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Preparation and Characterization of Activated Carbon derived from olive stone as adsorbent for Congo Red

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ABSTRACT

Carbon activated powdered was prepared from activated carbon derived from olive stone. Then by using the surface methodology, many parameters such as pH, furnace temperature (T), acid ratio, time of activation that affect on the qualities prepared activated carbon produced and its efficiency were investigated. In addition, the adsorption of Congo Red onto the activated olive stone carbon active was studied and removal or adsorption percent as response was reported. By applying surface methodology we obtained optimum conditions, at the other hand next researches can use these conditions to produce activated carbon by high efficiency from Olive stone as natural adsorbent.

Keywords: Activation; Carbonization; Olive stone; Adsorption; Surface methodology; Congo Red

INTRODUCTION

biodegradation degradation is a difficult task and required great attention and emphasis potentiall. their dyes, especially cationic dyes may be toxic, carcinogenic and even mutagenic and generate serious hazards to aquatic living organisms and ecosystems [1-7]. The applicability of conventional physiochemical methods for treating reactive dye waste is limited and the lack could be overcome by adsorption phenomenon as a powerful low cast procedure. In this respect the design and development of locally nin-toxic, cheep and abundant adsorbent with prous structure area is a challenging requirement. [8-10]. Congo red (CR) or 1-naphthalenesulfonic acid, 3,3_-(4,4_-biphenylenebis (azo)) bis (4-amino-) disodium salt is a benzidine-based anionic diazo dye (Figure 1)[11]. This anionic dye can be metabolised to benzidine(known human carcinogen)[12]. Effluent containing CR is largely produced from textiles, printing, dyeing, paper, and plastic industries [13].

The change negative nature of dye (sodium salt form) giving it very good water solubility. Treatment of contaminated Congo red in wastewater is not straightforward.

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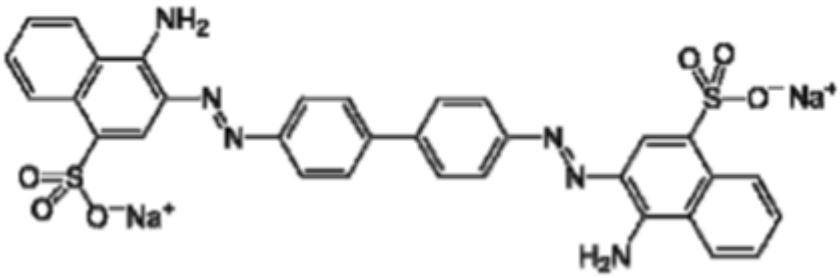

Fig. 1. Chemical structure of Congo Red.

Several studies have been reported for Congo Red removal by adsorption.[14-19] . Due to urgent need for its fast and quantitive removal in short time through economic pathway, application of agriculture carbon waste is highly recommended. In this research, activated carbon was prepared from olive stone and efficiently was applied for the removal of Congo Red [20-23]. In this regard, two branch of variables are important and must be optimized. In the first, the effective variables on the activation and preparation of activated carbon was investigated and optimized. The criterion for optimization of variables is the removal percentage [24]. Subsequently, the influence of effective variables such as pH, amount of adsorbent and contact time was optimized using experimental design. Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for designing experiments, building models and analyzing the effects of the several independent variables (factors). At the other hand response surface method combined all conditions to reach the best experimental design. In this research two design methods were applied, first for dye concentration, pH, adsorbent dose and agitation time and other design applied for carbon active production and its conditions[25,26]. In order to produce the carbon active we select olive stone because this agriculture waste is widely in hand and no more useful to applied reported for it. Response surface methodology (RSM) is a combination of mathematical and statistical techniques that can use for developing, improving and optimizing the adsorption processes and is used to evaluate the relative significance of various process parameters even in the presence of complex interactions[27,28]. The main objective of RSM is to determine the optimum operational conditions of the process [29]. This methodology is widely used in chemical engineering and applied sciences to optimize process variables. RSM usually contain three steps: (a) design and experiments, (b) response surface modeling through regression, (c) optimization. RSM makes it possible to represent independent process parameters in quantitative form as:

