Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1012122

57 (2016) 7040–7046
March

Evaluating the optimum working parameters for the removal of methyl orange from aqueous solution based on a statistical design

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Received 30 September 2014; Accepted 18 January 2015

ABSTRACT

In this study, a 2^3 full factorial design, rather than a conventional method, was used for determining the optimum working parameters and choosing the best adsorbent for removal of methyl orange (MO) from aqueous solution. Regenerated multiwall carbon nanotubes (reg-MWCNT), which had been used in previous studies, and granular-activated carbon (GAC) were selected as adsorbents for this application. The experimental design determined the effect of three factors (temperature, pH, and initial dye concentration) and the interactions between them. The extent of removal of MO by reg-MWCNT was higher than by GAC. All experimental factors were examined and their interactions were found to be significant for percentage removal of MO, with pH being the most significant. Using only eight experiments, the highest percentages of MO removal on reg-MWCNT and GAC were 98.51 and 84.66%, respectively, achieved when the pH of the dye solution was 2 at 25˚C and with 20 mg/L initial dye concentration.

Keywords: Regenerated carbon nanotubes; Active carbon; Adsorption; Factorial design; Dye removal

1. Introduction

Rapid industrial development plays a significant role in water contamination. Industries such as those producing textiles, leather, plastic, paper, and dyestuffs produce water contaminated by dyes. The removal of dyes from aqueous solution has become an important issue [1] because water quality is affected by color. Most dyes are synthetic chemical compounds that are harmful to ecosystems and water sources and have carcinogenic and mutagenic influences on humans [2]. Methyl orange (MO) is one of the most frequently used acidic and anionic dyes in the textile, printing, paper, and food industries and in many research laboratories. The removal of dyes from water is difficult because most are stable to light and oxidation [3]. Methods such as ion exchange, precipitation, ultrafiltration, reverse osmosis, and electrodialysis are typically used [4]. However, the most promising method is adsorption, which is currently considered effective, efficient, and economical, with easy handling and high dye-removal performance [5]. Adsorbents studied for the removal of MO from aqueous solutions include bentonite [6], modified clay [7], hybrid materials [8], organometallic materials [9], and nanoparticles [10–12]. Activated carbon and carbon nanotubes are also frequently used for adsorption. Activated carbon is a structurally homogeneous material with a high

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surface area and microporous structure [13] and exhibits important advantages, such as comparatively low cost, high stability, and easy control of its structural properties. Adsorption of contaminants by activated carbon has been one of the most useful techniques in water treatment, particularly for the removal of odor and color [14]. Carbon nanotubes (CNTs) are attracting increasing research interest as new adsorbents for the removal of organic and inorganic contaminants from water, owing to their large specific surface areas, small size, and hollow and layered structures. CNT walls are not reactive but can be made reactive under strong chemical conditions (e.g. by incorporating hydroxyl or carboxyl groups into the side walls). Functional groups make CNTs more hydrophilic and suitable for the adsorption of polar compounds [15].

Factors such as pH, initial concentration of dye, amount of adsorbent, time, and temperature influence adsorption. In classical methods, experiments are performed by systematically varying the studied factor while keeping the others constant, and thereby determining the optimum conditions [16]. Factorial design is used to reduce the total number of experiments required compared with conventional methods and to provide the best optimization system [17]. The relationships between the different factors and the optimum results can be calculated using a factorial design. Factorial design techniques can be used in all research and development activities, having the advantages of improving quality, reducing costs, and increasing the reliability of results. Because factorial design simultaneously changes the values of the variables, less time, fewer experiments, and less analysis are required than for the independent investigation of each factor [18]. The basic experimental design is a two-level full factorial, in which each factor is investigated at only two levels. This is also referred to as a 2^k design, where k denotes the number of factors being investigated. The two levels of the factors are denoted as −1 (low level) and +1 (high level).

In this study, the optimum working parameters and selection of the best adsorbent for removal of MO from aqueous solution were evaluated using a factorial design. This method allows results to be achieved easily, quickly, inexpensively, and in an environmentally friendly way. Regenerated multiwall carbon nanotubes (reg-MWCNT), which had been used many times for other purposes in our laboratory, and commercial granular-activated carbon (GAC) were selected as adsorbents. The process was modeled with a two-level full factorial design with three experimental factors to determine the maximum percentage removal of MO that could be achieved and optimum conditions for its removal. The effects of pH, temperature, and initial dye concentration and their interaction effects were examined using a reaction time of 20 min with 2.5 mg adsorbent in 25 mL dye solution.

