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Research Article

Modeling and optimizing acid cyanine 5R removal from aqueous solutions using immobilized MgO nanoparticles on glass

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ABSTRACT

In this study, the nanoadsorbents were immobilized on an inert support (glass) to minimizetheir release to the environment.The initial dye concentration (acid cyanine 5R, an azo dye), pH and contact time parameters were optimized using central composite design under response surface methodology. The experiments weredone in a 10 liter glass reactor with MgO nano (as good dye adsorbent) coated glass partitions. COD and dye removal efficiency were determined by assessing before and after the adsorption. The COD removal efficiency and the remaining dye were close-fitting well to thequadratic model in the experimentations range of variables. The experimental study showed that fixed MgO on the glass waseffective in AC 5R adsorption.
The optimal operating point (initial dye=30 mgl^{-1}, pH= 9 and contact time= 90 min) giving maximum dye and COD removal was found using DesignExpert 7.0.0 software (85% and 83%, respectively).

Keywords: Azo dye, Chemical Oxygen Demand, Silicone adhesive, Textile wastewater.

1. INTRODUCTION

The discharges of untreated industrial waste water play an important role in the emission of pollutants to the environment. Colored effluents from industries such as leather and textile are major environmental challenges because some of the dyes in these effluents are carcinogen and persistent in the environment and can cause other environmental and aesthetical problems (the dyes are visible even at low concentrations ~0.005 ppm)[1, 2].Within various industries, textile industries are the largest consumers' dyes (about two-thirds of the manufactured dyes)[3]. Typically, the textile industries consume about 130m^3 of water per ton of product (Kocabas et al., 2009).High water consumption leads to producing a high volume of colorful effluent. According to Lu et al. in 2010, textile wastewater treatment and reuse can be possible and economically reasonable (Lu et al., 2010).Textile industry's effluents contain a variety of dyes, which are usually synthetic and have high molecular weight, complex chemical structure and low biodegradability[4]. Therefore, these dyes must be removed using appropriate methods prior to discharge to the environment. Among the various utilized methods, adsorption is a favorable method for the treatment of these wastes because of its

simplicity in design, cost-effective feasibility, recycling of adsorbent and absence of unsafe residues[5]. Adsorption refers to the gathering of an ingredient (adsorbate) at the interface between two phases (liquid–solid interface)[6].

Nanoadsorbents are usually used as the suspended slurry of fine particles in reactors. Although the suspended adsorbent makes a higher surface area for the adsorption and degradation of pollutants and reactors have simple design, this type of reactor has the drawback of low energy utilization and it is difficult to separate or recover the adsorbent after the reaction. To minimize their release to the environment and overcome the disadvantage of the suspended adsorbent-based slurry system for practical applications, nanoadsorbents are immobilized on an inert support (such as glass).These immobilized nanoadsorbents have been synthesized using various chemical methods such as hydrothermal [7],sol–gel[8] and chemical vapor deposition[9].

Recent studies have shown that MgO nanoparticles have significant adsorption capacity for the dye removal of wastewaters because of high surface to volume ratio, great adsorption surface area, large numbers of highly reactive edges and the destructive

sorbents[10, 11]. Adsorbates reactin adsorption surface and convert into less poisonousness compounds, which is known as destructive adsorption[12]. MgO nanoparticles are of the cheapest and most easily prepared adsorbents[13].Studies have indicated that MgO nanoparticles can be used for the removal of azo acidic reactive dyes from wastewaters[14]. Azo dyes are an important group of synthetic organic dyes and used in textile industries. They have one or more azo bonds (N = N)[15]and constitute more than 60% of the total produced dyes[14]

In this work, the potential efficiency of immobilized MgO nanoparticles in the removal of an azo dye was investigated. However, the immobilization of MgO nanoparticles with the above-listed methods was not successful. Therefore, attempts were made to immobilize MgO nanoparticles using simple adhesives. Initial tests showed that immobilizing MgO nanoparticles on the glass by silicone adhesive was better than other adhesives, such ascyanoacrylate. Therefore, silicone adhesive was used for this purpose. Acid cyanine 5R (AC 5R), an azo dye, was employed as the model dye. Also, chemical oxygen demand (COD)was used as the supplementary index for assessing the treatment efficiency.

