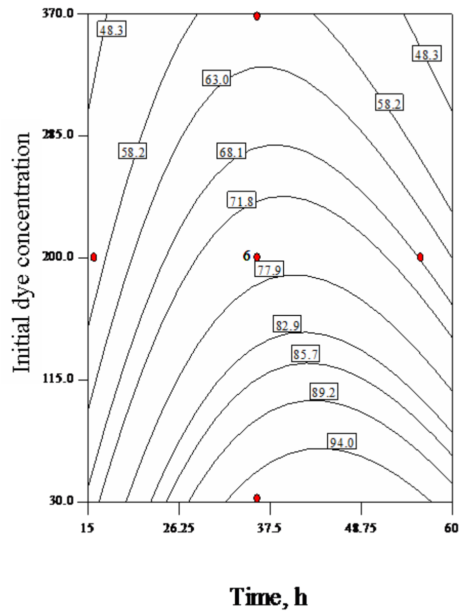


Fig. 3 Contour plot of removal of the dye concentration. The effect of initial dye concentration, contact time and their mutual interaction on removal of Reactive Blue 4 for 20 g/L adsorbent concentration.

Fig. 3 represents that interaction between contact time and initial dye concentration for 20 g/L waste aluminium hydroxide sludge. Removal of the dye increased with decreasing initial dye concentration.

According to model optimum initial dye concentration, adsorbent concentration and contact time were found as 108.83 mg/L, 29.36 g/L and 33.57 h respectively. At these conditions, the maximum removal of the dye was found as 95%.

## IV. CONCLUSION

Removal of a reactive dye (Reactive Blue 4) from aqueous solutions by adsorption using waste aluminium hydroxide sludge was investigated. Response surface methodology was used to determine the optimum reaction conditions for the maximum removal of the dye. It was found that the most effective parameter was adsorbent concentration. An equation was obtained by which removal of the dye can be calculated at the coded values of independent variables. Optimum initial dye concentration, adsorbent concentration and contact time were obtained as 108.83 mg/L, 29.36 g/L and 33.57 h respectively. At these conditions, maximum removal of the dye was obtained as 95%. The experiments were performed at the optimum conditions to verify these results and the same results were obtained. Since removal of the reactive dyes from the wastewaters is difficult, this results is important.

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