2. Materials and methods

2.1. Materials

A commercial charcoal-activated granule with a 5 mm diameter (Merck, Germany), also known as GAC, was used after drying at 100°C for 24 h. The MWCNT (OD-30–50 nm) was previously studied [15] and was used after regeneration. The regeneration procedure involved stirring 5.0 g used MWCNT in 100 mL of 1.0 M HCl solution for 24 h. The solids were filtered and washed with deionized water until the filtrate reached pH 7.00. The cleaned reg-MWCNT was dried at 100°C for 24 h. Both samples were stored in airtight polyethylene containers and kept in a desiccator. MO was supplied by Merck. A stock solution of 500 mg/L MO was prepared and the working solutions were obtained by diluting the stock solution with deionized water.

pH adjustments of solutions were performed with 0.1 M NaOH and 0.1 M HCl using a Hanna pH 211 Microprocessor pH meter that was calibrated using NBS buffers before each measurement. Dye concentrations were measured using a PG INST. T80 + ultraviolet–visible wavelength spectrophotometer.

All glassware were cleaned by soaking in diluted HNO_3 (1:9) and rinsed with double-distilled water before use.

2.2. Batch adsorption experiments and full factorial design

All experiments were conducted in 50 mL Erlenmeyer flasks using 2.5 mg adsorbent (GAC or reg-MWCNT) and 25 mL of MO solution. The flasks were placed in a thermo-controlled water bath and shaken for 20 min. The shaking speed was 120 times/min. After reaching equilibrium, each mixture was filtered through filter paper (1238-Filter-Lab). It was noted that the filter paper absorbed some dye. Various concentrations of MO were used and the concentrations of the dye solutions before and after filtration were measured to determine the amount of dye adsorbed on filter paper. Concentration measurements for all adsorption experiments are corrected for adsorption by the filter paper. Dye concentrations in the supernatant solutions were measured (diluted if necessary) at 462 nm, which is the wavelength of maximum absorption of 25 mg/L MO dye solution. Calibration concentrations varied from 5 to 25 mg/L and a calibration correlation coefficient of 0.9997 was achieved. The percentage removal of adsorbent was calculated from the following equation:

$$\%R = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

where $\%R$ is the percentage removal of MO, and C_0 and C_e are the initial and equilibrium concentrations of MO in the solution (mg/L), respectively.

For the 2^3 experimental design, the high (+1) and low levels (−1) of the three independent factors (pH (A), temperature (B), and initial dye concentration (C)) are listed in Table 1. Appropriate choices of high- and low-level values for the factors were determined during previous experiments.

MINITAB 15 statistical software was used for creating the 2^3 full factorial design table and for analyzing the results. $\%R$ was identified as the average value of results of two parallel experiments. The order in which the experiments were carried out was randomized to avoid systematic errors.

3. Results and discussion

The decision regarding the selection of the best adsorbent was based on the full factorial experimental results determined by combining all factor levels. The main effects, the Pareto plot, interaction plot, and variance analysis of experiments were evaluated to define the optimum conditions and the effects of the factors on percentage removal of MO by each adsorbent. A 2^3 full factorial design has eight experiments. The coded values of variables with the experimental results (percentage removal, $\%R$) are illustrated in Table 2 for duplicate experiments.

3.1. Analysis of variance

The statistical parameters were determined by analysis of variance (ANOVA). Interactions between independent factors and the quality of model fitness were performed by ANOVA based on a p value with a greater than 95% confidence level [4]. These p values were used as a tool to determine the importance of the interactions between the factors and to check

Table 2
Experimental design matrix with coded values and replicate results for the two adsorbents

Run no	pH (A)	T (B)	C (C)	%R (GAC)		%R (reg-MWCNT)	
				I	II	I	II
1	−1	−1	−1	84.31	85.01	98.46	98.55
2	1	−1	−1	49.59	49.60	97.38	97.34
3	−1	1	−1	69.33	69.30	98.19	98.24
4	1	1	−1	57.80	57.39	81.04	81.09
5	−1	−1	1	78.02	78.09	97.29	97.13
6	1	−1	1	58.32	58.33	72.47	72.50
7	−1	1	1	73.97	73.89	97.06	97.10
8	1	1	1	64.99	65.02	77.52	77.60

coefficient significance [19]. Table 3 shows the main and two- and three-way interaction effects, coefficients of the model (Coeff.), standard error (SE) coefficients, Students' test values (t), and probability (p) results for the adsorbents.