2. MATERIALS AND METHODS

2.1 Materials

Magnesium oxide nanoparticles (MgO nanoparticles)with the size of 20 nm,purity of 98% and surface area of>60 m^2g^{-1} were purchased from US-Nano Co.Acid cyanine 5R was obtained from Alvan Sabet Company, Iran. The chemical structure of acid cyanine 5R is shown in Figure 1. Sodium hydroxide and other required compounds such as HCl were procured from Merck, Germany.

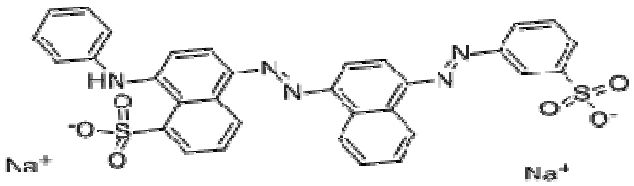

Figure 1 schematic demonstration of the chemical structure of Acid cyanine 5R dye (synonym: Acid Blue 113).

2.2 Sample preparation

The stock solutions at the desired concentration were prepared by liquefying the dye in distilled water. The experimental samples (with the concentrations in the range of 5-50 mg l^{-1}) were made up by these solutions. The pH of the sample solutions was adjusted using 0.1N HCl or NaOH solutions. The dye removal experiments were accomplishedin a10 L liter glass batch reactor with MgO nanocoated glass partitions. Each test consisted of preparing thedye solution with thechosen initial

concentration and pH by diluting the stock dye solution by distilled water. After the experiments (with different retention times), the supernatant was analyzed for the residual dye and COD. Efficiency of the dye and COD removal was calculatedby the following equation:

Eq. 1 Dye and COD removal efficiency (%) =

$$\frac{C_i - C_e}{C_i} \times 100$$

where $C_i$indicates the initial AC 5R and initial COD andC_e indicates the end (following adsorption) AC 5R dye concentrations and COD. All the experimentations were done at room temperature and at least three times independently. The average of the three measurements is also presented.

2.3 Dye concentration and COD analysis

The primary and residual color (after adsorption in different predefined conditions) weremeasured using a spectrophotometer DR 5000[16]. The maximum absorption of the dye AC 5R was atλ_max = 574 nm. Standard curve was plotted at this wavelength. Chemical oxygen demand (COD) was measured using the open reflux standard method 5220 B[17].

2.4 Response surface methodology

The initial dye concentration, pH and contact time parameters for maximum removal efficiency wereoptimized using central composite design (CCD) under response surface methodology(RSM). RSM was applied for the determination of simultaneous effects of pH (X1) initial AC 5R concentration (X2) and contact time (X3) on % COD removal (R1) and the AB113 remaining concentrations (R2).

The experimental variables and their ranges of variation are summarized inTable 1.

Table 1 Used independent variables and their ranges for experimental design

Variable	Unit	Range
Initial Dye Concentration	Mg l^{-1}	5-50
pH	--	3-9
Time	Min	0-120

The total number of design points in theCCD was calculated by Eq. 2:

Eq. 2 $n = n_0 + 2k + 2^k$

where n, k and n_0 are the number of required runs, number offactors and number of central points, respectively[18]. To determine the optimum values of the three selected factors, 20 experiments wereplanned using a 23 full-factorial central composite design with 6 replicates at the centralpoint.

A quadratic (second order) model as shown in Eq. 3 was used to estimate the interaction between dye removal and COD as responses (R) and three independent variables.

Eq. 3 $R = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=1}^{k} b_{ij} X_i X_j + \varepsilon$

whereR is the dependent variable, b_0 is constant value, bi, b_{ii} and b_{ij} refer to the regression coefficient for linear, second order and interactive effects, respectively, Xi and Xj are the independent variables and ε is the error of prediction. The CCD analysis and the associated statistical analysis were acquired using Design Expert 7.0.0 software. In Table 2, the actual and coded levels of the design are shown.

Table 2 Real and coded values of independent variables used for experimental design

Variables	Coded level				
	-alpha	-1	0	1	+alpha
	Real Values				
pH	3	4.216		7.784	9
Initial dye concentration	5	14.121		40.879	50
Time	0	24.324		95.676	120

MgO NPs were fixed onthe glass using siliconeadhesive. Ambient temperature were ranging from 18 to 25°C.

