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RESPONSE SURFACE METHODS OPTIMIZATION OF Ni^{2}+ ADSORPTION ON ACTIVATED CARBON PREPARED FROM HAZELNUT SHELLS

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ABSTRACT

The optimization of the adsorption of Ni^{2+} from aqueous solutions was investigated by ultrasound-assisted preparation of activated carbon from alkaline impregnated hazelnut shells. To investigate the effects of independent variables such as particle size, ultrasonic power density, impregnation ratio, impregnation time, activation temperature and activation time on the adsorption of Ni^{2+} from aqueous solutions, the experiments were designed by using the fractional factorial and central composite design method. Furthermore, the results were modelled statistically and optimized by using constrained optimization technic by means of the Matlab. The ultrasonic irradiation used for the alkaline impregnation into hazelnut shells was found to be beneficial for preparation of activated carbon for use as adsorbents to remove Ni^{2+} from aqueous solutions.

Key words: Hazelnut shell, Activated carbon, Ultrasound, Ni^{2+} adsorption, Constrained optimization

1. INTRODUCTION

Heavy metal pollution is one of the most serious environmental problems facing the world. Therefore, the heavy metal concentration in waste and potable water must be reduced to the maximum allowable level [1]. Industrial wastewaters containing heavy metals in high concentration are treated with the ion exchange, reverse osmosis, chemical neutralization and precipitation, adsorption, sorption and the membrane evaporation methods [2, 3, 4].

Adsorption by using activated carbon which is one of the oldest known methods for removal of pollutants from wastewater has gained an increasing importance in industrial applications compared to the other purification and separation methods due to its efficiency and economic feasibility [5, 6, 7]. Activated carbons are generally produced by either chemical or physical activating from various carbonaceous raw materials such as wood, peat, coal, lignite and wastes of vegetable (e.g. grape seeds, palm-tree cobs, nutshells and fruit stones) [8, 9, 10]. At first stage, in the chemical activation, a solution containing a dehydrating agent (e.g., KOH, H_2SO_4) is impregnated to the raw agricultural materials to retard the formation of tars during the carbonization process. Secondly, in the physical activation, carbonaceous materials are washed, dried and carbonized in an inert atmosphere to produce the final activated carbon [8, 9, 13, 15, 16]. The combination of the chemical and physical activation processes leads to the production of activated carbon with specific surface properties. Todays, the aim of the researches for the production of cheap and highly efficient an activated carbon is the use of cheap and readily available non-classical materials such as hazelnut shell, coconut shell, olive-waste cakes and corn cob. [5, 7, 9-17].

Nowadays, the use of ultrasound has gained increasing importance. Ultrasound has several beneficial mechanical effects in solid-liquid systems by means of the cavitation phenomenon. Therefore, ultrasound increases the surface area and cleans solid or catalyst particle surfaces by causing the formation of many micro cracks on the solid surface [18].

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The emphasis of this paper is to investigate optimum conditions of Ni^{2+} adsorption from aqueous solution on activated carbon production conditions. The adsorption experiments were designed statistically and carried out in a batch equilibrium conditions. The particle size, ultrasonic power density, impregnation ratio and time, activation temperature and time were chosen as independent variables. The regression models obtained by means of variance analysis were used in a constrained optimization to find optimum process conditions for maximum Ni^{2+} adsorption capacity.

2. MATERIALS AND METHODS

2.1. Materials

Activated carbon used in the adsorption experiments were supplied from project number 2003/38 supported by Atatürk University Research Foundation, Erzurum/Turkey [19].

