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# Magnetic Removal of Acidic Dyes from Waste Waters Using Surfactant- Coated Magnetite Nanoparticles: Optimization of Process by Taguchi Method

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**Abstract.** The presented work is aimed at utilization of magnetite nanoparticles modified with Cetyltrimethylammonium bromide (CTAB) for removal of Nyloset Yellow E-RK (NY) dye from water and waste water by magnetic force. First the $Fe_3O_4$ nanoparticles were synthesized via co-precipitation method. Fe3O4 and CTAB were added to the dye solution then adjusted the pH. After equilibration the adsorbed dye on the nanoparticles was removed magnetically from the solution and eluted with ethanol. Taguchi method was applied as an experimental design to determine optimal conditions for the effective removal of dye. L16 orthogonal array for experimental design and the smaller the best criterion (based on reduction of residual dye) were used for this purpose. The chosen experimental parameters and their ranges were: pH, 7-10; amount of CTAB, 0.02- 4 mL of 0.1 %( w/v) solution; extraction time, 30-180 sec; NaCl concentration, 0-4%(w/v), respectively. The optimum parameters were found to be pH, 10; CTAB, 2 mL of 0.1% solution; extraction time, 60 sec; electrolyte concentration, 0% NaCl. The adsorption equilibrium data were fitted to Langmuir isotherm rather than Freundlich isotherm. The maximum adsorption capacity, $q_{max}$, obtained from Langmuir's model was 136 mg $g^{-1}$. The results indicated the applicability of the method for removal of anionic dyes from aqueous solutions.

**Keywords**: Dye removal, Magnetic nanoparticles, Taguchi experimental design.

## 1. Introduction

The rapid industrialization and urbanization result in the discharge of large amounts of waste to the environment, which in turn creates more pollution. Majority of colored effluents consist of dyes, released to the environment from textile, dyestuff, and dyeing industries [1]. The presence of these dyes in water even at very low concentration is highly visible and undesirable [2]. Nyloset Yellow E-RK (NY) is an acidic dye that is used at exhaust dyeing and printing. The degradation by-products of organic dyes such as synthetic azo-dyes have dangerous impacts on the environment since it contains toxic aromatic amine compounds and the removal rate of these materials during aerobic waste treatment are still low [3]. Therefore, there is an urgent requirement for development of innovative, but low-cost processes, by which dye molecules can be removed. Adsorption technique is quite popular due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents [4]. Various adsorbents have been tested and used for the removal of dyes from polluted water [5]. Among the kinds of adsorbents, nano-sized iron oxides have been attracted interesting recently; In particular, magnetic iron oxides such as magnetite ($Fe_3O_4$) and maghemite ($\gamma$-$Fe_2O_3$) have been investigated intensively for environmental and bio-applications [6,7]. In addition to convenient magnetic properties and low toxicity and price, iron oxide (e.g. $Fe_3O_4$) nanoparticles exhibit high surface area to volume ratios, depending on the particle size, which associated to their ability for surface chemical modification, can show enhanced capacity for heavy metal uptake in water treatment procedures [8]. Super

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paramagnetic NPs such as $Fe_3O_4$, are attracted to a magnetic field but retain no residual magnetism after the field has been removed. This property makes them particularly suitable for pollutant removal because no centrifugation or filtrations (versus non-magnetic NPs) of the sample are then needed [9].

In presented work, magnetite NPs were synthesized and modified by cethyltrimethyl ammonium bromide (CTAB) in alkaline media to form addmicelles for the extraction of NY from waste waters. In continue the affecting parameters on the adsorption of the dye by an orthogonal array design, four factor-four level $4^4$ matrix, were optimized. Then isotherm of the dye's adsorption was discussed.

# 2. Experimental

## 2.1. Reagents and apparatus

All reagents and standards were of analytical grade unless otherwise stated, and dilutions have been carried out with doubly distilled water. Nyloset Yellow E-RK was obtained from Setas (Turkey). Sodium hydroxide, hydrochloric acid (37% m/m), Ferric chloride ($FeCl_3.6H_2O$), ferrous chloride ($FeCl_2.4H_2O$), CTAB, methanol, ethanol, acetone were all purchased from Merck ( Darmstadt, Germany). A buffer solution (pH= 10) was prepared by mixing sodium hydroxide (0.1 mol $L^{-1}$) with concentrated phosphoric acid solution. The spectrophotometric measurements were performed with a Shimadzu UV 160(Japan) UV-Vis spectrophotometer. The samples were characterized with a scanning electron microscope XL30 Philips (Netherlands). The pH measurements were carried out by a Metrohm 692 pH/ Ion meter (Herisau, Switzerland), equipped with a combined glass-calomel electrode. The IR spectra were recoded with FTIR Tensor 27, Bruker/ 078. The magnetic field was obtained with a 1.4 Tesla (10 × 5 × 4 cm) magnet.