$$Y = f(X_1, X_2, X_3, \ldots X_n) \pm \varepsilon \qquad (1)$$

where, Y is the response (yield), f is the response function, ε is the experimental error, and $X_1, X_2, X_3, \ldots X_n$ are independent parameters. By plotting the expected response (Y), give a surface, known as the response surface. The form of f is unknown very complicated. Thus, RSM aims the approximation of f by a suitable lower-ordered polynomial in some region of the independent process variables. If the response can be well modeled by a linear function of the

independent variables, the function (Eq. (1)) can be written as:

$$Y = C_0 + C_1X_1 + C_2X_2 + \cdots + C_nX_n \pm \varepsilon \quad (2)$$

Curvature nature of responses show a higher order polynomial such as quadratic model (Eq. (3)) with following equation:

$$Y = C_0 + \sum_{i=1}^{n} C_i X_n + \sum_{i=1}^{n} d_i X_i^2 \pm \varepsilon \quad (3)$$

By careful studying the response surface model and considering their interaction a point with known value of variables that gives the best response, can then be established and known as optimum point [30]. The optimization of Congo Red removal was carried out by four chosen independent process variables (Adsorbent dose, pH, initial dye concentration and contact time) with six replicates at center points and six star points known as central composite face-centered (CCFD) design. The ranges and the levels of the variables (high and low) investigated in this work are given in Table 1. Four factors were studied and their low and high levels are given in Table 1. Percentage adsorption was studied with a standard RSM design called central composite design (CCD). Thirty experiments were conducted in duplicate according to the scheme mentioned in Table 2. Design Expert Trial Version 6.0.10 (Stat Ease, USA) was used for regression and graphical analysis of the data.

The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots (Montgomery, 2001). The dependency and interaction of variables was explained by the multiple coefficient of determination (R^2) and the model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range (Elibol and Ozer, 2002). In next step we applied experimental design to produce the best activated carbon from olive stone by optimizing heat of furnace, time of heat, activated reagent and contact time and coded according to Table2. All sample of activated carbon were prepared according to Table 3 by applying central composite design.

Table 1. Experimental range and levels of independent variables

Parameters	**Factors**				
Range and levels (coded)	-2	-1	0	1	2
Initial dye concentration(mg/L)	5	10	15	20	30
Adsorbent dose(g)	0.05	0.1	0.2	0.3	0.4
pH	1.5	2.5	3.5	4.5	5.5
Contact time (min)	2	15	25	30	40

Table 2. Experimental range and levels of independent variables

Parameters	**Factors**				
Range and levels (coded)	-2	-1	0	1	2
furnace temperature(℃)	200	250	300	350	400
time of carbonization (h)	0.5	1.5	2	2.5	3
activation time (h)	2	10	16	20	24
acid ratio (HCl/HNO_3)	1	2	1/2	3	1/3

Table 3. The central composite design for the four independent variables

Trial no	X_1	X_2	X_3	X_4	Trial no	X_1	X_2	X_3	X_4
1	-1	-1	-1	-1	16	1	1	1	1
2	1	-1	-1	-1	17	-2	0	0	0
3	-1	1	-1	-1	18	2	0	0	0
4	1	1	-1	-1	19	0	-2	0	0
5	-1	-1	1	-1	20	0	2	0	0
6	1	-1	1	-1	21	0	0	-2	0
7	-1	1	1	-1	22	0	0	2	0
8	1	1	1	-1	23	0	0	0	-2
9	-1	-1	-1	1	24	0	0	0	2
10	1	-1	-1	1	25	0	0	0	0
11	-1	1	-1	1	26	0	0	0	0
12	1	1	-1	1	27	0	0	0	0
13	-1	-1	1	1	28	0	0	0	0
14	1	-1	1	1	29	0	0	0	0
15	-1	1	1	1	30	0	0	0	0

where X_1, X_2, X_3 and X_4 are four independent variables respectively: furnace temperature, time of carbonization, activation time and activated reagent ratio (HCl/HNO_3).