2.2. Methods

Batch mode adsorption experiments for determination of the nickel ions were performed in a shaker. Samples of 200 mg of activated carbon were poured to 100 mg/L initial concentration of Ni^{2+} solution prepared by dissolving the solid $NiSO_4.6H_2O$ in distilled water in 250 mL Erlenmeyer flasks and shaked at 18 ˚C, 170 rpm for a contact time of 6 h. At the end of the experiments, the solutions of Ni^{2+} were separated from the samples activated carbons by filtering and filtrates were analyzed by using an Atomic Absorption/Flame Emission Spectrophotometer Shimadzu Model AA-670.The amount of Ni^{2+} adsorbed was calculated as follows:

$$Y_{Ni^{2+}} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where, $Y_{Ni^{2+}}$ is the amount of Ni^{2+}adsorbed onto per unit weight of adsorbent at equilibrium (mg/g); C_o is initial Ni^{2+} concentration (mg/L) and C_e is final Ni^{2+} concentration (mg/L) in solution at equilibrium time (mg/L); V the solution volume (L); m is adsorbent dosage (g).

2.3. Design of Experiments

The orthogonal central composite design was applied for fitting a second-order model. The experimental design consists of a 2^n factorial or fractional (coded to the usual ±1 notation) augmented by 2n axial points (±β,0,0. . . , 0), (0,± β,0, . . . , 0), . . . , (0, 0, . . .,± β), and m_0 center points (0, 0, 0, . . .,0), where each parameter runs at two levels [20, 21]. Meanwhile, as the number of parameters, n, increases, the number of runs for a complete replicate of the design increases rapidly. In this case, main effects and low-order interactions may be estimated by fractional factorial designs by assuming high-order interactions negligible. Individual second order effects cannot be estimated separately by 2^n factorial designs. Therefore, the central composite design was applied in this study using expressions as described in our previous detailed papers [22-25]. The responses and the corresponding parameters were modelled and optimized by using constrained optimization program by means of the Matlab and statistical computer software by means of response surface methods.

3. RESULTS AND DISCUSSION

In the light of pre-experiments, six parameters, namely, particle size (X_1), ultrasonic power density (X_2), impregnation ratio (X_3), impregnation time (X_4), activation temperature (X_5) and activation time (X_6) were chosen as the independent parameters for response analysis and modeling of Ni^{2+} adsorption from aqueous solutions on activated carbon prepared from ultrasound-assisted alkaline impregnated hazelnut shell. The parameter levels with coded values were shown in Table 1.

Table 1. The parameter levels with coded values

Parameter		+β	+1	0	-1	-β
Particle size (mm)	X_1	1.85	1.55	1.29	0.93	0.78
Ultrasonic power density (W/L)	X_2	190	76	19	6	2
Impregnation ratio (g/mL)	X_3	0.06	0.05	0.038	0.025	0.015
Impregnation time (min)	X_4	143	120	90	60	37
Activation temperature (^{0}C)	X_5	839	800	750	700	661
Activation time (min)	X_6	72	60	45	30	18

The central composite design was applied to estimate main effects and second-order effects as well as interaction effects for modeling of Ni^{2+} adsorption from aqueous solutions on activated carbon prepared from ultrasound-assisted alkaline impregnated hazelnut shell. As usual, the selected experiments were performed in random order to minimize the effect of systematic error. Furthermore, three central replicates were also employed to calculate pure experimental error. The experimental results were evaluated by using constrained optimization program by means of the Matlab and statistical computer software by means of response surface methods. The second order models obtained by regression analysis of Ni^{2+} adsorption from aqueous solutions on activated carbon are given as follows.

$$\begin{aligned} \mathbf{Y}_{Ni}^{2+} = {} & 7.07857 + 0.5872\,X_1 + 0.3190\,X_2 - 0.3833\,X_3 + 0.6992\,X_4 - 0.4980\,X_5 \\ & - 0.4782\,X_6 - 0.2327\,X_1X_1 - 0.2709\,X_2X_2 - 0.2422\,X_3X_3 - 0.3555\,X_4X_4 \\ & + 0.0033\,X_5X_5 - 0.4703\,X_6X_6 + 0.3494\,X_1X_2 - 0.7406\,X_1X_3 + 0.5706\,X_1X_4 \\ & - 0.3444\,X_1X_5 + 0.3031\,X_1X_6 - 0.3444\,X_2X_3 + 0.0269\,X_2X_4 - 0.7406\,X_2X_5 \\ & - 1.2356\,X_2X_6 - 1.2356\,X_3X_4 + 0.3494\,X_3X_5 + 0.0269\,X_3X_6 + 0.3031\,X_4X_5 \\ & - 0.3444\,X_4X_6 + 0.5706\,X_5X_6 \end{aligned} \quad (2)$$

