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Removal of Methyl Red from Aqueous Solutıons with Natural and Biochar Prina: A Full Factorial Modeling Study

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Abstract: Wastewater from various industries contains a high concentration of dyes. Dyeing wastewater is discharged into natural receiving waters without treatment; they are dangerous for both the environment and human health. Therefore, it is necessary to remove the dyes before it is discharged to the receiving environment. In this study, full factorial modeling of methyl red removal was studied by using an adsorption method, which is widely used in dye rsemoval with natural and modified prina adsorbent. 2^3 factorial design is used in the modeling method. In there 3 factors; adsorbent content (0.03g/30mL - 0.3g/30mL), initial dye concentration (30mg/L - 300mg/L) and adsorbent type (natural and biochar pomace) were selected. These factors were studied in two low (-1) and high (+1) levels. Effects of selected factors on adsorption efficiency; adsorbent type > initial concentration> adsorbent dosage. Besides, removal efficiencies up to 88% were obtained with biochar prina and it was found that prina is a good alternative adsorbent for methyl red removal.

Keywords: Adsorption, biochar, dye, full factorial, prina

1. Introduction

Dyes are widely used in various industries, such as textiles, paper, plastics, cosmetics, ceramics and leather, for coloring their final products. To remove dyes from aqueous solutions, many chemical or biological treatments have been used either individually or together. (Kose 2008). There are several dye removal methods, such as adsorption, oxidation-ozonation, coagulation, coagulation-flocculation and biological methods. Among these removal methods, adsorption is an attractive alternative method. Many adsorbents have been tested on the possibility to lower concentrations from aqueous solutions, such as active carbon, peat, olive oil waste (prina), chitin, red mud, calcite, clay, natural zeolites, bentonite, sepiolite, perlite, iron oxide coated sand, birnessite and others (Yin and Zhou 2015; Zhao and Chen 2012).

The olive processing industry disposes around four million tonnes of waste in olive stones (prina) each year. According to the International Olive Council, the world annual production of olive oil in 2012 was more than 3 million tons, translating to approximately 15 million tons of olive cakes as the by-products. Turkey is one of the Mediterranean countries which are in the first range of olive and olive oil-production. The annual production of olive oil in Turkey is 100.000–250.000 tons. This production amount creates 100.000–250.000 tons of solid wastes (Jaikumar et al. 2009; Luo et al. 2010).

These oil-producing wastes are commonly disposed of in the fields or burnt there with the loss of energy as well as causing different environmental problems such as fires, plagues CO_2 emissions to the atmosphere. Olive stone waste is a lignocellulosic material, with hemicellulose, cellulose and lignin as main components. Many current studies aim to develop methods of recovering the lignocellulosic material or biomass to produce solid, liquid, or gas biofuel. Therefore, widespread prina use is directed towards its use as a solid fuel or its derivatives fuel as a renewable energy (Luo et al. 2010). Other uses include activated carbon as biosorbent, animal feed, furfural production, plastic-filled, abrasive etc. In this study, we investigated the adsorption properties of prina by varying these factors at two levels. Interaction between these factors was studied and optimization was done.

2. Materials and Method

2.1. Materials

Prina was supplied by an olive oil producer from Ayvalık, Turkey. The wastes were rinsed three times with water then dried in an oven at 103°C until constant weight. They were ground and sieved for a particle size of 2.0–4.75mm. This material was named as natural prina. The carbonization step was carried out at 600 °C for 1 hour under purified nitrogen (99.99%). After carbonization, it was named biochar prina.

2.2. Method

In this study, a Full Factorial Design of Experiment was designed to investigate the effect of adsorbent amount, initial dye concentration and adsorbent type on removing methyl red ions with natural and biochar prina. The samples were mixed at predetermined periods at a temperature of 23°C in a shaker at 150 rpm until equilibrium was reached. The concentrations were measured with a Thermo brand Aquamate model UV spectrophotometer at 525nm wavelength. The removal efficiency (E) of natural and biochar prina on methyl red dye was calculated according to the following formula Equation 1;

$$E(\%) = [(C_0 - C) / C_0]x100 \qquad (1)$$

Where; C_0 is the initial concentration of the dye solution (mg/L) and C is the dye solution's final concentration.

Full Factorial Design of Experiments examines every possible combination of factors at the levels tested (Lian et al. 2009; Iram et al. 2010). The general notation for a full factorial design run at b levels is bk=# Runs, where k is the number of factors.

This study aims is to maximize the removal of methyl red dye ions (response variable). In this respect, experimental factors, which are adsorbent amount, initial dye concentration and adsorbent type, were selected as possible candidates affecting the removal percentage. By considering the earlier studies, two levels for each factor were determined. The 2^3 factorial design with high and low levels of factors are given in Table 1 (b=2 and k=3).