The significance of each coefficient was determined by the p values listed in Table 3. The main and interaction effects were all significant for MO removal by GAC and reg-MWCNT at a 5% probability level ($p < 0.05$). Furthermore, adjusted regression coefficient $R\text{-}Sq$(adj) values of 99.90 and 99.87% for reg-MWCNT and GAC, respectively, were obtained, which indicates the measure of goodness of fit of the model to the experiment data [19]. The model equations for MO removal by GAC and reg-MWCNT, showing the resultant coefficients, are, respectively:

$$\%R_{AC} = 67.06 - 9.34A - 0.60B + 1.77C + 4.27AB + 2.27AC + 1.24BC - 1.57ABC \quad (2)$$

$$\%R_{rej-MWCNT} = 89.94 - 7.82A - 1.46B - 3.85C - 1.35AB - 3.24AC + 2.69BC + 2.65ABC \quad (3)$$

These equations represent which factors and their interactions affect the percentage removal of MO by the two adsorbents. Many studies have found that the pH of the dye solution is very influential on removal

Table 1
Low and high levels of factors

Factors	Low level (−1)	High level (+1)
(A) pH	2	8
(B) T (°C)	25	55
(C) Initial dye concentration (mg/L)	20	200

Table 3
Estimated effects and coefficients for MO removal by reg-MWCNT and GAC

	reg-MWCNT					GAC				
Term	Effect	Coeff.	SE Coeff.	*T*	*P*	Effect	Coeff.	SE Coeff.	*T*	*P*
Constant		89.94	0.0139	6,487.33	0.00		67.06	0.0512	1,309.46	0.00
A	−15.64	−7.82	0.0139	−563.90	0.00	−18.86	−9.34	0.0512	−184.14	0.00
B	−2.91	−1.46	0.0139	−104.95	0.00	−1.20	−0.60	0.0512	−11.69	0.00
C	−7.70	−3.85	0.0139	−277.80	0.00	3.54	1.77	0.0512	34.54	0.00
AB	−2.70	−1.35	0.0139	−97.38	0.00	8.54	4.27	0.0512	83.35	0.00
AC	−6.49	−3.24	0.0139	−233.98	0.00	4.53	2.27	0.0512	44.25	0.00
BC	5.38	2.69	0.0139	194.13	0.00	2.46	1.24	0.0512	24.16	0.00
ABC	5.30	2.65	0.0139	191.24	0.00	−3.14	−1.57	0.0512	−30.61	0.00

Notes: reg-MWCNT: $S = 0.0554527$, $R^2 = 99.94\%$, $R^2(\text{adj}) = 99.90\%$, GAC: $S = 0.204848$, $R^2 = 99.88\%$, and $R^2(\text{adj}) = 99.87\%$.

effectiveness [6,7,20,21]. From the above equations, a highly effective factor is indicated for pH (coded A) for both adsorbents for the removal of MO. The negative signs of the effects in Eqs. (2) and (3) indicate that the low-factor value results in a high percentage removal [22]. Decreasing the pH of dye solutions increases the dye percentage removal on both adsorbents. This result can be associated with both the surface of adsorbents and the ionization state of MO, which depends on the pH of the solutions [23]. At lower pH, the adsorbents may become positively charged and electrostatically attract the negatively charged sites of reactive dyes, thereby increasing the dye removal [24–26].

The effects of the other factors varied according to the adsorbent. The pH–temperature interaction (coded AC) had high effect on %*R* for GAC, but a very low effect for reg-MWCNT. The three-factor interaction (ABC) had the same effect on %*R* for both adsorbents, and all main factors and interactions were significant on %*R*. The positive and negative signs in the equations above indicate high- or low-factor settings.

The removal percentages of MO removal on reg-MWCNT and GAC were found at optimum conditions to be 98.51 and 84.66%, respectively. These results are comparable with the results when utilizing bentonite-supported nanoscale zerovalent iron removal percentage of MO was 99.74% [6]. And the removal percentage was found to be 76.22% on almond shell wastes [2].

