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Application of Factorial Design in the Analysis of Factors Influencing Textile Dye Adsorption on Activated Carbon

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Abstract

In this study, the use of factorial design software is applied to evaluate efficiently factors influencing the adsorption capacity of activated carbon in treating textile dyes. Activated carbon is usually used to treat wastewater effluents from textile industries in order to remove textile dyes before discharge into the environment. Most treatment facilities, particularly large industrial or wastewater treatment facilities use continuous flow reactors or packed columns to treat the dye. Due to the limited residence time in these types of reactors, adsorption equilibrium is not necessarily reached, and the absorption rate becomes an important factor in this treatment process. Other factors influencing the capacity of activated carbon used in this study included pH, ionic strength, the type of the dye and the type of carbon. In this study, we use Minitab software to design an experiment to evaluate collectively these factors, each under various levels ($3^3 \times 2^2$ factorial design). The novelty of this study is the utilization of factorial design in the experimental approach.

Keywords: Activated carbon; Textile dye wastewater; Factorial design; Dye adsorption

Introduction

Effluents from textile industries may contain high concentration of commercial dyes; such waste may impact receiving water-bodies aesthetically and by reduction of light penetration which affect biological processes. In addition, studies showed that dyes can be toxic to aquatic life and the expanded use of azo dyes have shown that some of them and their reaction products such as aromatic amine are highly carcinogenic [1,2]. Guidelines and legislation for dye effluents are currently enforced by many countries across the world [3]. Wastewaters containing dyes are difficult to treat, since many of the commercial dyes are resistant to aerobic digestions, and stable to light, heat and oxidizing agents. Several physico-chemical and biological techniques have been developed to remove dyes from textile wastewater. Such techniques include activated carbon (AC) in straightforward adsorption processes, others may involve adsorption-enhanced processes [4-6]. These techniques rely on and many will benefit from AC. The application of adsorption technique is still the most versatile method in the removal of dyes from wastewater effluents.

Typical treatment facilities used for wastewater containing dyes include batch reactor processes when the volume of the wastewater is small. However, in wastewater treatment facilities with large flows, the typical treatment processes that are used include preliminary treatment (screening), primary treatment (coagulation/flocculation and sedimentation), secondary treatment and tertiary treatment processes. The secondary stage is typically activated sludge treatment (biological oxidation), while the tertiary stage is focused on removal of dye. In the later process when continuous flow reactor is used, the contact time of the adsorbent with the dye (residence time) is normally limited to 2-5 hours. Contact time longer than that requires much larger tank which can be cost prohibitive. Under such shorter contact times, the time needed to achieve adsorption equilibrium may not be fully achieved. Thus, adsorption kinetics becomes a factor that need to be addressed in AC adsorption of dyes. The rates of AC adsorption of most dyes were found to conform to pseudo-second-order kinetics with good correlation [7-9].

In addition to time, previous review studies have shown that other factors that may influence activated carbon adsorption include pH, salinity, type of AC, type of dye and temperature [9]. It has also been shown that adsorption capacity of AC increases with the increase of pH and that the optimum pH found for adsorption of the Reactive Black

Dye on AC was alkaline [8]. Other studies showed that AC adsorption of Acid Yellow 36 dye decreases with the increase of pH [10]. Such variation in the effect of pH emphasizes the fact that adsorption of dyes on AC can be dye-specific. Moreover, the wastewater salinity (ionic strength) was found to impact the AC capacity. Increase of the ionic strength to 1 M was found to cause an increase of the adsorption of reactive dyes on AC [8].

The size of the dye molecule will determine whether the dye will be adsorbed in the region of macropores, mesopores or micropores of AC. According to IUPAC, pore sizes in AC can be classified into three categories: macropores >50 nm; mesopores 2-50 nm and micropores <2 nm. The pore distribution of commercial AC activated carbon was studied extensively by many researchers and found to depend on the method of AC preparation. In general, the average pore size in AC can be between 0.25 to 1.0 nm [11-13]. The survey of chemical literature shows that the prevalent research work associated with AC adsorption has involved *in situ* measurements on the discharging sites and the studies in which AC adsorption isotherms are evaluated in traditional "one factor at a time" method [9,14].