Table 1 The levels of experimental factors

Factor	Low Level (-1)	High Level (+1)
Adsorbent Amount (g/30mL) **(A)**	0.03	0.3
Methyl Red Dye Concentration (mg/L) **(B)**	30	300
Adsorbent Type **(C)**	Natural Prina	Biochar Prina

Interaction is a variation among the differences between means for different levels of one factor over different levels.

Using plus and minus signs to represent high and low levels of a factor, the main effects given in Table 2 were calculated by using the following general equation (Ai et al. 2006; Erbas and Semra 2006; Montgomery et al. 2001; Senoglu and Acıtas 2014; Tibet and Coruh 2017).

Table 2 Experimental design matrix of methyl red dye removal efficiency

Run No	Factor			Efficiency (%)		
	A	B	C	Replicate I	Replicate II	Average
1	-1	-1	-1	72.16	65.83	68.99
2	+1	-1	-1	71.51	65.70	68.60
3	-1	+1	-1	79.61	78.65	79.13
4	+1	+1	-1	88.71	85.21	86.96
5	-1	-1	+1	82.75	83.40	83.07
6	+1	-1	+1	83.66	83.14	83.40
7	-1	+1	+1	77.62	87.76	82.69
8	+1	+1	+1	89.91	86.08	87.99

3. Results

The residuals also appraised the sufficiency of the models. The observed residuals are plotted against the expected values, given by a normal distribution in Figure 1. Trends seen in Figure 1 reveal reasonably well-behaved residuals. In these graphics, the residuals seem to be randomly scattered.

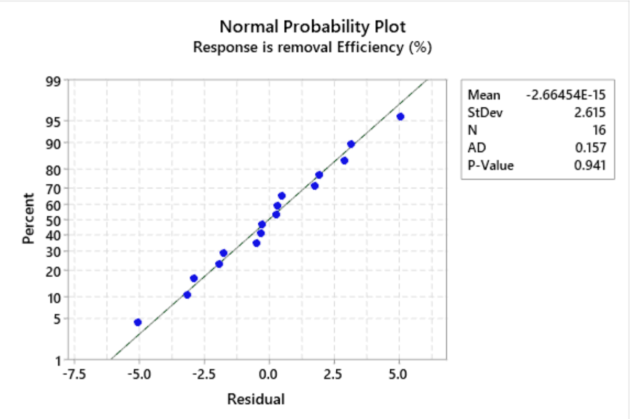

Fig. 1 Normal Probability plot

The Cube Plot in Figure 2 shows the predicted removal efficiency at combinations of the low and high experimental factors. In the study, the highest predicted value for the response variable is obtained at methyl red concentration at a high level, adsorbent amount at a high level and the adsorbent type at biochar prina.

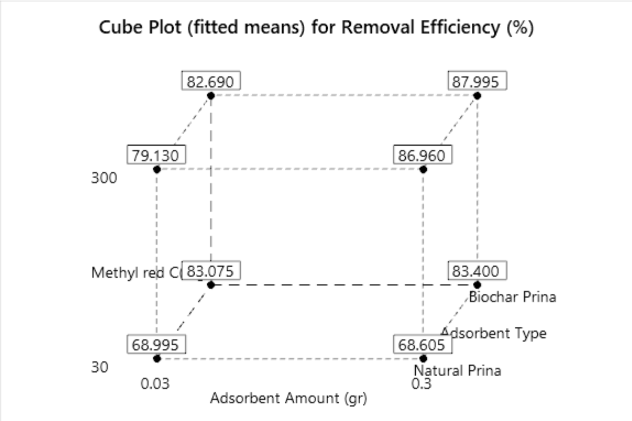

Fig. 2 Cube plot for methyl red removal efficiency

The R-square of the model (88.43%) was higher than the predicted value (78.32) % and fitted well the model's results. These results argued good agreements between the predicted and experimental values of methyl red removal efficiency (Table 3). In this way, the methyl red adsorption by natural prina and biochar prina could be expressed.

Table 3 Estimated Effects and Coefficients for removal efficiency

Term	Effect	Coef	SE Coef	T	P
Constant	-	80.106	0.895	89.48	0.000
Adsorbent Amount (g)	3.267	1.634	0.895	1.82	0.105
Methyl red C(mg/L)	8.175	4.088	0.895	4.57	0.002
Adsorbent Type	8.368	4.184	0.895	4.67	0.002
Adsorbent Amount (g)*Methyl red C(mg/L)	3.300	1.650	0.895	1.84	0.103
Adsorbent Amount (g)*Adsorbent Type	-0.453	-0.226	0.895	-0.25	0.807
Methyl red C(mg/L)* Adsorbent Type	-6.070	-3.035	0.895	-3.39	0.009
Adsorbent Amount (g)*Methyl red C(mg/L)* Adsorbent Type	-0.810	-0.405	0.895	-0.45	0.663

S = 3.58101 PRESS = 410.356

R-Sq = 88.43% R-Sq(pred) = 53.74% R-Sq(adj) = 78.32%

In Table 4, the most important parameters that affect the adsorption process's efficiency are adsorbent Type, methyl red concentration and interaction of methyl red concentration* adsorbent type. To effects these parameters, experiments were performed at different combinations of the physical parameters using statistically designed experiments.

