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CASE STUDY

Reactive dye extraction utilizing regenerated bleaching earth

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ABSTRACT: Bentonite bleaching earth is utilized for purifying used motor oil through a recovery process in order to improve the quality and stability of the final product. Indeed, spent bleaching earth is generated due to adsorbing oil impurities. Polluted spent bleaching earth contains 20-40% (w/w) oil and is flammable. Its disposal without pre-treatment leads to loss of oil along with environmental impacts. Accordingly, similar studies have been conducted since 1979 until now. This research was a laboratory study on reactive dye adsorption. Cleaning bleaching clay, thermal remediation and acid washing activation methods were utilized. Response surface methodology was used to design the experiments and determine the optimal parameters in order to run the dye adsorption process. The main experimental parameters have been concluded as temperature (200-800 °C), acid solution concentration (0.1-3 M), dye solution concentration (1-35 ppm), and ratio of activated earth to dye solution (0.1-2 %, w/w). Results revealed that dye adsorption process along with oil removal at a temperature of 650 °C, acid solution concentration of 0.83 M, dye solution concentration of 11.75 ppm and ratio of activated earth to dye solution of 1.52 % (w/w) results in an adsorption efficiency of 68.57%. This removal efficiency is a bit higher than activated virgin bleaching earth and much higher than virgin bleaching earth, which has adsorption capacities of 66.75% and 51.56%, respectively. Considering this recycling process, the purified material is quite acceptable technically, environmentally and economically.

KEYWORDS: *Acid washing activation; Activated virgin bleaching earth (AVBE); Reactive dye adsorption; Response surface methodology (RSM); Spent bleaching earth (SBE); Thermal remediation.*

INTRODUCTION

Mineral oils lose their capabilities during operation as a result of reacting with oxygen, breaking down under temperature, and in combination with external substances; such as dust, different types of fuel, carbon, and metal particles. Such oils are known as used oil. One of the steps in recycling used oil is the final refinement operation or the application of bleaching clay which is aimed at improving the quality of the end products, based on the stability of oil color bleaching clay consists of clays which have capacity of adsorbing color and other undesirable materials of the remained oil from the treatment processes in their natural or activated status (Shahi *et al.,* 2015). The clay is usually bentonite from montmorillonite group with compact masses of crystalline aluminum silicates, containing various amounts of alkali and transition metals. Bleaching process is usually carried out by bentonite clay which is called virgin bleaching earth (VBE). The most important function of bleaching clay is to improve the appearance and stability of the final oil product (Tsai *et al*., 2002). Bleaching clay brightens the oil and removes its pigments and impurities through chemical changes in the oil (Hussin *et al*., 2011). As the impurities are adsorbed by the adsorbent, spent bleaching earth (SBE) remains in the form of residue. The residue is flammable and may cause fire, if it is not disposed properly. Since SBE contains a large amount of oil, its disposal with any