Herein, we attempt to gain better understanding of AC adsorption of dyes under five different factors including type of dye, type of carbon, pH, salinity and time of contact, each at multiple levels. The novelty of this study is the utilization of factorial design of experiment approach. This is performed by means of factorial designs, the Analysis of Variance (ANOVA) and multiple regression analysis. The factorials are useful in assessing the statistical significance of the design factors. This provides information about what happens when the factor is changed and about the potential interactions between the factors. An interaction occurs when the effect of one main factor depends on the levels of another factor (or factors). The use of ANOVA ensures that the real effect can be

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distinguished from those arising from the random error. The procedure leads to a set of F-statistics and P-statistics to test the hypotheses that each factor, including interactions, is non-significant.

Materials and Methods

Materials

Adsorbents: The activated carbons used in this study were supplied by CalgonCarbon, Pittsburgh, PA, USA. The three types of AC used in the study are Filtersorb 600-M, AP4-60 and SGL 8X30.

Adsorbates: The two dyes are pure dyes commonly used for commercial applications. The dye structures are presented in Table 1.

Design of experiment

In this study, a factorial experiment was conducted in order to evaluate collectively the impact of multiple factors and levels on adsorption of the commercial dye on AC. A $3^3 \times 2^2$ factorial design of experiment was applied, which means three factors were evaluated at three levels and two additional factors were evaluated at two levels. The response variable of interest in this study is the “adsorption capacity” of activated carbon, mg dye/g AC, calculated collectively under the five factors and their levels. The selection of these factors and levels are substantiated by the background discussion presented in section 1. Table 2 presents the selected factors and their levels. A total of 216 isotherms were conducted in the randomized order and conditions dictated by Minitab¹⁶ software [15]. Example of the first 10 randomized run orders and criteria for each run is presented in Table 3.

Isotherm studies

Preparation of the dyes’ stock solutions: Six liters stock solution of each of the two dyes were prepared in tap water. Enough dye was

added into each to bring the absorbance level of the dye to around 2.6 absorbance, measured on Shimadzu UV-Vis 1800 spectrophotometer. The prepared values of absorption were selected using preliminary runs and found to give measurable levels after the AC is added at the longest run used in the study (8 hours). The six liters of each dye were split in half and to each, sea salt “Instant Sea” was added to bring the level of salinity to 0.01 and 1.0%. After the salinity was adjusted to the two levels each solution was then transferred into one-liter bottles. The stock solution in each bottle was adjusted to the required pH level (4, 7, or 10) by the addition of drops of 0.1 M HCl or NaOH which did not substantively change the volume. The 12 liters prepared were enough to run the 216 isotherms in duplicate runs.

50 mL of the stock solutions for each of the run specifications generated by the design of experiment were removed and added into a 125-mL brown bottle which was previously cleaned and dried. Each bottle contained exactly 0.50 grams of one of the three specific carbons selected by the design of experiment. A magnetic stir bar was inserted into each bottle and all bottles were placed on a multi-magnetic stir plate and allowed to spin at very low speed at room temperature. The isotherm bottles with duplicates, a total of 216 experiments were all prepared similarly. Since there were only three stir plates with a maximum capacity of 45 bottles, all the experiments were not run simultaneously. At the proper times, 2, 4 and 8 hours the bottles were removed off the stirrer for analysis. An aliquot of the solution in the bottle was removed and centrifuged to remove any potential carbon in suspension before the dye absorption is measured.

