Adsorption of the Methylene Blue from Aqueous Solution by the Thermally Regenerated Spent Bleaching Earth

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Abstract— Effects of temperature (500, 600 and 700°C) and time (30, 75 and 120 min) on the thermal regeneration of spent bleaching earth were investigated. Regenerated samples were used to adsorb the methylene blue from the aqueous solution. Experiment carried out at pH=5.6, temperature=25°C, initial concentration of methylene blue=4 ppm and mixing time=60 min. During the experiments, the pH of the solutions was fixed using the potassium hydrogen phthalate buffer and concentration of methylene blue was measured using the spectrophotometer at 657 nm. The maximum observed removal was found 97.05 %. The optimum temperature and time were found 587°C and 78 min, respectively. The optimum removal was found 97.38% at optimum conditions while virgin bleaching earth revealed the removal of 89.89%. According to perturbation diagram, both temperature and time have a peak at the middle of the ranges.

Keywords— Methylene blue, Response surface methodology, Spent bleaching earth, Thermal regeneration.

I. Introduction

MANY industries such as textile, leather, paper, plastics, etc., use different synthetic chemical dyes in order to various purposes [1]. These dyes were classified as direct, reactive, acid and basic. Basic dyes have been classified as toxic colorants. The most important basic dye is Methylene Blue (MB) that has wide applications [2]. MB has various harmful effects on the human beings. For example MB can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [3]. So it is of utmost importance to be removed from wastewater. There are several physical, chemical and biological decolorization methods have been reported. Among these methods, adsorption as a well-known equilibrium separation process is known as one of the most effective ways for removing dyes from aqueous solutions. In this regard, activated carbon has been evaluated extensively for the removal of color resulting from the different classes of dyes, however adsorption using carbon adsorbent still remains an expensive process due to the high cost in the use of activated carbon and the difficulty in the regeneration of spent activated carbon [4]. For this reason, many investigations have involved low cost and waste material adsorbents such as biomass, industrial waste sludge and clay based geo-materials. Use of industrial waste materials has become particularly attractive because of extra advantages such as waste elimination and cost reduction on the part of industrialists [5]. Spent bleaching earth (SBE) is an industrial waste generated at the vegetable oil refining industry after the bleaching (discoloration) of crude oil [6]. The bleaching step is realized using of acid activated clay, called bleaching earth [7]. Virgin bleaching earth (VBE) has a significant capacity to adsorb non-glyceride components and impurities such as carotenoids, chlorophylls, trace metals, free fatty acids and hydro-peroxides from oils. At the end of the process, the oil/bleaching earth mix is filtered to separate the treated oil from the waste clay, which then forms SBE. SBE typically contains 20–40% (w/w) of residual vegetable oil and pigments, oxidation products, free fatty acids (FFA), phosphatides and trace metals. As a result SBE is classified as a hazardous waste in many countries and is banned from landfill due to flammability, producing unpleasant odors, high organic content and so on [8]. Regeneration and reuse of SBE as an adsorbent for the removal of pollutants from water and wastewater, is one of the solutions to this environmental problem. Heat treatment, solvent cleansing and chemical treatment using acids, bases and salt solutions have been used in SBE regeneration for adsorption of various adsorbates [5]. The main objective of this paper is to reduce the environmental risks arising from SBE by making a new adsorbent for removal of MB from aqueous solutions. Thermal method is used to regenerate SBE. Experiments were carried out to find the optimum regeneration temperature and time using response surface methodology (RSM).

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II. Experimental

A. Experimental design and statistical analysis

Statistical design of experiments and data analysis was performed using Design Expert software (version 7.0.0, Stat-Ease, Inc., Minneapolis, MN). A center central composite design (CCD) on three levels (-1, 0, +1) was constructed for the independent variables i.e. time and temperature for the regeneration phase. Results were analyzed with response surface methodology (RSM) to evaluating the effects of operation conditions and finding the best conditions for desirable responses with limited experiments. Response can be expressed as second-order polynomial equations, according to Eq. 1.