## 2.2. Preparation of $Fe_3O_4$ NPs

The chemical co-precipitation method was used for preparation of $Fe_3O_4$ NPs. $FeCl_3$. $6H_2O$ (10g), $FeCl_2$. $4H_2O$ (3.85g) and HCl (12mol $L^{-1}$, 1.6 mL) were dissolved in 50 mL deionized water (degassed with nitrogen gas before use) to prepare a stock solution. 400 mL of 1.5 mol $L^{-1}$NaOH solution was heated to 80° C and was degassed for 15 min. The stock solution was then added drop wise under nitrogen gas protection and vigorous stirring using a glassware stirrer. After the reaction, the obtained $Fe_3O_4$ NPs precipitate was separated from the reaction medium by magnetic field, and washed four times with 100 mL of deionized water. Finally, the obtained NPs were re-suspended in 500 mL of degassed deionized water. The average size of NPs was about 28 nm as shown in the SEM image (Fig. 1).

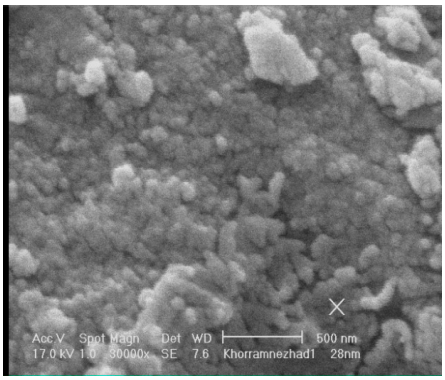


Fig. 1: The SEM image of the $Fe_3O_4$ NPs.

## 2.3. Separation process

About 24mg of $Fe_3O_4$ and 0.2 mL CTAB (10 mg $mL^{-1}$) were added to 40 mL of NY solution (10 mg $L^{-1}$) in a beaker. The solution pH was adjusted to 10 by addition of 2mL of 0.1 mol $L^{-1}$ phosphate buffer. The mixture was stirred by a glass rod for about 1 min and the beaker was then placed on the magnet. The $Fe_3O_4$ NPs which adsorbed NY, were separated magnetically and the initial yellow colored solution became colorless. The residual dye concentrations in the supernatant clear solutions were determined spectrophotometerically using suitable calibration curves. The dye removal efficiency was calculated by the following equation:

$$\text{Dye removal efficiency (\%)} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

Where, $C_0$ and C are the initial and residual concentrations of the dye in the solution (mg $L^{-1}$), respectively.

# 3. Results and discussion

## 3.1. Characterization of the $Fe_3O_4$ NPs

The scanning electron microscopy (SEM) image of prepared NPs shown in Fig. 1 demonstrated the agglomeration of many ultrafine particles with a diameter of about 28 nm. The comparison of FTIR spectra of pure $Fe_3O_4$ NPs (a) and CTAB-coated $Fe_3O_4$ NPs (b) showed that $Fe_3O_4$ NPs surface was well modified by CTAB.

## 3.2. Experimental design and data analysis

In this study Taguchi orthogonal array design (OAD) method that is a type of fractional factorial design and a four-factor four-level design ($4^4$) was used to evaluate the effects of factors. In order to estimate the best conditions for the extraction of dye, sixteen experiments were done. The factors and their respected levels are reported in Table 1. The ANOVA results for calculated model based on the dyes absorbance are shown in Table 2. The comparison of calculated F values of each factor with their critical values at confidence level of 95% ($P < 0.05$) was applied to recognize significant parameters (when $F_{calculated} > F_{critical}$ , the factor is significant).

## 3.3. Effect of pH

For $Fe_3O_4$ NPs, the surface charge is neutral at $pH_{zpc}$, which are about 7.0. Based on the ANOVA results (Table 2), pH significantly affects the adsorption of dye. Also, it was observed that the maximum adsorption efficiency of NY is at pH10. In alkaline pH, surface of $Fe_3O_4$ NPs is negatively charged and CTAB molecules interact with the negatively charged surface of $Fe_3O_4$ NPs and create a positive surface at pH10 via coating the surface of $Fe_3O_4$ NPs by forming addmicells, then the dye can interact.

## 3.4. Effect of surfactant amount

The ANOVA results showed that the amount of CTAB significantly affects adsorption of the dye. In alkaline pH, the dye adsorbs via CTAB on the surface of $Fe_3O_4$ NPs. In this condition, with the increasing amount of CTAB, adsorption of dye increased remarkably. The optimum amount of CTAB was found to be 0.2 ml of 10 mg $mL^{-1}$.

## 3.5. Effect of ionic strength

The effect of ionic strength was investigated with different concentrations of NaCl (0- 4% w/v). The ANOVA results indicated that by increasing NaCl concentration, the adsorption capacity of the $Fe_3O_4$ NPs is significantly decreased. Since the electrostatic interaction plays an important role in the extraction, increased salt may reduce the electrostatic interaction between MNPs and analyte and CTAB molecules.

## 3.6. Effect of Adsorption Time

The effect of contact time on percent removal of dye was investigated in the range of 0.5 to 3min. Extraction with magnetic nanoparticles was established very fast because of the shorter diffusion route for NPs and very high surface area, from the sample solution. 1 min was chosen as optimum time (Table 2).