EXPERIMENTAL

All chemicals including NaOH, HCl, HNO3 and other reagent, with the highest purity available were purchased from Merck, Darmstadt, Germany. CR was used as received without any further purification; while its color was stable at experimental. A stock solution of CR was prepared by dissolving the required amount in distilled water and the working solutions with desired concentrations were prepared by successive dilutions of the stock solution. The concentration of the dye was determined at 569 nm using Jusco UV-Visible spectrophotometer model V-530, pH/Ion meter model-686, Metrohm, international ASTM sieves and Stirrer model IKA.

Preparation of Adsorbent From Olive Stone

Olive stone firstly washed to remove dirt from its surface and dried overnight in an oven at 105 ◦C. The dried stone was crush and loaded in a stainless steel vertical tubular reactor in furnace. Heating the mixture until 250ºC with heating rate of 10 ºC/min for 2h make possible to achieve porous carbon. The porous carbon grinded and pass through various mesh size. The carbon was activated following mixing with concentrated then the mixture was dehydrated in an oven overnight at 105 ◦C to remove moisture.

The adsorption of Congo Red from aqueous solution was performed in a static mode. Experiments were performed according to the first central composite design (CCD) matrix as expert design. In all stages for investigation of the influences of variables and evaluation of their interaction, 100 mL CR solution with various initial concentration and pH, mixed by known adsorbent dose and stirred for different time at 400rpm. The mixture was agitated in an orbital shaker at room temperature at desired speed. Finally, mixture was separated by centrifugation at 4000 rpm for 10 min. The residual concentration was determined using Jusco UV-Visible spectrophotometer model V-530nm. The response (removal efficiency) of CR was calculated as:

$$Y(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (4)$$

At all experiments and stages, the concentration of CR was evaluated using

calibration curve obtained at the same conditions. Removal percentage for each run was measured and optimum values of initial dye concentration, adsorbent dose, pH and contact time was obtained as following variables: initial dye concentration 15 mg/L, adsorbent dose 0.2 g, pH 1.5 and contact time 25 min. The application of the response surface methodology admit to achieve an empirical relationship between the response and input variables expressed by the following quadratic model (Eq. (5)):

$$\%\ \text{Congo Red Removal} = 190.228 - 113.446X_1 - 11.837X_2 + 2.363X_3 - 1.461X_4 + 19.189X_1^2 - 34.469X_2^2 + 0.042X_3^2 - 0.086X_4^2 + 18.75X_1X_2 - 0.775X_1X_3 - 0.529X_1X_4 - 7X_2X_3 + 3.612X_2X_4 - 0.016X_3X_4 \quad (5)$$

where X_1, X_2, X_3, X_4 are four independent variables.

Finally each sample of activated carbon was used as above optimum condition to removal dye from Congo Red solutions (pH, contact time, initial concentration and adsorbent dose was constant).

The results for each trial performed as per the experimental plan are given in Table 4. The application of the response surface methodology based on the estimates of the parameters indicated an empirical relationship between the response and input variables expressed by the following quadratic model (Eq. (6)):

$$\%\ \text{Congo Red Removal} = 26.71 + 0.47810.094X_1 + 3.52X_2 - 0.72X_3 - 5.36X_4 - \big(6E(-4)\big)X_1^2 - 0.8X_2^2 - 0.08X_3^2 + 2.5X_4^2 - 0.047X_1X_2 + 0.0044X_1X_3 - 0.024X_1X_4 + 0.77X_2X_3 + 2.315X_2X_4 - 0.043X_3X_4 \quad (6)$$

where X_1, X_2, X_3 and X_4 are furnace temperature, carbonization time, activation time and acid ratio.