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

where R is the predicted response used as a dependent variable; k is the number of independent variables (factors); x is the independent factor; β0 is the constant coefficient, and βi , βij and βii are the coefficients of linear, interaction and quadratic terms, respectively. Design Expert was also used to find the 3-D surface and perturbation plots of the response models.

B. Materials

The spent bleaching earth (SBE) was obtained from an edible oil refining factory (Salamat oil factory , Ardabil, Iran).The virgin bleaching earth (VBE) was provided by Kanisaz jam (Iran). Methylene blue was purchased from Merck (Germany). All other chemicals used in this study were analytical grade and obtained from Merck. All solutions were prepared with deionized water.

C. SBE treatment

According to Table I, subsamples of the SBE were separately heated in a muffle furnace at defined times and temperatures. All of the regenerated samples were washed with hot deionized water and centrifuged several times, suction-filtered and dried at 85°C overnight. Finally they were crushed and sieved (< 90 µm).

D. Methylene blue adsorption test

All of the thermally regenerated samples, VBE and powdered activated carbon (PAC) were tested for MB uptake in the same conditions. The experimental procedures for the adsorption of MB were described as follows: (1) prepare a MB solution with a concentration of 8 ppm and a potassium hydrogen phthalate buffer solution with pH=5.6, mix the buffer and MB solution (1:1 v/v), and distribute 50 mL of this solution to a series of 100 mL Erlenmeyer flasks; add 0.05 gr of regenerated SBEs, VBE and PAC into the solutions separately except one of them (blank); shake these bottles on a thermal shaker at 200 rpm for 1 h at 25°C; filter the suspension and determine the residual MB concentration in the supernatant using a spectrophotometer at a wavelength of 657 nm. The blank tests (without adsorbent) were performed to avoid possible adsorption of MB on the Erlenmeyer flasks and the filter apparatus. Using the adsorption efficiency results, the optimum regeneration temperature and time was found by response surface methodology (RSM), and then a sample was prepared by these optimized conditions.

TABLE I
VARIABLES AND THEIR LEVELS FOR THE REGENERATION

Variable level	Time (min)	Temperature (°C)
-1	30	500
0	75	600
1	120	700

III. Results And Discussion

The prepared samples were used to determine the feasibility of the thermally regenerated SBE to adsorb the methylene blue from aqueous solution. The adsorptions of all samples were higher than 90% which means that the selected times and temperatures are in proper ranges. It must be noted that these conditions were selected based on the preliminary experiments (results are not shown) and response surface methodology was used to find the optimum conditions in these ranges.

A. Effects of regeneration temperature and time

As mentioned before, SBE contains some residual oil and other organic materials. Due to the high temperature of the furnace, these mentioned organic materials burn in presence of the air and the burnt materials coated on the surface of the used bleaching earth which acts as a carbonic layer. This layer is responsible for the increase in adsorption in comparison with VBE. For this reason, the adsorption of the samples was higher than VBE.

By increase in time and/or temperature, this carbonic layer destroy and the adsorption efficiency falling down.

According to Fig. 1, the maximum of the adsorption is almost in the middle of the ranges. At this point, the carbonic layer is stable and has the best structure. Fig. 2 shows the perturbation plot of the adsorption. It is clear that effect of temperature is more sensible than time, especially for the higher temperatures which reduce the adsorption because of the destruction of the organic layer.

B. Statistical analysis

Statistical analysis of the results is shown in Table II. The Model F-value of 10.26 implies the model is significant. There is only a 2.23% chance that a "Model F-Value" this large could occur due to noise