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pre-treatment in a landfill leads to the loss of a large amount of oil as well as financial losses due to loss of clay, while disposal of SBE in landfill causes hazards to the environment (Lee *et al*., 2000). Indeed, landfilling results in dangerous pollution and fire. These are due to the presence of oil in clay and consequently the potential for its leakage into the watercourse, and the possibility of spontaneous combustion. These environmental problems can be solved by removing oil from the clay, while the cleaned and activated spent bleaching earth (ASBE) can be used for removing color from industrial sewage such as textile plants. Textile industry produces colored wastewaters which are very sustainable in the environment. Studies show that about 15-20 % of dye enter into textile wastewater. The three major factors affected bleaching performance: type of clay, bleaching method, and oil quality. Under the third were response of different color pigments to bleaching, effect of moisture, oxidation, and organic impurities in the oil. Of the three factors, oil quality has the greatest influence upon bleaching performance (Rich, 1967). (Santos and Boaventura, 2008) The most problematic pollutants in textile sewage are the chemical colors, which are used in this industry. Sadri *et al.* (2010) presented a comparison between dried sewage sludge (DSS) and sewage sludge ash (SSA) for Acid Red 119 dye removal. Results revealed that the maximum adsorption capacities of DSS and SSA were found 90.91 and 98.87%, respectively. Reactive dyes, which have bright color, easy usage and low energy consumption, were consumed in textile industry widely. Reactive dyes usually have a synthetic origin and complex aromatic structures, making them stable and difficult to biodegrade (Bapat and Jaspal, 2016). Untreated disposal of effluents contaminated by reactive dyes may result in adverse effects on human/aquatic life (Karimifard and Alavi Moghadam, 2015; Gupta *et al*., 2015). Textile wastewater dye adsorption via bleaching clay has aroused a great interest among many researchers. El-Geundi (1991) studied the adsorption of two basic dyestuffs (Atrazon Blue and Maxilon Red) and two acid dyestuffs (telon blue and erionyl red) onto maize cob. High adsorptive capacities was observed for the adsorption of basic dyestuffs, namely, 160 and 94.5 mg dye per g maize cob for Astrazon Blue and Maxilon Red, respectively. Also, lower capacities were obtained with the acid dyestuffs, namely, 47.7 and 41.4 mg dye per g maize cob for erionyl red and telon blue, respectively. Khoo *et al.* (1979) found various bleaching earths for removal of β-carotene from acetone solution including tonsil, fuller's earth, silica, and kaolin. Results indicated that except for silica, in addition to physical adsorption, processes involving chemisorption and subsequent chemical reaction proceeded on the surface of the clay minerals. Low *et al*. (1996) examined potential of carbonized spent bleaching earth (CSBE) for removal or reduction of basic and acid colors in aqueous solutions. It was found out that CSBE is useful for removing basic colors. Therefore, CSBE is considered as an absorbent in treatment of basic colors in sewage. Lee *et al.* (1997) investigated some organic dyes from aqueous solution by hexane-extracted spent bleaching earth, a waste material from the palm oil industry. It was noted that the material had better affinity for basic than acid dyes. Lee *et al*. (1999) resulted that refined acidic bleaching earth from treating bleaching waste of palm oil industry was treated with 20% acid sulfuric at a temperature of 350 °C for 3 hours. The resulting material adsorbed a wide range of organic colors (including reactive and acidic dye) with an adsorption capacity of 2-300 mg/g. Al-Zahrani and Daous, (2000) performed extraction experiments on spent bleaching clay to recover oil using organic solvents at optimum conditions. The bleaching efficiencies of the clays de-oiled by methylethylketone (MEK), acetone, petroleum ether and hexane were 73, 65, 51 and 27%, respectively. The corresponding percentages of extracted oil were 72, 67, 60 and 42%, respectively. The optimum values of temperature and heating time were determined for each type of deoiled clay. The bleaching efficiency of the reactivated clays varied between 86 and 94%. Rossi *et al.* (2003) studied the adsorption characteristics of three bleaching clays in a palm oil physical refining process. Different clay types and concentrations were used in combination with a fixed amount of synthetic silica. Clay concentration demonstrated that acid-activated clays were more efficient than natural clay in removing carotene pigments. The phosphorus adsorption capacity of clay seemed also to be positively affected by acid activation. Forgacs *et al.* (2004) complied with various methods of removal synthetic dyes from waters and wastewater such as adsorption on various sorbents and chemical decomposition. Tsai *et al*. (2005) examined regenerated

bleaching earth for adsorption and adsorption kinetics of the three basic dyes; violet 4, violet 3 and red 9 from aqueous solution. The rate of adsorption investigated under various parameters such as initial dye concentration, pH and temperature. The adsorption of the basic dyes by regenerated bleaching earth at lower initial concentrations had the following order: basic violet 4>basic violet 3>basic red 9 due to the molecular weights and molecular sizes of the basic dyes. Weng and Pan (2007) investigated the adsorption characteristics of methylene blue (MB) onto spent activated clay from an edible oil manufacturer. Adsorption increased with increasing MB concentration, temperature, and pH. Maximum adsorption capacities were ranged for MB from 0.94×10^{-4} to 3.41×10^{-4} mol /g and between 5 and 45 °C. Woumfo *et al.* (2007) used three Cameroonian clay materials with high smectite content were used for decolouration of palm oil with a clay / oil ratio of 2%. Their performances were compared to those of a commercial bleaching earth before and after acid activation. Optimization of bleaching capacities was determined. Rafatullah *et al.* (2010) reviewed the scattered available information on various aspects of a wide range of potentially low-cost adsorbents for Methylene Blue (MB) removal as a pollutant, from wastewaters of textile industry. It is evident that low-cost adsorbents have demonstrated outstanding removal capabilities for MB. Arulkumar *et al.* (2011) used raw material from Thespesia populnea (kind of tree) for the preparation of activated carbon as an adsorptive removal of Orange G dye from aqueous system. The effects of various parameters were studied using response surface methodology (RSM). RSM results showed that 0.54 g of activated carbon was required for the maximum adsorption.