3. RESULTS

The design along with the removal efficiencies obtained is provided inTable3.Accordingly, COD removal efficiencies werebetween 0 and 99.35%, which was related to the run numbers 3 and 4, respectively.The findings of thestudy were in goodagreement with those of Meriç et al. [19].

Table 3 central composite design and experimental results.

Run	Factor 1 A:pH	Factor 2 B: dye in	Factor 3 C:Time	Response 1 COD %Removal	Response 2 Remaining Dye_e mg l^{-1}
1	6	50	60	55.6453	22.65
2	6	28	60	39.1068	16.23
3	6	28	0	0	28.00
4	7.78	40	95.68	99.35	1.23
5	4.22	14	95.68	40.564	7.26
6	6	28	60	39.279	17.32
7	4.22	40	24.32	11.043	35.00
8	6	28	120	90.97	1.98
9	4.22	40	95.68	71.693	12.26
10	3	28	60	26.58	20.14
11	6	28	60	38.150	17.25
12	4.22	14	24.32	8.4107	12.84
13	7.78	40	24.32	20.63	31.75
14	6	5	60	15.156	4.65
15	9	28	60	51.39	13.98
16	6	28	60	40.696	16.45
17	7.78	14	24.32	12.664	12.30
18	6	28	60	40.3371	16.35
19	6	28	60	40.3422	16.85
20	7.78	14	95.68	51.4707	6.56

Neamtu et al.[20]reported 10 min as the optimum reaction time for the photo-Fenton process to the removal of 85%color and more than 90%COD removal.The comparison of the above-mentioned results with the current study showed similar findingsatdifferent contact times of dye and COD removal.

Analysis of variance (ANOVA) of quadratic modelof COD removal efficiency and the remaining dyeare presented in Tables 4 and 5, respectively.Based on the ANOVA results (Table 4 and Table 5), the effect of contact time was found to be the highest among the studied variables on COD and dye removal. In Table 4, the modelF-value of 705.12 indicatedthe model wassignificant. There wasonly 0.01% chance that the"modelF-value" withthis large size could occur due to noise. Also in Table 5,the model F-value of 518.65 impliedthe model wassignificant. There is only 0.01% chance that the "modelF-value" withthis largesizecould occur due to noise. The COD removal efficiency and remaining dye were close-fitting well to the quadratic model in the experimentations range of variables. A stepwise model reduction was done for COD removal and remaining dye concentrations models to omit the non-significant model terms and the

reduced model is shown in Eqs. 4 and 5,respectively.

The graphical representation provides a method to visualize the relation between the response and experimental levels of each variable, and the type of interactions between the test variables.

The optimum value of each variable was located based on the hump in the three-dimensional plot or from the central point of the corresponding contour plot.

Response surface plot for the combined effect of pH and initialdye concentration on COD removal is demonstrated in Figure 2. As can be seen in this figure, the percent of dye removal was increased with the increaseof the pH and initial dye dosage. COD removal was raised with the increaseof pH and initial dye concentration. AccordingtoMoussavi and Mahmoudi[12], MgOwaseffective for decolorization and COD removal.

It is seems that the high dye and COD removal in the alkaline pH region wasrelated to the high adsorption efficiency of azo dye with MgO nanoparticles at more basic pH [21]and near the point of zero charge pH(pH_{pzc}). The pH, at which the net surface charge is zero, is calledthe point of zero charge[22].The MgO pH_{pzc} is about 12.4[23], which indicates the adsorption ability of the surface.This means that the surface wasnot saturated by dye adsorption at the alkaline pH and stayed available for more dye fragments[24].