Table 4 Estimated Effects and Coefficients for removal efficiency

Source	DF	Adj SS	Adj MS	F	P
Model	7	784.472	112.067	8.74	0.003
Linear	3	590.089	196.696	15.34	0.001
Adsorbent Amount (gr)	1	42.706	42.706	3.33	0.105
Methyl red C(mg/L)	1	267.323	267.323	20.85	0.002
Adsorbent Type	1	280.060	280.060	21.84	0.002
2-Way Interactions	3	191.759	63.920	4.98	0.031
Adsorbent Amount (g)*Methyl red C(mg/L)	1	43.560	43.560	3.40	0.103
Adsorbent Amount (g)*Adsorbent Type	1	0.819	0.819	0.06	0.807
Methyl red C(mg/L)*Adsorbent Type	1	147.380	147.380	11.49	0.009
3-Way Interaction	1	2.624	2.624	0.20	0.663
Adsorbent Amount (g)*Methyl red C(mg/L)*Adsorbent Type	1	2.624	2.624	0.20	0.663
Error	8	102.589	12.824	-	-
Total	15	887.060	-	-	-

A normal probability plot of the standardized effects, which is to determine the statistical significance of both primary and interaction effects, is given in Figure 3. The insignificant effects will fall along a line; on the other hand, and the significant effects will stray farther from the line. According to Figure 3 and Figure 4, the main effects B and C and the interaction BC are statistically significant. Since B and C lie on the right-hand side of the line, their contributions have a positive effect on the model.

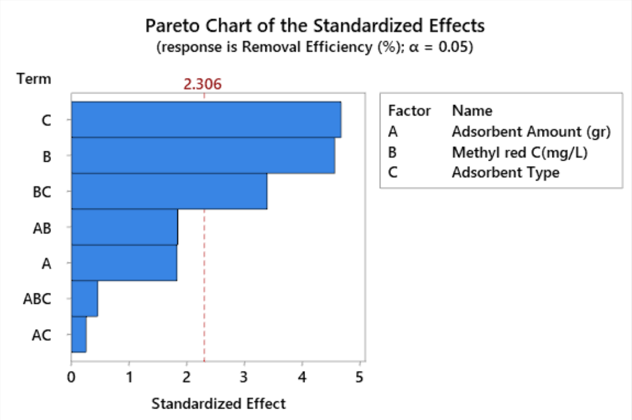

Fig. 3 Pareto chart of the standardized effects for methyl Red removal

The reverse is valid for the rest of the significant effects, which lie on the left-hand side. The adsorbent type appears to have the most enormous effect because it lies furthest from the line.

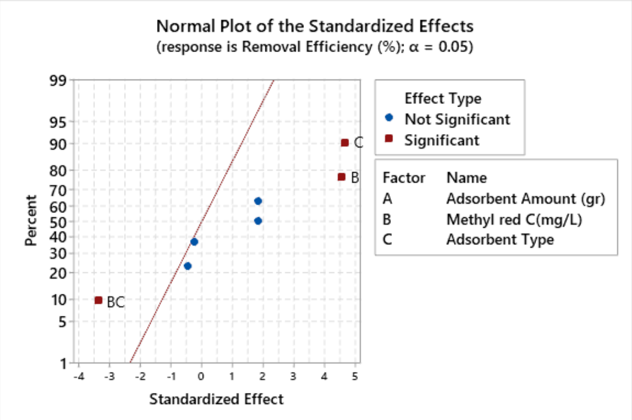

Fig. 4 Normal plot of the standardized effects for methyl red removal

Figure 5 shows the main effects plot, offering the effect of each variable on the response factor. The main effect is significant if the mean for one level of the factor is sufficiently different from the mean for another factor level. That is, lines with steeper slopes (up or down) have a more significant impact on the output than lines with little or no slope (horizontal). This type of figuration shows the contribution to the response factor of changing one of the influential variables. When a factor's effect is negative, removal efficiency decreases as the factor changes from low to high levels. In contrast, if the effect is positive, an increase in removal efficiency occurs for a high level of the same factor. If the magnitude of the main effect is small, the slope would be close to zero.