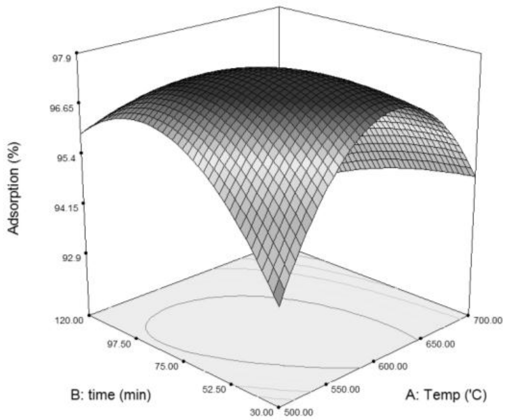

Fig. 1 3D surface of the adsorption

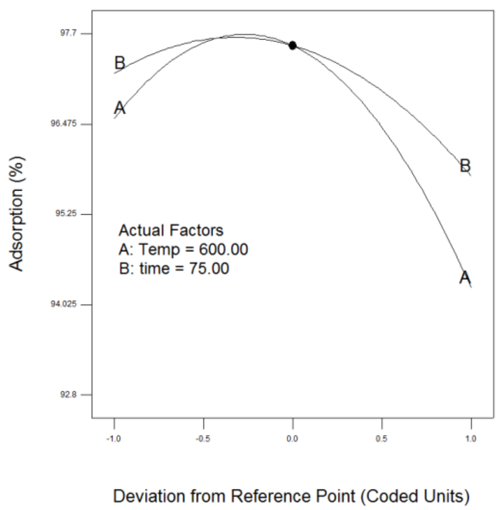

Fig. 2 Perturbation plot of the adsorption

TABLE II
ANALYSIS OF VARIANCE TABLE OF THE ADSORPTION

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	22.13	4	5.53	10.26	0.0223	significant
A-Temp	*3.3*	*1*	*3.3*	*6.11*	*0.0688*	
AB	*5.35*	*1*	*5.35*	*9.92*	*0.0345*	
A2	*10.77*	*1*	*10.77*	*19.98*	*0.0111*	
B2	*2.71*	*1*	*2.71*	*5.03*	*0.0884*	
Residual	2.16	4	0.54			
Cor Total	24.29	8				

For the selected significant model, the R-Squared and Adj R-Squared values are 0.9112 and 0.8224, respectively. The "Pred R-Squared" of 0.6334 is in reasonable agreement with the "Adj R-Squared. The Final Equation in Terms of real Factors is presented in Eq. 2:

$$Ads = 97.32 - 0.74\times Temp - 1.16\times Temp\times time - 2.32\times Temp^2 - 1.16\times time^2 \qquad (2)$$

C. Optimization

The optimum conditions was found 97.38% at time =78 min and temperature=587°C. The adsorption of the optimum sample was measured 97.26%. Based on Fig. 3, all of the darkest area has efficiency higher than 97% and could be selected as operational conditions.

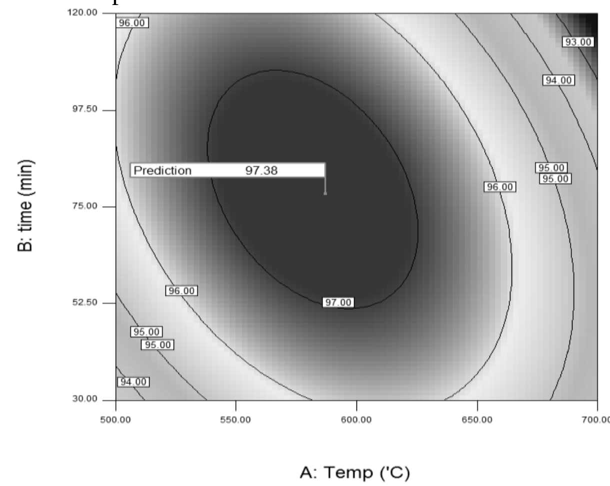

Fig. 3 Optimisation of the adsorption

IV. CONCLUSION

Thermal regeneration as an effective method was used to make a new adsorbent from the solid wastes of the edible oil refining factories. Spent bleaching earth (SBE) successfully regenerated using thermal treatment and used as an alternative absorbent for removing the methylene blue from the aqueous solutions. Due to the low cost of SBE, the introduced process conditions reveal the acceptable removal efficiency in comparison to the commonly used adsorbents such as virgin bleaching earth and powdered activated carbon. Response surface methodology could be used to optimize the treatment conditions.

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