Dye concentration measurements: For each dye, a Beer-Lambert plot was previously prepared. The 12 stock solutions’ initial absorption was also previously measured. At the end of each run, the bottles were removed from the stirrer and allowed to settle. For each, an aliquot was

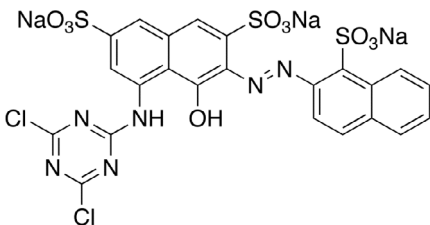
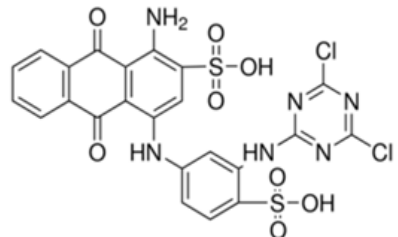
Dye	Structure	Size, A ^o	
		Length	Width
Procion Red 308 reactive dye		14	16
Procion Blue 406 reactive dye		21	7.5

Table 1: Dyes structures and sizes.

Factor	Factor, (level)		
Type of activated carbon	F600 (1)	SGL (2)	4-60(3)
Type of dye	B406 (1)	R308 (2)	-----
Salinity, %	0.01, (1)	1.0, (2)	-----
Time, hours	2.0, (1)	4.0, (2)	8.0, (3)
pH	4.0, (1)	7.0, (2)	10, (3)

Table 2: Factors and levels.

Run order	Dye	pH	Salinity, %	Activated carbon	Time, hours
1	1	10	1	1	2
2	1	4	0.01	2	2
3	2	7	1	2	2
4	1	4	1	3	8
5	2	7	0.01	2	4
6	2	10	1	1	2
7	2	4	0.01	1	4
8	2	4	0.01	2	2
9	2	7	0.01	1	4
10	2	7	0.01	1	4

*The table only presents the first 10 of 216 runs with various combinations of factors and levels performed in this study generated by MiniTab16® [15]

Table 3: Design of experiment order of runs.

removed, centrifuged and a portion of the solution placed in a cuvette and the absorbance measured at the lambda-max specific for that dye. A Shimadzu UV-Vis 1800 was used for all measurements. All bottles were similarly treated and measured after until all 216 runs were completed. The absorbance measurements were converted to concentrations in mg/mL using the Beer-Lambert best fit equation for the dye. Because each bottle had 50 mL this was easily converted to mg of dye which was subtracted from the initial amount of dye to calculate total dye adsorbed onto AC in mg. The response factor mg dye adsorbed/gram of AC was then calculated for all 216 samples and the data generated used in the factorial analysis.

Results and Discussion

Adsorption capacity

The adsorption capacity of the carbon (which we define as mg dye adsorbed/gram activated carbon) was calculated as explained in the methodology. This adsorption capacity ranged from values of 0.71 to 21.3 (mg dye adsorbed/g carbon) for one dye and from 1.8 to a 16.2 (mg dye adsorbed/g carbon) for the other dye within our experimental factors and their levels. The adsorption of dyes is clearly a complex process and is impacted by many factors. As such, it is difficult to describe the impact and the relationships of the factors since they are interconnected. Our approach, factorial analysis, allows us to evaluate the most influential factors efficiently without regard into how each factor individually may affect the adsorption.

Analysis of results

Factorial experiments are useful in assessing the statistical significance of multiple design factors. This provides information about what happens when the factor is changed and about the potential interactions between the factors. An interaction occurs when the effect of one main factor depends on the levels of another factor (or factors). The evaluation of the results of our experiments was done by means of the Analysis of Variance (ANOVA) and multiple regression analysis. The use of ANOVA ensures that the real effect can be distinguished from those arising from random error. The ANOVA procedure consists of decomposing the total sum of squares into components for each source of variability in the experiment. In our experiment there are 5 sources of variability: dye, carbon type, pH, salinity and the time; each with multiple levels. The interactions can be between any number of factors. The procedure leads to a set of F-statistics and P-statistics to test the hypotheses that each factor, including interactions, is non-significant.

From the ANOVA analysis presented in Table 4, it can be seen that the total sum of square (Seq SS) reflects the variance in the entire sample. The subtraction of all the sums of squares of the individual

factors from the total sum of squares yields the residual mean square (error). Each sum of square is calculated as a comparison between two sets of results (averages for the high and low level) for the two-level factors, with one degree of freedom (DF). The three-level factor will have 2 DF. The F-criterion must be compared with critical values from statistical tables.