As discussed in previous section, experimental designs model [the central composite face-centered experimental design] and response surface methodology was used with four process variables in two step to evaluate their effect on the carbon active produced process. The response equation was obtained (Eq. (6)) for the percentage removal of Congo Red.To investigate the interactive effect of two factors on the removal percentage of the Congo Red, the response surface methodology was used and three dimensional and contour plots were drawn. Effects of pair conditions on carbon active production procedure are discussed below.

Effect of furnace temperature (T) and carbonization time (t)

To investigate the combined effect of furnace temperature and carbonization time, the RSM was used and results were shown in the form of contours and 3D plots. Figs. 2, 3 shows that with increase in furnace temperature and decrease in carbonization time high efficiency of olive carbon active was obtained. The result of Figs.2, 3 clearly show the optimum condition for carbonization time and furnace temperature and used in future carbon production and its subsequent activation.

Effect of furnace temperature (T) and activation time (t)

Figs. 4 and 5 shows the effect of furnace temperature and activation time. Figs. 4, 5 shows that with increase in furnace temperature and decrease in activation time adsorption percentage increased. On the other hand, by increase in furnace temperature one of the time consuming procedures essentially for carbon active production was shortened.

Table 4. The central composite design for the four independent variables

Coded values of variables, Responses and model data													
Trial no	**X_1**	**X_2**	**X_3**	**X_4**	**Exp ads %**	**predicted**	**Trial no**	**X_1**	**X_2**	**X_3**	**X_4**	**Exp ads %**	**predicted**
1	-1	-1	-1	-1	94.0	95.29	16	1	1	1	1	97.8	102.1
2	1	-1	-1	-1	84.3	99.65	17	-2	0	0	0	93.8	87.60
3	-1	1	-1	-1	94.6	96.18	18	2	0	0	0	95.3	104.10
4	1	1	-1	-1	81.6	95.84	19	0	-2	0	0	96.2	100.51
5	-1	-1	1	-1	82.6	85.78	20	0	2	0	0	93.4	100.75
6	1	-1	1	-1	98.4	94.54	21	0	0	-2	0	93.7	92.35
7	-1	1	1	-1	98.7	94.37	22	0	0	2	0	98.5	93.20
8	1	1	1	-1	95.6	98.43	23	0	0	0	-2	91.9	99.41
9	-1	-1	-1	1	94.3	99.46	24	0	0	0	2	97.2	102.96
10	1	-1	-1	1	98.2	101.42	25	0	0	0	0	94.4	101.85
11	-1	1	-1	1	78.4	102.66	26	0	0	0	0	90.9	101.85
12	1	1	-1	1	94.6	99.92	27	0	0	0	0	95.1	101.85
13	-1	-1	1	1	94.3	89.52	28	0	0	0	0	93.0	101.85
14	1	-1	1	1	68.9	95.88	29	0	0	0	0	93.6	101.85
15	-1	1	1	1	97.1	100.42	30	0	0	0	0	93.7	101.85

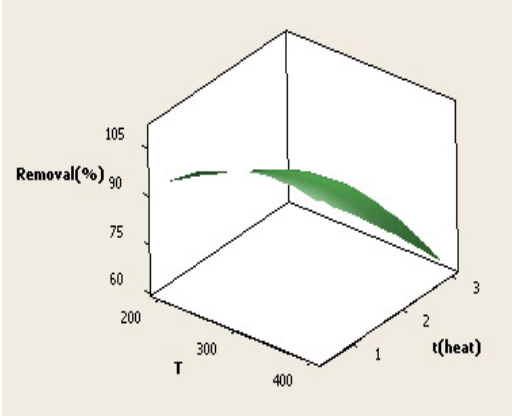

Fig. 2. 3D plot showing effect of furnace temperature and carbonization time on percentage adsorption of Congo Red.