The adsorption characteristics of basic yellow 87 from aqueous solution were investigated using carbon aerogel. The mesopores adsorbent was highly effective as adsorbents for basic yellow 87 from aqueous solution (Wu *et al.,* 2012). Zhong *et al.* (2012) utilized Peanut hull (agricultural solid waste in China) as a precursor for preparation of activated carbon via microwave. The activated carbon yield was investigated by response surface methodology (RSM). The optimum activated carbon obtained with phosphoric acid concentration of 33.04 vol. %, had a yield of carbon of 42.12%. Koupaie *et al.* (2012) investigated the application of anaerobic sequencing batch reactor (An-SBR) for treatment of wastewater containing Acid Red 18 (AR18). The results showed that the dye de-colorization rate increased with increasing its concentration in the feed solution. This process was optimized by using response surface methodology (RSM) in design expert software. Radaei *et al.* (2014) applied RSM in order to optimize Reactive Blue 19 removal by activated carbon from pomegranate residual. Results showed that the decrease of initial dye concentration and the increase of initial pH, adsorbent dose, and contact time are beneficial for improving dye removal efficiency. Analysis of variance (ANOVA) results presented high R^2 value of 99.17% for Reactive Blue 19 dye removal. Ayazi *et al.* (2016) prepared magnetite/graphene oxide (MGO) nanocomposite and applied for adsorption removal of Reactive Blue 19 (RB19). Optimization and modeling of the removal of RB19 using MGO were performed through RSM. The analysis of variance showed a high correlation coefficient ($R^2 = 0.954$). Karimifard and Moghaddam, (2016) investigated the adsorption capacity (211.02 mg/g) of Reactive Blue 19 (RB19) onto multi-walled carbon nanotubes (MWCNTs). In addition, response surface methodology was utilized to simulate and determine the optimum conditions of RB19 removal by MWCNTs. The activated or neutral form of bentonite-based spent bleaching earth/clay (SBE) is a by-product generated during the bleaching process in edible oil refinery. To overcome environmental problems, SBE is regenerated and reused for water/wastewater treatment (Loh *et al.,* 2017). According to the results of previous studies, using SBE from edible oil manufacture in different types (carbonized or acidic) was the most common methods of removing dye from colored solution such as industrial sewage. In the past, experiments on dye adsorption were carried out traditionally, without an experiment design, while the interactions among the parameters did not study.

This study is an experimental investigation on the process of dye adsorption utilizing ASBE. Experiments are designed by means of RSM, while considering the interactions among variables, and the most efficient conditions along with the least number of experiments to find the optimal results. Comparing results from ASBE, VBE and AVBE (Activated Virgin Bleaching Earth), Specific values can be achieved. The study was carried out in order to achieve optimal parameters for reactive dye adsorption through ASBE at K. N. Toosi University of Technology, Tehran, Iran in 2015.

MATERIALS AND METHODS

All laboratory containers and equipment were washed with detergents and distilled water, and dried prior to performing the experiments. Determining adsorption of ASBE, homogenized samples were used, and experiments were conducted on the size of 2-3 mm clay particles. In order to take advantage of RSM, some parameters are to be determined through some preliminary tests.

Utilized materials

Materials used in this research included VBE (ω=2.6%), SBE contained motor oil, hydrochloric acid (HCl), and reactive red dye of the textile industry. SBE used in this research was obtained from the treatment section of Engine Oil Production Company, which is one of the large industrial oil engine production units. The VBE used in this plant was raw calcium bentonite. The utilized hydrochloric acid (37%) was produced by Merck Company. A textile reactive red dye ($C_{27}H_{18}ClN_7Na_4O_{15}S_5$) produced by Dye Stuff Company in China, were utilized (Fig. 1). Taking advantage of the results of abovementioned experiments, the main experiments of this research were conducted by means of RSM: design expert software.

Experiments

In this section, thermal remediation and acid washing activation tests were run to obtain the clay sample as dye adsorbent. Carrying out dye adsorption test, the degree of dye adsorption by the adsorbent was measured.

Clay sample preparation

Thermal remediation of SBE was carried out in furnace at various temperatures to obtain clay without contaminants. Afterwards, acid washing of the remediated sample was performed by using HCl 37 % to activate the clay.

Thermal remediation

The flash point of motor oil is 226 ˚C. Hence, 50 g SBE sample was measured by means of an electronic balance with a precision of 0.001 g (model FH-303B made by AND Company). Then the clay was placed into the furnace (model Gallen Kamp with accuracy of 0.1 ˚ C) and heated up in the range of 200 to 800 °C for 1 h (Shahi, 2015). Cooling down the temperature of the sample to laboratory temperature (24 °C), this sample was named regenerated spent bleaching earth (RSBE).

Acid washing

In this test, hydrochloric acid (37 %) with low rate of evaporation and convenient was used to provide solutions with concentration of 0.1-3 M, while RSBE/ acidic solution ratio were kept 20 % (w/w). Measuring the amount of acidic solution and RSBE, they were mixed with a magnetic mixer (model PLOE IDEAL PARS HMS8805 with accuracy of ± 1%) at the ambient temperature for one hour at a speed of 300 rpm. After complete mixing, acidic phase and leached RSBE were separated by centrifuge (model Segurita BHG 1100 with accuracy of ± 2 ppm). Also, acid washing was continued until reaching neutral pH (through injecting $AgNO_3$ for this assurance). The clay and acid solution passed through a filter paper No. 2 (Nr. 598[2], Ø 12.5 mm). The remaining clay on the filter paper was put inside an oven for 24 hours at a temperature of 80 °C. Taking the sample out of oven, it was grinded with porcelain mortar to turn it into powder and increase the clay absorbability. This sample was named ASBE (Shahi, 2015).