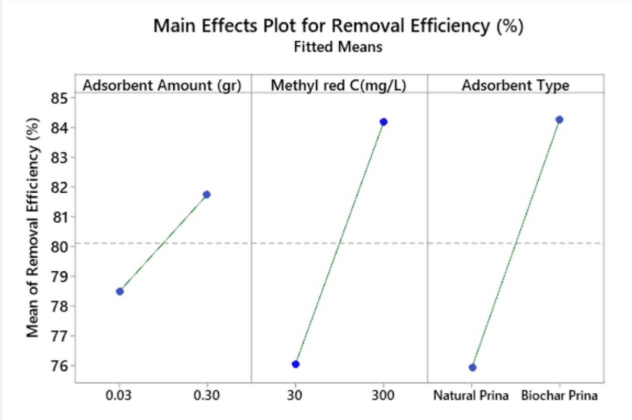

Fig. 5 Main Effects plot for Methyl Red removal efficiency from aqueous solutions

The interaction plot shows the possible interaction between the mean responses of the factors under assessment. An interaction plot circumstance the impact that changing the settings of one factor has on another factor. Graphically, two parallel lines of factors indicate no interaction between them; however, non-parallel lines suggest that they interact together. The interaction plot in Figure 6 confirms the interaction of methyl red concentration* adsorbent type is significant.

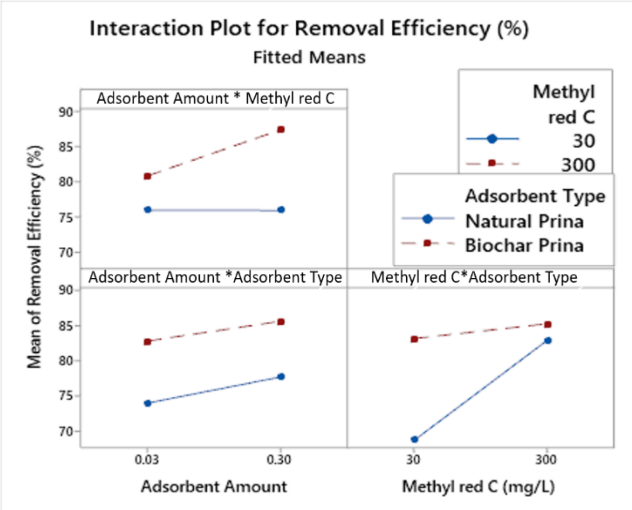

Fig. 6 Interaction plot for methyl red removal efficiency from aqueous solutions

To see the effects of interactions between experimental factors, a multi-vari chart was generated (Figure 7). From this chart, the effect of adsorbent type is observed for the biochar prina to be more efficient than the natural prina.

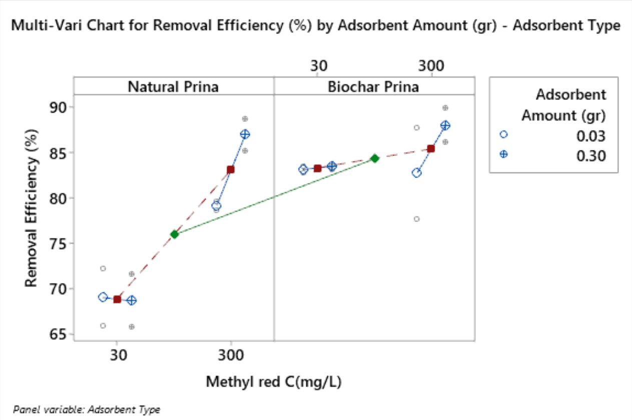

Fig. 7 Multi-Vari Chart for methyl red removal efficiency from aqueous solutions

4. Conclusion

The scope of this study was to investigate the effectiveness of the prina to remove methyl red dye ions from aqueous solutions. For this purpose, a 2^3 full factorial design (three factors, at two levels) was employed to evaluate the importance and interactions of adsorbent amount, initial dye concentration and adsorbent type. The factorial design results show that the adsorbent type (factor C) had the most potent effect on the methyl red dye's removal efficiency. The negative coefficient in the equation means that increasing factor C decreases removal efficiency. On the other hand, the positive sign of initial dye concentration (factor B) means a direct relation between this factor and the response. That is, increasing adsorbent amount increases removal efficiency. This study clearly shows that the interaction between adsorbent type and initial dye concentration was significant for the removal efficiency of methyl red ions.

Authors' contributions: SED was interested in performing the experiments, calculating the results, interpreting the data and arranging them according to the format. YT was interested in applying the experimental results to the model program and preparing the graphics. SC was interested in organizing the study.

Conflict of interest disclosure: Our work has not been carried out with any organization or employees.

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