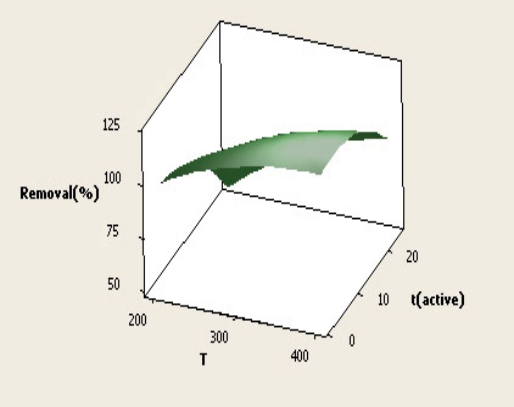

Fig. 4. 3D plot showing effect of furnace temperature and activation time on percentage adsorption of Congo Red.

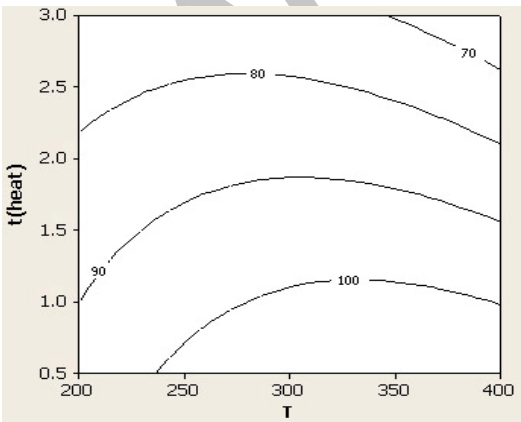

Fig. 3. Contour plot showing effect of furnace temperature and carbonization time on percentage adsorption of Congo Red.

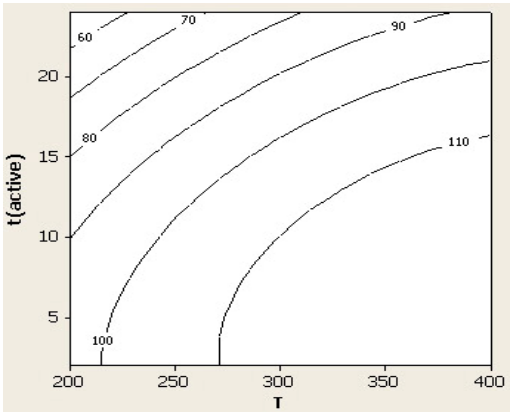

Fig. 5. Contour plot showing effect of furnace temperature and activation time on percentage adsorption of Congo Red.

Effect of furnace temperature (T) and acid ratio

Figs. 6 and 7 shows the effect of furnace temperature and acid ratio. Figs. 6, 7 shows that with increase in furnace temperature and decrease in the acid ratio, the removal percentage significantly enhance. Acid ratio effect show the minimum rise in adsorption

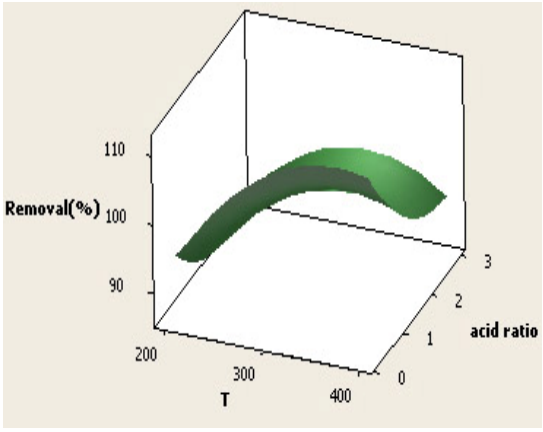

Fig. 6. 3D plot showing effect of furnace temperature and acid ratio on percentage adsorption of Congo Red.