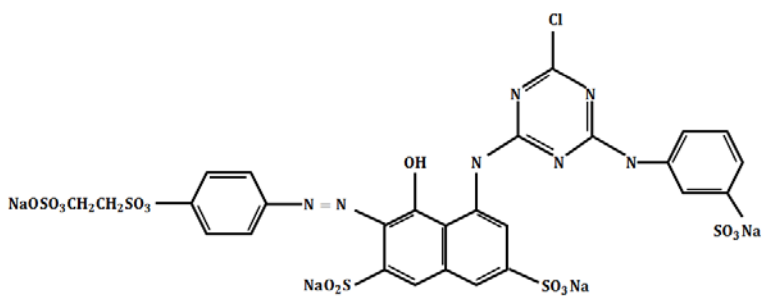


Fig. 1: Molecular structure of reactive red dye

Furthermore, the same process (thermal remediation and acid washing activation) was applied on VBE sample in order to compare AVBE with ASBE sample in terms of oil removal efficiency.

Dye adsorption

ASBE sample was utilized as an adsorbent to measure the cleaned sample absorbability. This measurement was done through utilizing reactive textile dye absorbability produced by Dye Stuff Company, China. Considering the results of standard curve for reactive red dye, the dye solution concentration was set to 1-35 ppm. ASBE and dye solution were mixed with 0.1-2 % (w/w) ratio and the mixture was agitated thoroughly at 150 rpm for 15 minutes using a magnetic mixer (Alam, 2007). Then, the mixture phases were segregated via a centrifuge. Passing through filter paper No. 3(Nr. 598[3], Ø 125 mm), the separated dye was prepared for spectrophotometry with Lovibond PCSPECTRO with wavelength accuracy of ± 2 nm. Using spectrophotometry and obtained criterion wavelength by means of standard curve of reactive red dye, ASBE sample absorbability was measured.

Experiment design

Considering the 3 above mentioned tests, the main experiments design was done via RSM utilization to optimize the approximate ranges of parameters and select the optimal point. Referring to previous studies, temperature and dye solution concentration were evaluated as essential influential parameters in this research. A total of 30 experiments were carried out for dye adsorption processes. From each experiment, one response was obtained. After analyzing the experiment data with design expert 7, the second-order polynomial model expressed according to the Eq. 1 was adapted to the experiment results to provide optimization process.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i} \sum_{j} \beta_{ij} X_i X_j \quad (1)$$

Where, Y the result predicted by the model, β_e a constant coefficient, β_i the linear coefficients, β_{ii} the quadratic coefficients, β_{ij} the interaction coefficients, and X_i and X_j the coded values of the tested variables.

RESULTS AND DISCUSSION

Designing experiments via RSM, the optimum model is determined through definite temperature, acid solution concentration, dye solution concentration and ratio of ASBE to dye solution.

Standard curve for reactive red dye

Considering the standard wavelength of reactive red dye (513.32 nm) and dye adsorption, a standard curve for the reactive red dye at various concentrations is according to Fig. 2.

As shown in Fig. 2, there is a linear trend in adsorption in the range of 1-35 ppm. Hence, this trend is used in experiments design.

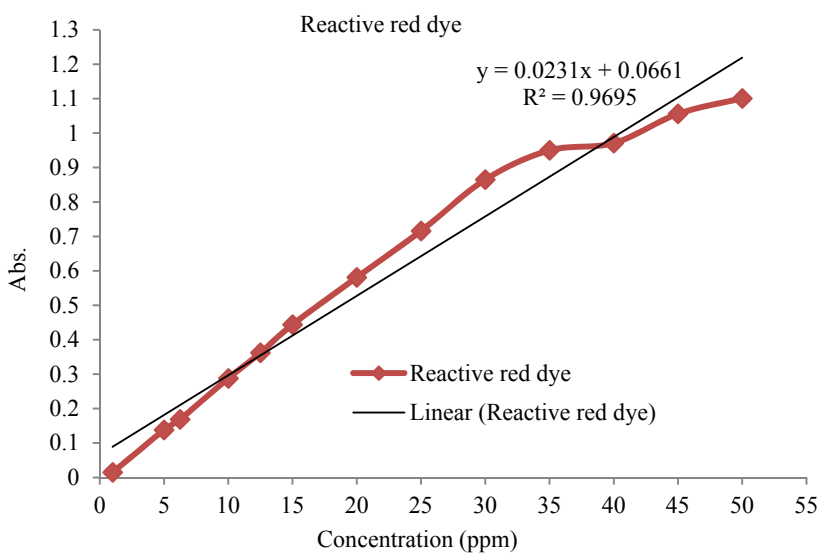


Fig. 2: Standard curve of reactive red dye

The ratio of ASBE to dye solution determination

Fig. 3 represents the adsorption of dye solution concentration for a vast range of ASBE/dye solution ratio. Increasing the ratio of ASBE to dye solution to 3 % (w/w), the dye solution adsorption goes beyond the linear region. Thus, a range of 0.1-2 % (w/w) for this ratio is acceptable.