For the five factors investigated for our response variable (mg dye adsorbed/gram activated carbon), the most significant are type of carbon, type of dye and the contact time ($0.00 < p < 0.001$) and ($12.0 < F < 287.9$). Less significant than time, carbon and type of dye, but still within 90% confidence level is the salinity ($p = 0.042$) and ($F = 4.21$). The three carbons tested had a range of pore size between 3-15 A. The dye molecules were modeled using Hyperchem software and minimized using a PM3 semi-empirical basis set in order to calculate the size [16]. As seen in Table 1, both dye molecules are larger than the largest pore size of all three activated carbons. Consequently, the dye must be adsorbed on the surface of the carbon granules and not within the pores. The ions involved can fit within the pores of the activated carbon. However, they are larger than hydrogen cations and since salinity is a factor affecting dye adsorbance, this may be due to the larger size of the ions leading to some surface adsorption which would affect binding sites for the dyes.

The pH was shown to be an insignificant factor in dye absorbance ($p = 0.242$) and ($F = 1.42$). In previous studies, pH was identified as a factor affecting absorbance. In our results, pH was not a significant factor. We speculate that the small hydrogen cations are diffused and adsorbed within the pores of the carbon whereas the larger dye molecules are strictly adsorbed on the surface so the capacity of dye adsorption is unaffected by changes in pH.

We also investigated the significance of the interactions between two variables. Of the ten possible interactions between two factors, four were shown to have no interaction. Three of these involved salinities. Salinity with time, pH, and dye were all insignificant with p values ranging between 0.077 to 0.468. The fourth of the two variable interactions which was insignificant was carbon and pH. Carbon with dye, time and salinity, dye with time and pH, and pH with time were all shown to be statistically significant. The R-squared value was 83.32% which indicates the validity of the significant variables and their interactions. In this study, we excluded the possibility of three-way interactions among the factors. This would have required running the study in additional replication runs which would have increased the number of runs substantially.

Figure 1 shows validation indicator plots of the model for our experiments. These plots are created by plotting the differences between the empirical and the predicted values (residuals) against

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Carbon	2	2632.4	2632.4	1316.2	287.91	0
Dye	1	55.15	55.15	55.15	12.06	0.001
pH	2	12.95	12.95	6.47	1.42	0.245
Salinity	1	19.26	19.26	19.26	4.21	0.042
Time	2	840.63	840.63	420.32	91.94	0
Carbon*Dye	2	101.14	101.14	50.57	11.06	0
Carbon*pH	4	7.52	7.52	1.88	0.41	0.8
Carbon*Salinity	2	38.95	38.95	19.47	4.26	0.016
Carbon*Time	4	148.6	148.6	37.15	8.13	0
Dye*pH	2	65.33	65.33	32.67	7.15	0.001
Dye*Salinity	1	14.43	14.43	14.43	3.16	0.077
Dye*Time	2	115.15	115.15	57.58	12.59	0
pH*Salinity	2	16.78	16.78	8.39	1.84	0.162
pH* Time	4	80.28	80.28	20.07	4.39	0.002
Salinity* Time	2	6.98	6.98	3.49	0.76	0.468
Error	182	832.01	832.01	4.57	-	-
Total	215	4987.56	-	-	-	-

Table 4: Analysis of variance, using adjusted SS for tests.