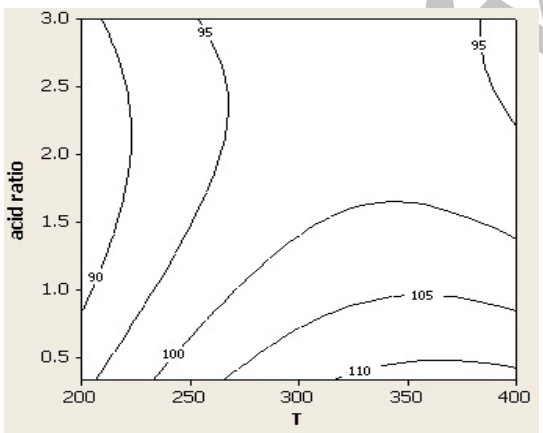

Fig. 7. Contour plot showing effect of furnace temperature and acid ratio on percentage adsorption of Congo Red.

Effect of time of carbonization and activation time

Figs.8 and 9 represents the effect of time of carbonization and activation time on the removal percentage of Congo Red. Two graphs show that with increase in carbonization time and decrease in activation time high efficiency of adsorbent was seen. These results may be attributed to the higher surface area and wide number of pores in carbon structure that significantly enhance the number of reactive atoms and adsorbent surface area.

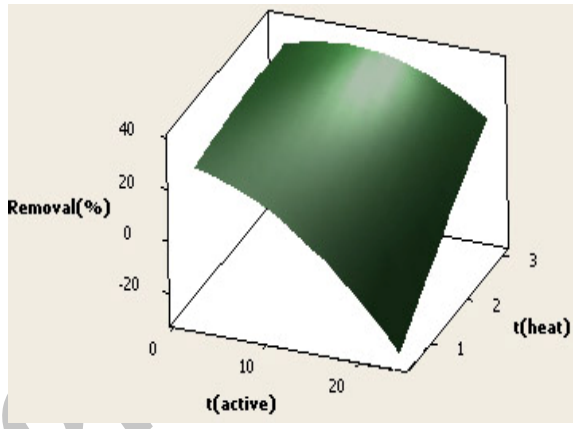

Fig. 8. 3D plot showing effect of effect of time of carbonization and activation time on percentage adsorption of Congo Red.

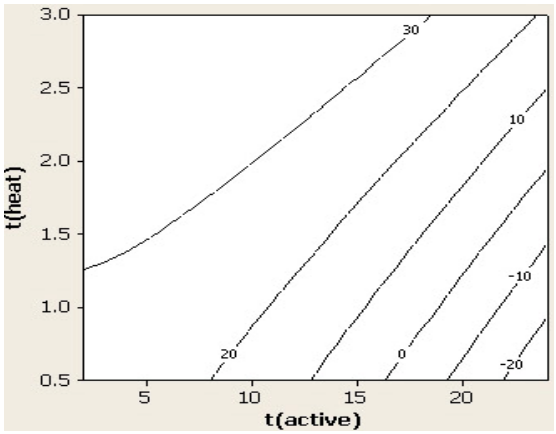

Fig. 9. Contour plot showing effect of time of carbonization and activation time on percentage adsorption of Congo Red.

Effect of time of carbonization and acid ratio

Figs.10 and 11 represents the effect of time of carbonization and acid ratio on the percentage adsorption of Congo Red. These graphs show that with increase in

carbonization time and acid ratio, the efficiency of adsorbent increased.

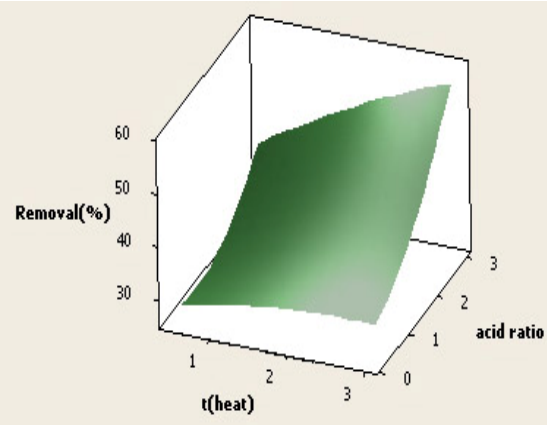

Fig. 10. 3D plot showing effect of effect of time of carbonization and acid ratio on percentage adsorption of Congo Red.