Modeling

The process of reactive red dye adsorption is modeled in the optimal areas by using RSM. Table 1 presents test results, which show adsorption efficiency via ASBE utilization.

Considering the regression coefficients, data analysis result a second-order polynomial model for adsorption is presented as Eq. 2.

$$Y = +57.71 + 6.70 * X_1 - 0.55 * X_2 + 7.84 * X_3 - 3.17 * X_4 - 1.86 * X_1 * X_2 - 13.12 * X_1 * X_3 + 11.43 * X_1 * X_4 + 1.07 * X_2 * X_3 - 0.025 * X_2 * X_4 - 10.13 * X_3 * X_4 - 8.07 * X_1^2 + 1.89 * X_2^2 - 11.36 * X_3^2 - 6.32 * X_4^2 \quad (2)$$

Where Y, X_1, X_2, X_3 and X_4 are dye adsorption, the coded temperature, the coded acid solution concentration, dye solution concentration and ASBE/ dye solution ratio, respectively.

Fig. 4 illustrates actual versus Predicted values for dye adsorption by ASBE. This figure shows that all estimated values by the model are very close to the experimental results. Decreasing the distance of resulting points from Y=X line, the adequacy of the model increases.

Model validation

Variance table analysis

Based on the experiment results and using RSM, the analysis of variance data is presented in Table 2.

According to Table 2, the probability value of model regression equation is equal to 0.0087 and smaller than 0.05 (confidence level of 0.95). This result shows that the second-order polynomial model fits the experiment results properly. Moreover, F-value (test statistic) is equal to 3.68 which is clearly larger than F-value in the table (equals 3.45 for α=0.05). On this basis, the findings confirm the competence of model fitness and significant. Moreover, the probability of model inadequacy is only 0.87%. F-value of suitable Lack of fit is 28.45, because the P-value is 0.0009. These two values show that inadequacy probability is only 0.09 % (<< 1) and model is acceptable.

Correlation coefficient

Correlation coefficient R^2 is an indicator of regression precision and reflects the relationship between the experimental data and predicted responses. A correlation coefficient close to 1 is highly desirable.