3.2. Main effects of each factor

The main effects of the three factors on percentage removal of the dye from solution with a change in the level of the factor are shown in Fig. 1. The sign of the main effect defines whether the effect is positive or negative on the outcome [27].

Fig. 1 shows that pH has a negative effect on the percentage removal of dye for both adsorbents: low pH of the dye solutions gives high dye percentage removal. Temperature shows slightly negative effects and the change in the temperature value does not affect the removal of the dye from solution [7]. Initial dye concentration shows different effects for the two

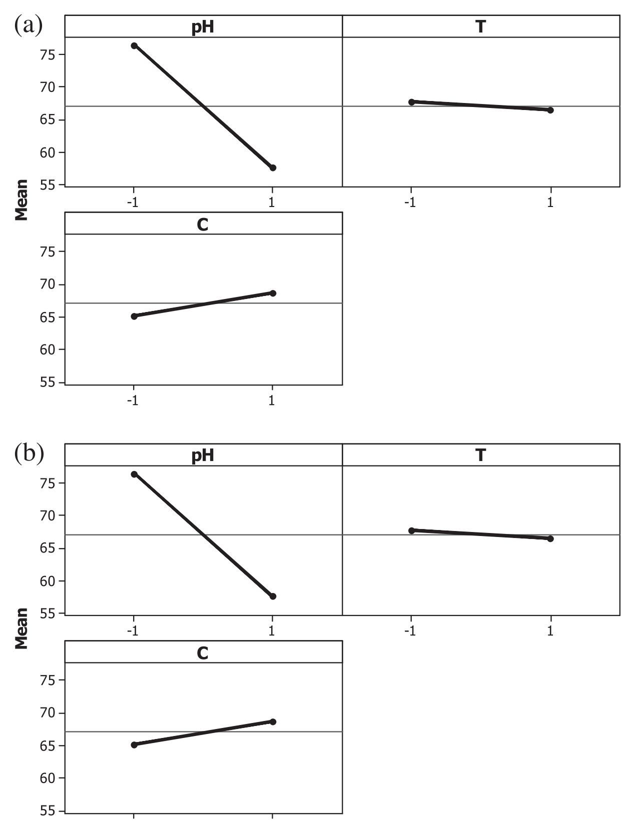

Fig. 1. Main effects of plots for %*R* of MO removal by (a) GAC and (b) reg-MWCNT.

adsorbents: a high level of initial dye concentration gives a high dye percentage removal by GAC, while reg-MWCNT shows the opposite effect. Percentage removal of MO decreases with increase in the initial dye concentration. It is due to the saturation of MWCNT sites [28]. This observation can be explained in terms of the differing granule size and surface structures of the two adsorbents. A similar effect has been reported for removal of Cr(VI) by two adsorbents using a two-level full factorial design [29].

3.3. Interaction effects of factors

The interaction plots of effects between different factors for dye percentage removal by both adsorbents can be seen in Fig. 2. A change in the response of a factor from a low to high level depending on the level of a second factor indicates that the interaction is effective when the lines do not run parallel [30]. The interaction plots for percentage removal of MO have different interaction effects for the two adsorbents: the pH–temperature and pH–concentration interactions are significant for GAC, while the pH–concentration interactions are important for reg-MWCNT. All low levels of factors for reg-MWCNT show a high percentage removal of MO. In the case of GAC, the percentage removal is high at low levels of pH and temperature factors, but high at the high level of concentration.

Interaction plots show the important interactions that influence the extent of dye removal from solution and are used to optimize the working conditions for the two adsorbents.

3.4. Pareto charts

Fig. 3 shows the Pareto charts that indicate the relative significance of the effects of the single and interaction factors on the removal of dye from solution. The Student's *t*-test was applied to determine whether the calculated effects are significantly different from zero. The horizontal columns in the Pareto chart indicate these values for each effect, while the vertical line shows the minimum statistically significant value for