3.1. Effects of Parameters

Contours of fitted second-order Eq. (2) and data from second-order design have been used to visualize the effects of independent parameters on removal of Ni^{2+} adsorption from aqueous solutions on activated carbon prepared from ultrasound-assisted alkaline impregnated hazelnut shell under experimental conditions in response surface contour plots of Figures. 1.

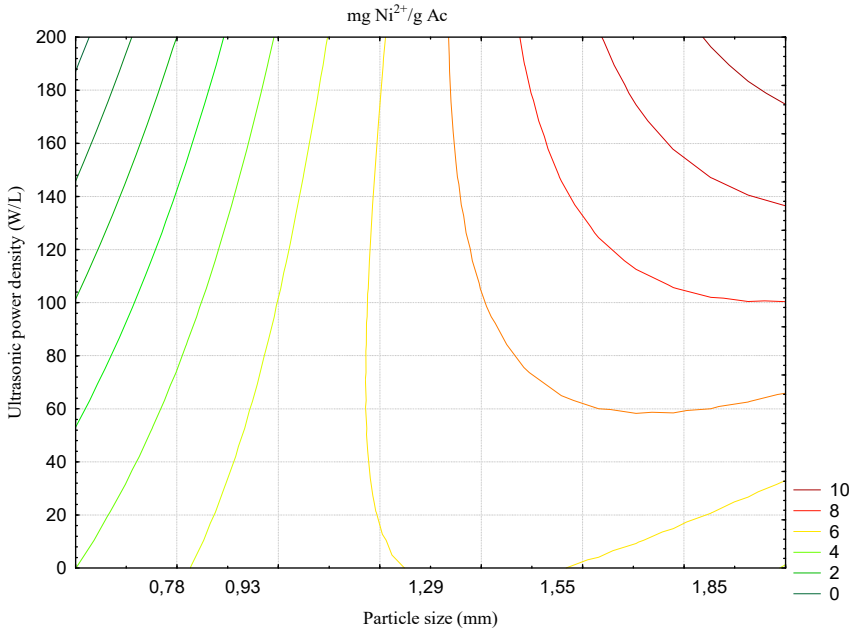

Figure 1.a. Response surface contour plots for the effects of ultrasonic power density and particle size