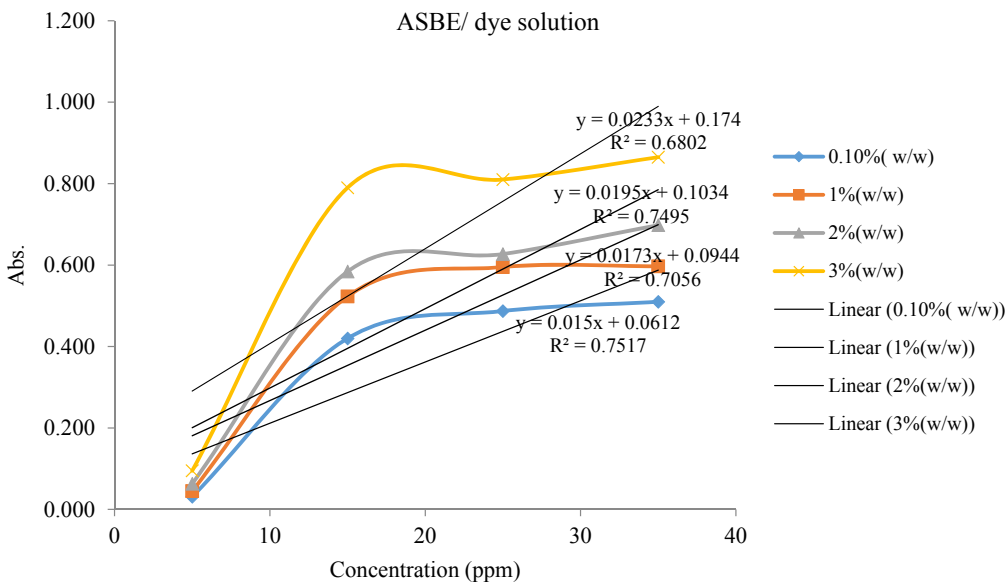


Fig. 3: Proper limit for ratio of ASBE to dye solution

Table 1: Clean clay dye adsorption test results

Run	Block	Variable				Adsorption (%)
		Temperature (°C)	Acid solution concentration (M)	Dye solution concentration (ppm)	ASBE/dye solution %(w/w)	
1	1	350	2.27	26.5	0.58	84.8
2	1	350	0.82	9.5	1.52	0
3	1	500	1.55	18	1.05	49.8
4	1	650	0.82	9.5	1.52	50.87
5	1	500	0.1	18	1.05	72.08
6	1	350	2.27	26.5	1.52	0
7	1	650	2.27	9.5	0.58	37.72
8	1	350	0.82	26.5	0.58	76.26
9	1	500	1.55	18	2	54.9
10	1	500	1.55	18	1.05	58.9
11	1	650	2.27	9.5	1.52	48.79
12	1	500	1.55	18	1.05	59.85
13	1	500	1.55	1	1.05	0
14	1	200	1.55	18	1.05	33.4
15	1	350	2.27	9.5	1.52	0
16	1	650	2.27	26.5	0.58	31.21
17	1	650	2.27	26.5	1.52	35.14
18	1	500	3	18	1.05	71.89
19	1	650	0.82	9.5	0.58	50.52
20	1	350	0.82	9.5	0.58	0
21	1	350	2.27	9.5	0.58	0
22	1	500	1.55	18	1.05	59.85
23	1	800	1.55	18	1.05	30.84
24	1	350	0.82	26.5	1.52	0
25	1	650	0.82	26.5	0.58	33.11
26	1	500	1.55	18	0.1	23.36
27	1	650	0.82	26.5	1.52	39.62
28	1	500	1.55	35	1.05	37.94
29	1	500	1.55	18	1.05	58.76
30	1	500	1.55	18	1.05	59.12

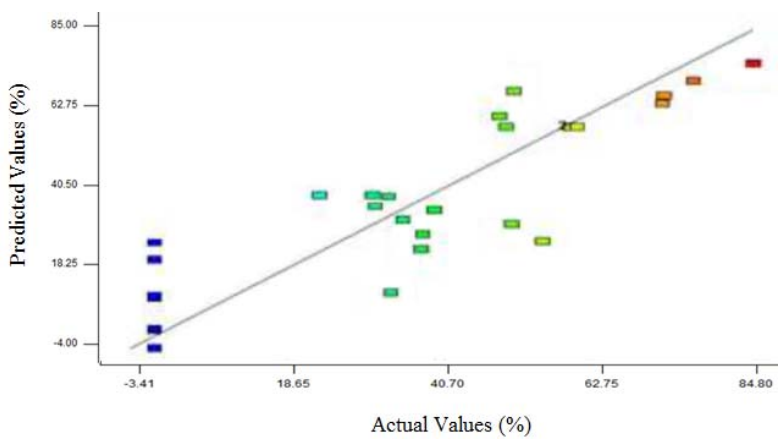


Fig. 4: Actual vs. predicted values for dye adsorption by cleaned clay

Regression coefficients of the adsorption model are calculated and presented in Table 3. These regression coefficients indicate that laboratory and predicted results matched very well and fitted model enjoyed very high conformity.

Model optimization

Achieving maximum adsorption in the defined ranges in the parameters is optimized. According to Fig. 5, the desirability of the optimal model is 0.908 which reflects the model optimality.

Table 2: ANOVA for dye adsorption

Analysis of variance table						
Source	Sum of squares	df	Mean Square	F Value	P- Value	Significant
Model	15146.34	14	1081.88	3.68	0.0087	✓
X_1-temperature	1077.36	1	1077.36	3.66	0.0750	
X_2- acid solution concentration	7.15	1	7.15	0.024	0.8782	
X_3- dye solution concentration	1474.55	1	1474.55	5.01	0.0408	
X_4-ASBE/dye solution	241.43	1	241.43	0.82	0.3794	
X_1X_2	55.50	1	55.50	0.19	0.6703	
X_1X_3	2753.10	1	2753.10	9.36	0.0080	
X_1X_4	2091.23	1	2091.23	7.11	0.0176	
X_2X_3	18.15	1	18.15	0.062	0.8072	
X_2X_4	0.010	1	0.010	3.398E-005	0.9954	
X_3X_4	1641.06	1	1641.06	5.58	0.0321	
X_1^2	1787.67	1	1787.67	6.07	0.0263	
X_2^2	98.30	1	98.30	0.33	0.5719	
X_3^2	3540.04	1	3540.04	12.03	0.0034	
X_4^2	1095.78	1	1095.78	3.72	0.0728	
Residual	4414.02	15	294.27			
Lack of fit	4337.79	10	433.78	28.45	0.0009	✓
Pure error	76.23	5	15.25			
Core total	19560.36	29				