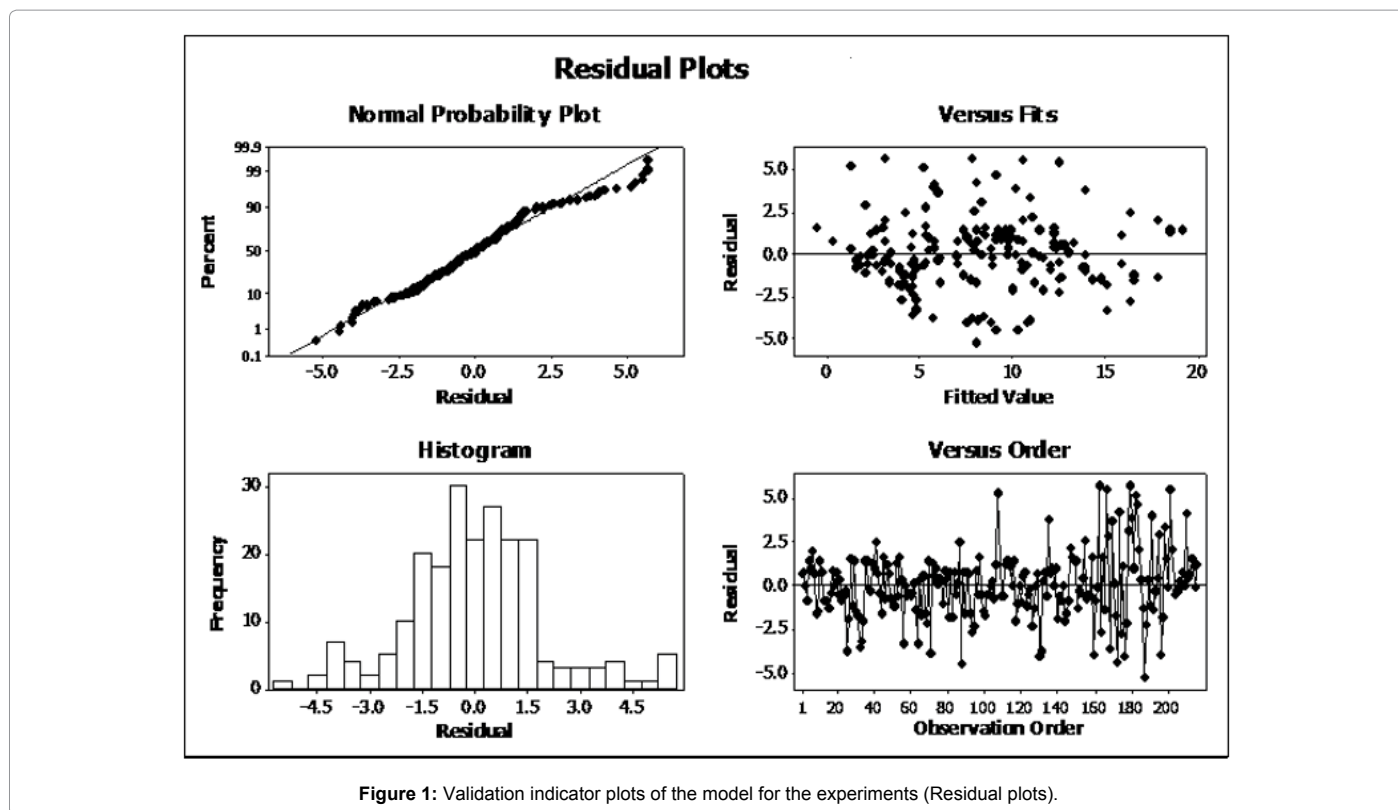


Figure 1: Validation indicator plots of the model for the experiments (Residual plots).

the empirical. Residuals of a well fitted model are randomly distributed around zero. The histogram and normality probability plots show a random distributes of values with no noticeable shape or trend across all the 216 runs conducted. The four plots all appear satisfactory, so we have no reason to suspect problems with the validity of our conclusion.

Conclusion

The applied factorial design of experiments approach used in this study offers many advantages over conventional “one variable at a time” experiments by allowing researchers the ability to determine

interactions between factors, more efficient utilization of data and statistical optimization of results.

In this study, time, type of carbon, and type of dye were all shown to be significant factors in the adsorption capacity of carbon. Additionally, two variable interactions with carbon and dye, time and salinity; dye with time and pH and pH with time were also identified as significant.

This statistical method of experimental design has potential in wastewater treatment because it can be used to optimize adsorption capacity in a non-equilibrium environment by identification or application of significant factors within the waste stream.

Future work should allow the development of multiple regression equations that can be used to predict dye adsorption under a variety of real-world conditions.

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