## 3.7. Effect of sorbent amount

Compared to ordinary sorbents, nanoparticles have higher surface area-to-volume ratio. Therefore, satisfactory results can be achieved with fewer amounts of NPs sorbents. By increasing the sorbent amount from 10 to 20 mg, extraction recovery slowly increased and remained constant then after. Hence 24 mg of $Fe_3O_4$ NPs was selected for all subsequent experiments.

## 3.8. Effect of eluent type

The desorption of NY from the CTAB addmicelles on surface of $Fe_3O_4$ NPs was studied using different kinds of organic solvents ( acetone, methanol, ethanol, 50% v/v methanol in HCl 0.1mol $L^{-1}$, 50% v/v methanol in HCl 0.5 mol $L^{-1}$). According to the results, pure ethanol and methanol both showed similar elution power. However ethanol was selected for desorption due to its non-toxicity.

### 3.9. Adsorption Isotherm

Equilibrium isotherm studies were carried out with different initial concentrations of NY (100-250 mg $L^{-1}$) at 25°C and pH 10, using 24mg of $Fe_3O_4$ and 2 hours equilibration. Langmuir and Freundlich models were used to analyze the equilibrium adsorption data. Langmuir's model states that the maximum adsorption capacity consists of a monolayer adsorption, and that the adsorption energy is distributed homogeneously over the entire coverage surface. The Freundlich isotherm model is an empirical equation describing the surface heterogeneity of the sorbent. It considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.

Freundlich model: $$log q_e = log K_F + \frac{1}{n} log C_e \quad (5)$$

Langmuir mode: $$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \quad (6)$$

The results indicated that the value of correlation coefficient for the fit of experimental isotherm data to Langmuir equation is more close to 1.00 than that for Freundlich equation. ($R_L^2$ = 0.9937, $R_F^2$ = 0.7). Therefore, the Langmuir model represents the experimental data better on the basis of values of regression coefficients. The values of maximum monolayer capacity and isotherm constant were obtained as $q_{max}$ =136 mg $g^{-1}$ and $K_L$ = 43.76 L $mg^{-1}$.

## 4. Removal of dye from simulated waste waters

Adsorption of NY from simulated waste waters was studied under optimum conditions. The simulated wastewater contained 26g $L^{-1}$ $Na_2SO_4$, 5.3 g $L^{-1}Na_2CO_3$, 1% w/v NaCl and 200 mg $L^{-1}$ of dye. The capacity of $Fe_3O_4$ NPs and its contact time was recognized in the simulated wastewater. The obtained results showed the relationship between the amount of adsorbent and required time in order to achieve removal efficiency higher than 90% in the wastewater sample. Compared with a similar work [10] reported for removal of some cationic dyes (adsorption time and capacity are = 60 min and 77.5 mg $g^{-1}$), our method is superior.

Table 1 Experimental Design Table for the Optimization of Nyloset yellow removal.

| Trial No. | pH | CTAB ,10 mg $mL^{-1}$ (mL) | Extraction time (sec) | Salt % ( w/v) |
|---|---|---|---|---|
| 1 | 7 | 0 | 30 | 0 |
| 2 | 7 | 0.2 | 60 | 1 |
| 3 | 7 | 0.4 | 120 | 2 |
| 4 | 7 | 0.6 | 180 | 4 |
| 5 | 8 | 0 | 60 | 2 |
| 6 | 8 | 0.2 | 30 | 4 |
| 7 | 8 | 0.4 | 180 | 0 |
| 8 | 8 | 0.6 | 120 | 1 |
| 9 | 9 | 0 | 120 | 4 |
| 10 | 9 | 0.2 | 180 | 2 |
| 11 | 9 | 0.4 | 30 | 1 |
| 12 | 9 | 0.6 | 60 | 0 |
| 13 | 10 | 0 | 180 | 1 |
| 14 | 10 | 0.2 | 120 | 0 |
| 15 | 10 | 0.4 | 60 | 4 |
| 16 | 10 | 0.6 | 30 | 2 |

Table 2 ANOVA Table for the Optimization of Dye's Removal.

| Factor | DOF[a] | Sum of Squares | Variance | F-ratio[b] | Pure sum of squares | PC%[c] | Type of effect | Optimum value |
|---|---|---|---|---|---|---|---|---|
| Sample pH | 3 | 2917.666 | 972.555 | 5.796 | 2414.331 | 12.116 | significant | 10 |
| [CTAB] | 3 | 3524.609 | 1174.87 | 7.002 | 3021.274 | 15.162 | significant | 0.2(mL) |
| Removal time | 3 | 2048.63 | 682.876 | 4.07 | 1545.295 | 7.754 | significant | 60(sec) |
| NaCl% | 3 | 8247.922 | 2749.30 | 16.386 | 7744.587 | 38.865 | significant | 0 |
| Error | 19 | 3187.783 | 167.778 | | | 26.103 | | |
| Total | 31 | 19926.61 | | | | 100 | | |

[a] Degree of freedom, [b] F critical $_{(3,\ 19;\ 0.05)=\ 3.13}$, [c] Percent contribution.

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