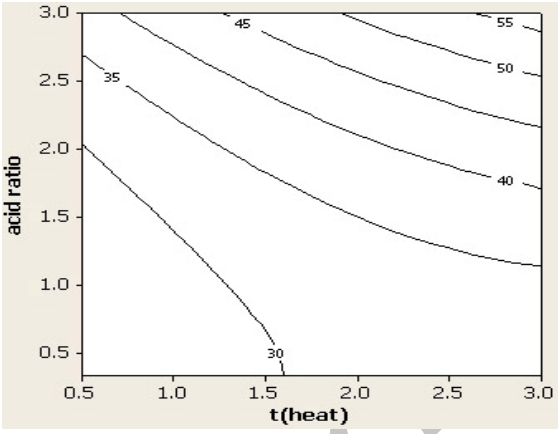

Fig. 11. Contour plot showing effect of time of carbonization and acid ratio on percentage adsorption of Congo Red.

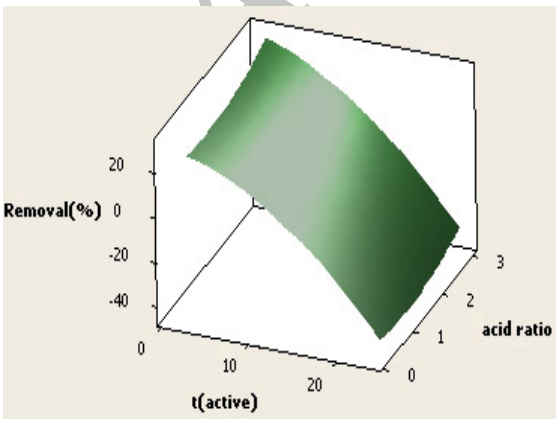

Fig. 12. 3D plot showing effect of activation time and acid ratio on percentage adsorption of Congo Red.

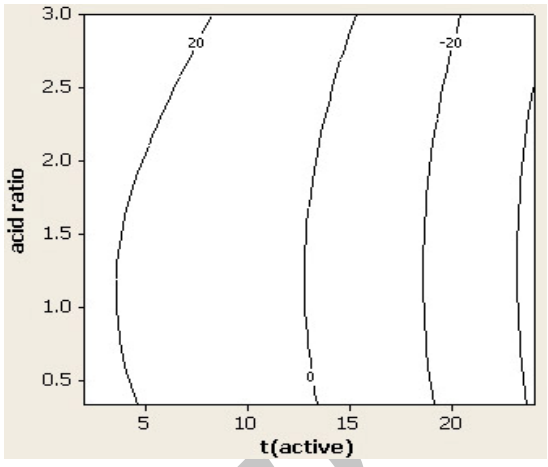

Fig. 13. Contour plot showing effect of activation time and acid ratio on percentage adsorption of Congo Red.

Effect of activation time and acid ratio

Figs.12 and 13 represents the effect of time of carbonization and acid ratio on the percentage adsorption of Congo Red. According to the Fig 12, increase in acid ratio with decrease in activation time caused the high removal efficiency.

CONCLUSIONS

The study was taken with the aim of finding the feasibility of produced carbon active from Olive stone by using Response Surface Methodological approach, which proves to be very effective and time saving technique for studying the influence of major process parameters on response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions. Results showed that we can use optimum values of activation time 2h, acid ratio 0.33, furnace temperature 200ºC and time of carbonization 0.5h to produce activated carbon from olive stone by high efficiency to removal Congo Red with initial dye concentration 15 mg/L at pH =1.5 and contact time 25 min by optimum value of adsorbent as 0.2 g.

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