Temperature = 650 °C

Acid solution concentration = 0.83 M

Dye solution concentration = 11.75 ppm

ASBE/Dye solution = 1.52 %w/w

Adsorption = 68.49 %

Fig. 5: Model optimization for dye adsorption

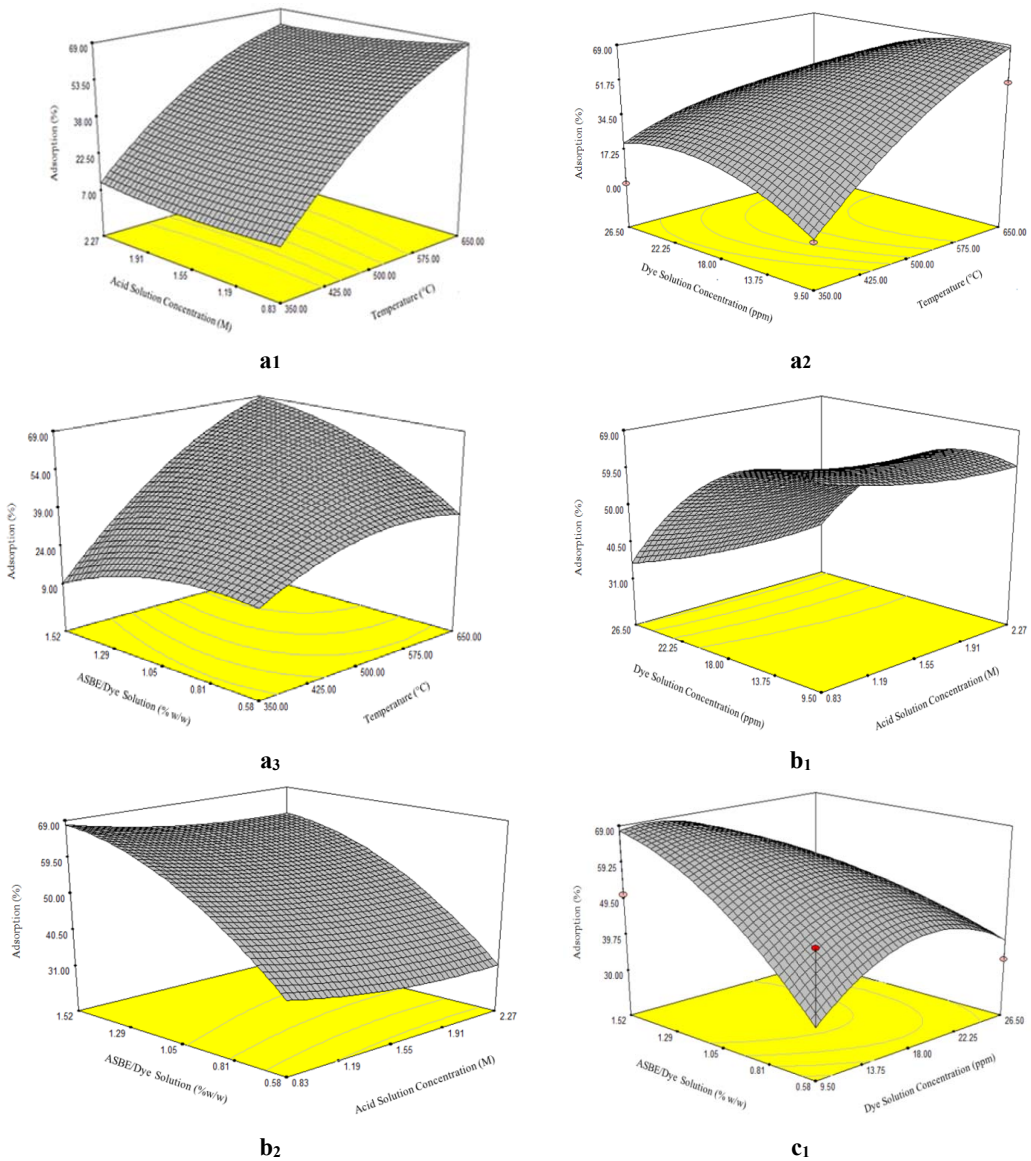
Dye adsorption sensitivity analysis

Using RSM, the parameters interactions effects on dye adsorption are measured and the results are examined.

Referring to Fig. 6, parameters interactions imply that increment of temperature and increase in the ratio of ASBE to dye solution (a_3, b_2, c_1) and a decline in acid solution concentration and decrease in dye solution concentration have brought significant increase to adsorption efficiency. Having very remarkable desirability, approximately 1 for optimum sample, the effects of parameters on results are described in the following sub- sections.