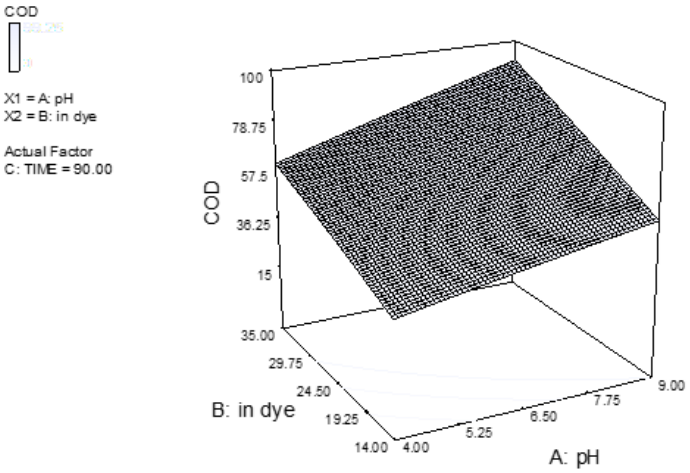

Figure 2 Response surface plot for combined effect of pH and initial dye concentration on COD removal efficiency.

Table 4 Analysis of variance (ANOVA) for Response Surface Reduced Quadratic Model of COD removal efficiency **

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	13047.31	8	1630.91	705.12	< 0.0001	significant
A-pH	661.78	1	661.78	286.12	< 0.0001	
B-initial dye	1816.23	1	1816.23	785.24	< 0.0001	
C-TIME	9743.17	1	9743.17	4212.40	< 0.0001	
AB	65.70	1	65.70	28.40	0.0002	
AC	80.63	1	80.63	34.86	0.0001	
BC	598.09	1	598.09	258.58	< 0.0001	
B^2	23.03	1	23.03	9.96	0.0092	
C^2	66.05	1	66.05	28.56	0.0002	
Residual	25.44	11	2.31			
Lack of Fit	20.72	6	3.45	3.65	0.0883	not significant

Pure Error	4.73	5	0.95

** Std. Dev.: 1.53, R-Squared: 0.9981, Adj R-Squared: 0.9966, Pred R-Squared 0.9866

Rotte et al.[21]showed that Safranin O dye adsorption on MgO decked multi-layered graphene was increased by the pH increasing. They concluded with pH increase, $[H^+]$ plausibly decreased and resultedin less protonation of Safranin O dye, which in turn increased the adsorption of Safranin O onto the adsorbent.

Optimization and validation

To obtain the optimum condition through the model equation predicted by RSM, DesignExpert 7.0.0 software was applied using practical criteria. The criteria were maximum COD removal, minimum remainingdye dosage in the studied range (5–50 mg l^{-1}) and initial pH in the studied range (3–9). In the optimum conditions,all the factorsconcurrentlymet the predicteddesirable criteria. Based on the assumptionsnoted, the predicted optimal conditions were initial dye of about 40 mg l^{-1}, pH of 8.9 and contact timeof90 min(COD removal efficiency 99.58%.). To check thevalidity of the results expected by the model, additionallaboratory experiments were conducted in 3 repetitions.Experimental data were in good consistency with those predictedthrough the regression model (97.56% vs. %99.58). According tothe results, both predicted and experimental data werein close agreement and the most interesting findingwas there was no significant difference between the results obtained experimentally**.**Rezaii Mofrad et al. [25] reported that optimum conditions of methylorange adsorption by MgO nanoparticles were300 mg l^{-1} initial dye concentration, 1.5 g l^{-1} MgO and 10 min contact time.Although the optimum contact time obtained in the currentstudy (90 min) wasmuch more than the optimum contact time of the foresaid research(10 min), not using thehigh concentration of absorbent, no need for separatingthe nanoparticles and good performance at low dye concentrations werethe advantages of the this work.

4. CONCLUSION

The experimental study showed that fixed MgO on the glass was effective in AC 5R adsorption. Also, the results for COD removal were promising and more than 99% removal was achieved (Table 3). Therefore, another set of experimentations was planned with only effective factors, i.e. pH, initial dye and time, on the dye and COD.The experimental values obtained for the AC 5R removal efficiencywere found to agree satisfactorily with the values predicted bythe proposed model with a high coefficient of determination (R^2 =0.998). The optimal operating point (initial dye: about 40 mg l-1, pH:8.9 and contact time: 90 min) giving maximum dye and COD removal was found using DesignExpert 7.0.0 software.The presentresults showed immobilized nanoMgO can be competitable with other processes such as photo Fentonin dye adsorption, but athigher contact time.

5. ACKNOWLEDGEMENT

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