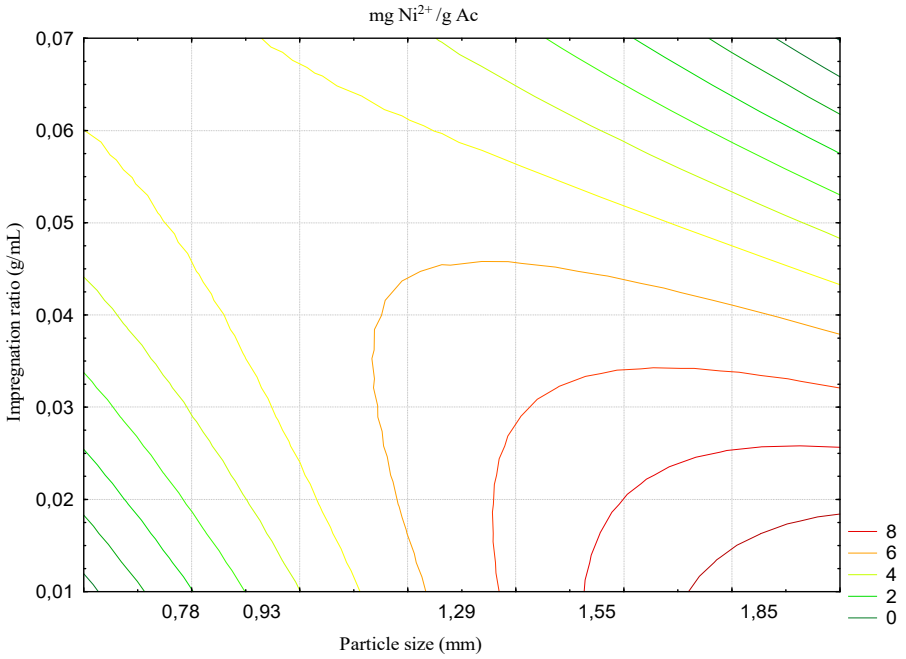

Figure 1.b. Response surface contour plots for the effects of impregnation ratio and particle size

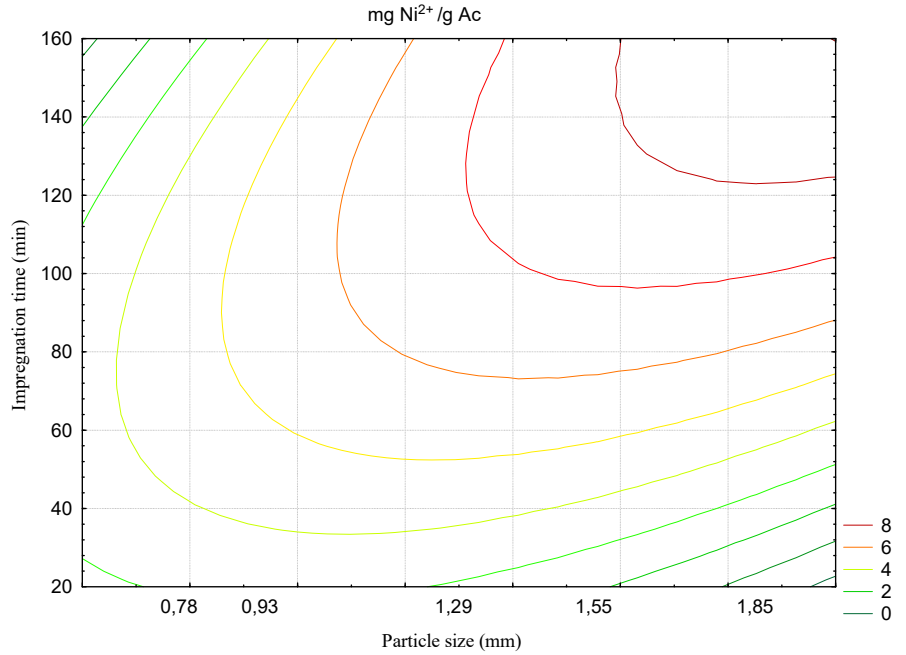

Figure 1.c. Response surface contour plots for the effects of impregnation time and particle size