Table 3 Regression coefficients for fitted model

Pred R-squared	Adj R-squared	R-squared
0.2	0.5637	0.7743



a1 **a2** **a3** **b1** **b2** **c1**

Fig. 6: RSM diagrams of parameters interactions on dye adsorption utilizing ASBE

Temperature

The oil and reactive red dye contain non-polar portion including C_6H_6 and SO_3, respectively. As non-polar portion react to each other, the color of dye solution is changed. The interlayer space and three-unit layers of Montmorillonite are occupied by hydrated cations. Moreover, presence of some organic ions in larger spaces is also acknowledged. In optimum temperature, clay minerals lose all of their hydrated molecules and organic ions. Resulting of this physical process, layers surfaces and interlayer spaces for dye solution adsorption are available. Higher Temperature leads to destruction of clay structure, layers surfaces and interlayer spaces loss. Consequently, a considerable reduction in clay adsorption occurs.

Acid solution concentration

Resulting of low-concentration acid, some of the inter-layer cations of the octahedral central atoms of clay are replaced by acid protons. The H^+ cation

Table 4: Dye adsorption by ASBE, VBE and AVBE in optimal conditions

Sample	Temperature (°C)	Acid solution concentration (M)	Dye solution concentration (ppm)	ASBE/dye solution (%w/w)	Response absorption (%)
ASBE	650	0.83	11.75	1.52	68.57
VBE	650	0.83	11.75	1.52	51.56
AVBE	650	0.83	11.75	1.52	66.75

enters three-unit layers when a mineral acid acts on Montmorillonite and the Al^{3+} cations inside the octahedral units are released. Releasing H^{+} cation in the space between Montmorillonite layers, it adsorbs pigment and forms a complex. Pigment is adsorbed into ASBE by electrostatic forces. Results of acid activation indicate that with an increase of Al^{3+} ions extraction, pores and surface area grow considerably until the grid collapses.

Dye solution concentration

The desired dye concentration is presented on linear portion of the standard curve. In spite of the specific amount of clay and lower dye solution concentration, adsorption level increases. There is an inverse relationship between dye concentration and adsorption in reactive red dye. Decrease in molecules number, the adsorption probability grows when the adsorption positions are equal. The transfer of adsorbing substance from dye solution to adsorbent continues until the adsorbate concentration in solution equals to the adsorbing concentration on adsorbent surface.

The ratio of ASBE to dye solution

Reducing dye solution in optimal sample along with an adsorbent increment, the level of adsorption escalates due to the growth of surface contact with dye solution.

Optimum sample determination

Considering the achievements of the optimal efficiency conditions of dye adsorption via ASBE are determined. Defining the optimal sample for obtaining the highest dye adsorption efficiency, another experiment was carried out under optimal conditions on VBE and AVBE in order to model validation.

Comparing adsorption levels in Table 4, it is possible to obtain a higher efficiency by cleaning contaminated clay and reusing ASBE for adsorbing the waste color resulted from textile industries instead of using VBE and AVBE. Accordingly, this solution can be cost effective and useful for preventing environmental damages.

CONCLUSION

Using data for modeling and employing RSM and interaction between data for experiment design, the maximum adsorption efficiency obtain. On the basis of RSM using central composite design model for experimental design and fitness of polynomial equation, optimal conditions for dye adsorption by ASBE are found to be temperature of 650˚C, acid washing solution concentration 0.83 M, dye solution concentration 11.75 ppm and 1.52 % (w/w) ratio of clay to dye solution. In general, the adsorption by thermal remediated clay is greater compared to those of raw and activated clay. Results indicated that activated bleaching clay is a suitable adsorbent for removing some dyes used in the textile industry, and that not only is effective in treating textile wastewater but also prevented environmental pollution. Since dyes are stable and toxic, releasing them into the environment will cause environmental and health-related problems. Accordingly, it is important to remove dyes from textile industry wastewater.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

ABBREVIATIONS

ANOVA	Analysis of variance
An-SBR	Anaerobic sequencing batch reactor
AR18	Acid Red 18
ASBE	Activated spent bleaching earth

$AgCO_3$	Silver carbonate
AVBE	Activated virgin bleaching earth
CSBE	Carbonized spent bleaching earth
^oC	Centigrade
df	RSM software parameter
DSS	Dried sewage sludge
g	Gram
F-value	Measure of significance
h	Hour
HCL	Hydrochloric acid
M	Molar
MB	Methylene blue
MEK	Methylethylketone
MGO	Magnetite/graphene oxide
min.	Minute
MWCNT	Multi-walled carbon nanotube
P-value	Probability of obtaining a result in hypothesis testing
ppm	part per million
RB19	Reactive Blue 19
RSBE	Regenerated spent bleaching earth
RSM	Response surface methodology
R^2	Correlation coefficient
SBE	Spent bleaching earth
SSA	Sewage sludge ash
VBE	Virgin bleaching earth
vol.	Volume
%	Per cent

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