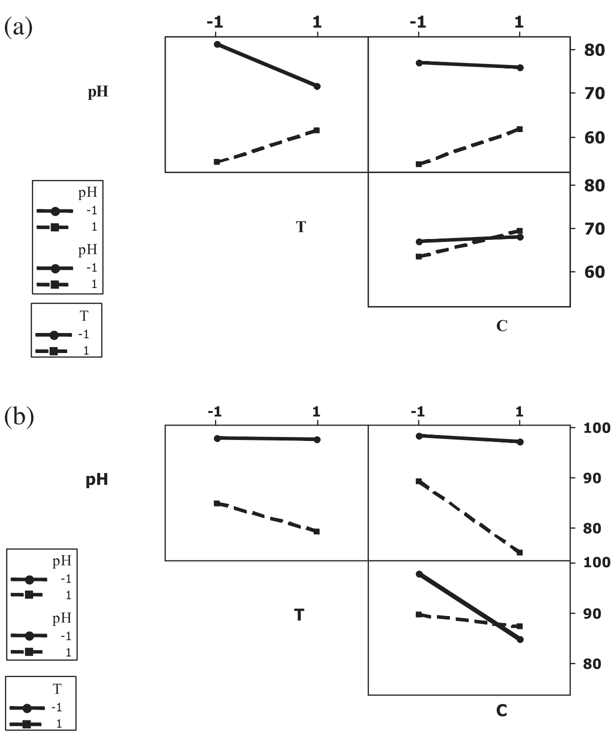

Fig. 2. Interaction plots of effects for percentage removal of MO on (a) GAC and (b) reg-MWCNT.

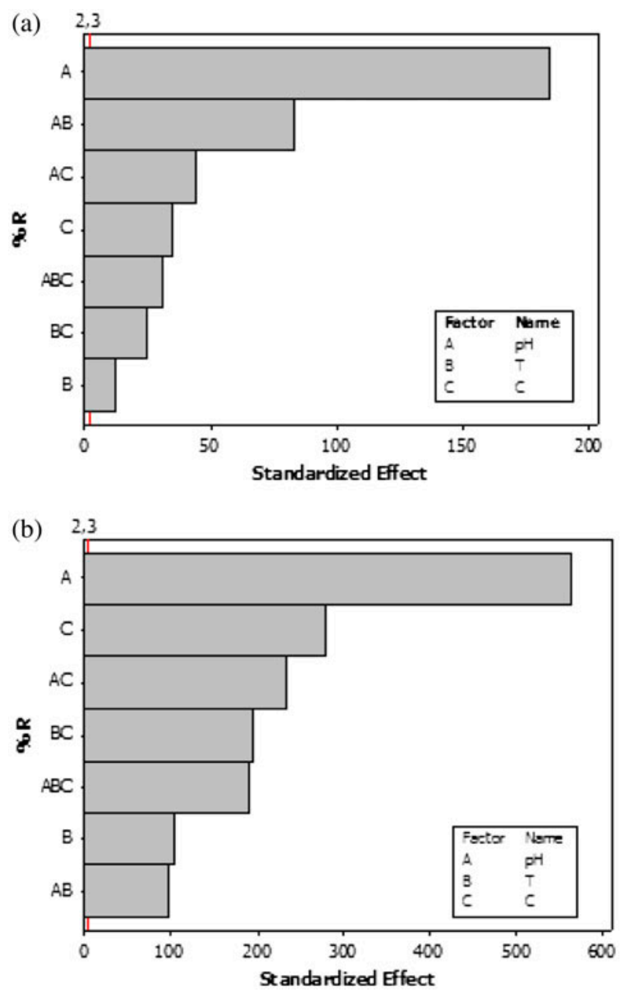

Fig. 3. Pareto chart of standardized effects on the dye percentage removal for (a) GAC and (b) reg-MWCNT.

each effect at a 95% confidence level [21]. At this confidence level, all main factors and interactions that extend beyond the vertical line are significant for dye removal by both adsorbents. pH has the greatest effect.

4. Conclusion

The effects of the main influencing factors and their interactions on the percentage removal of MO dye from solution by two adsorbents were examined. A full factorial design was carried out to reduce the number of experiments required compared with a conventional experimental method. This study demonstrates an easy and rapid way of selecting adsorbents and optimizing conditions. Although the MWCNT was regenerated, it demonstrated better removal of the dye from solution than the commercial GAC. This result can be attributed to the high surface area of reg-MWCNT. The effects of investigated factors and their interactions were examined. From the results of full factorial design, we also get optimum condition of MO removal from aqueous solution. The highest percentage removal by reg-MWCNT was obtained at a dye solution pH of 2 at 25°C with 20 mg/L initial dye concentration in 20 min when the amount of adsorbent is 0.1 mg/L.

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