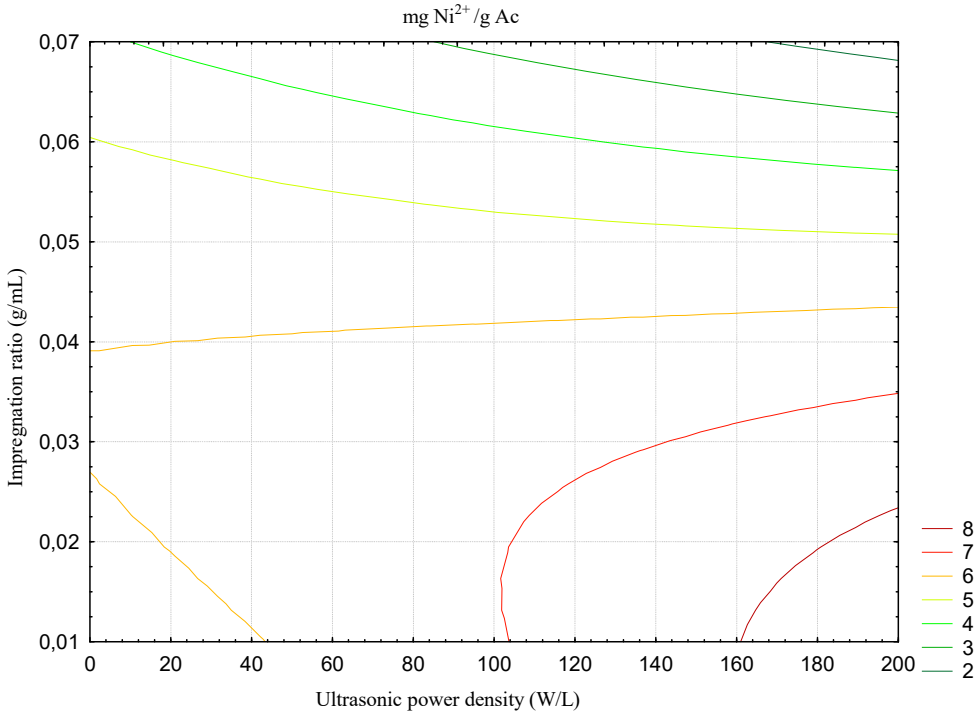

Figure 1.d. Response surface contour plots for the effects of impregnation ratio and ultrasonic power density

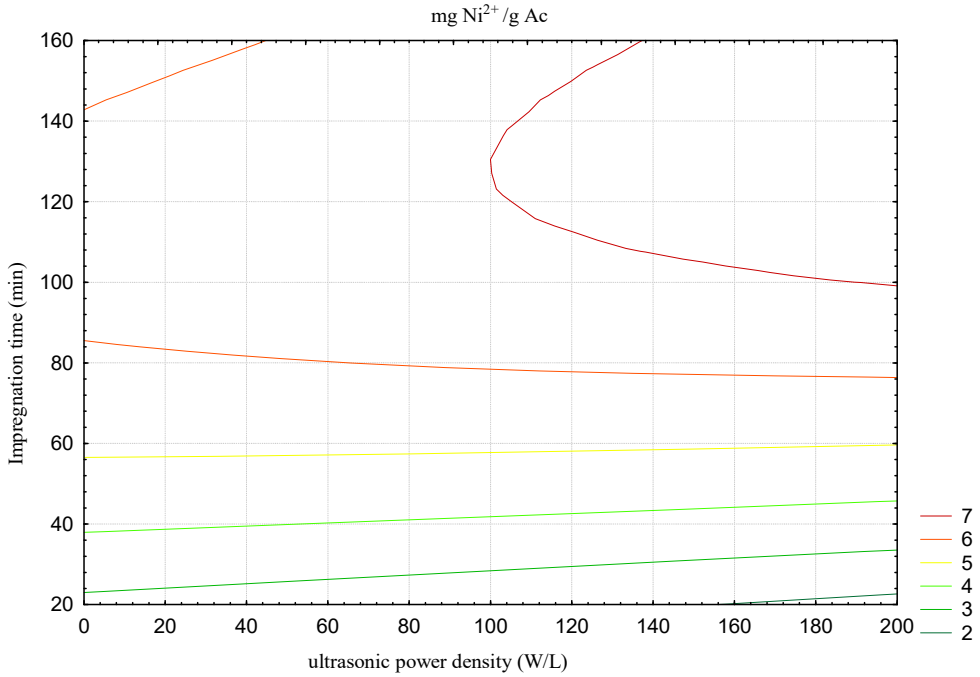

Figure 1.e. Response surface contour plots for the effects of impregnation time and ultrasonic power density

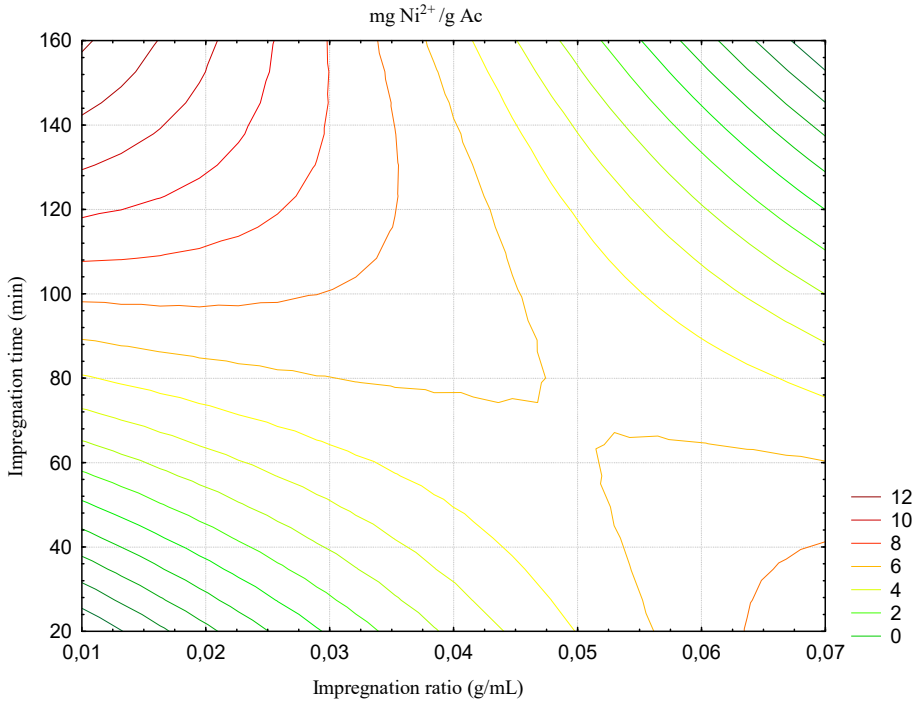

Figure 1.f. Response surface contour plots for the effects of impregnation time and impregnation ratio

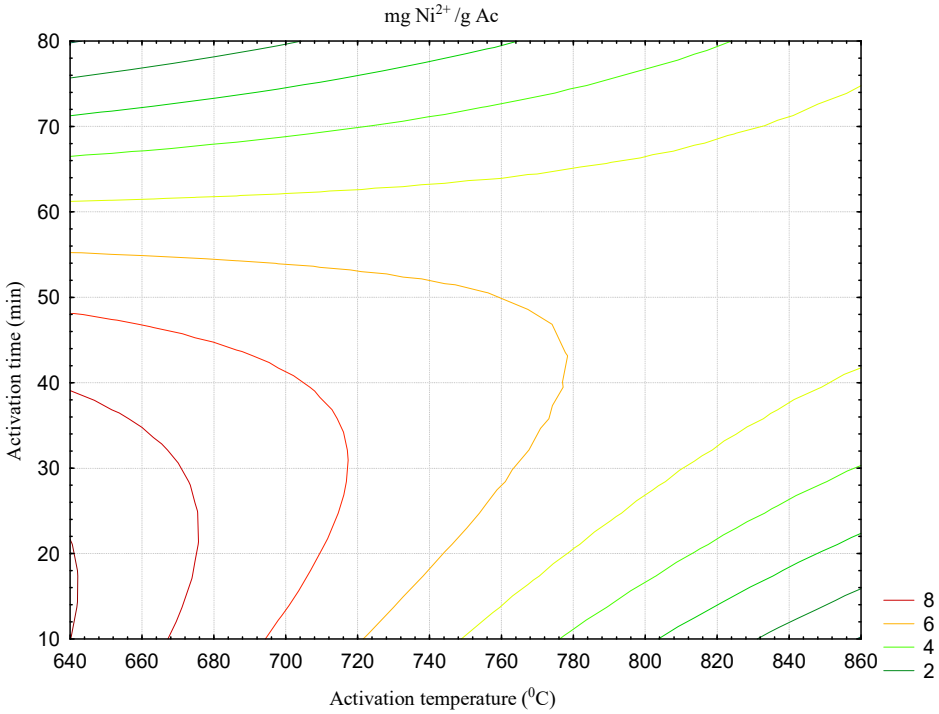

Figure 1.g. Response surface contour plots for the effects of activation time and activation temperature

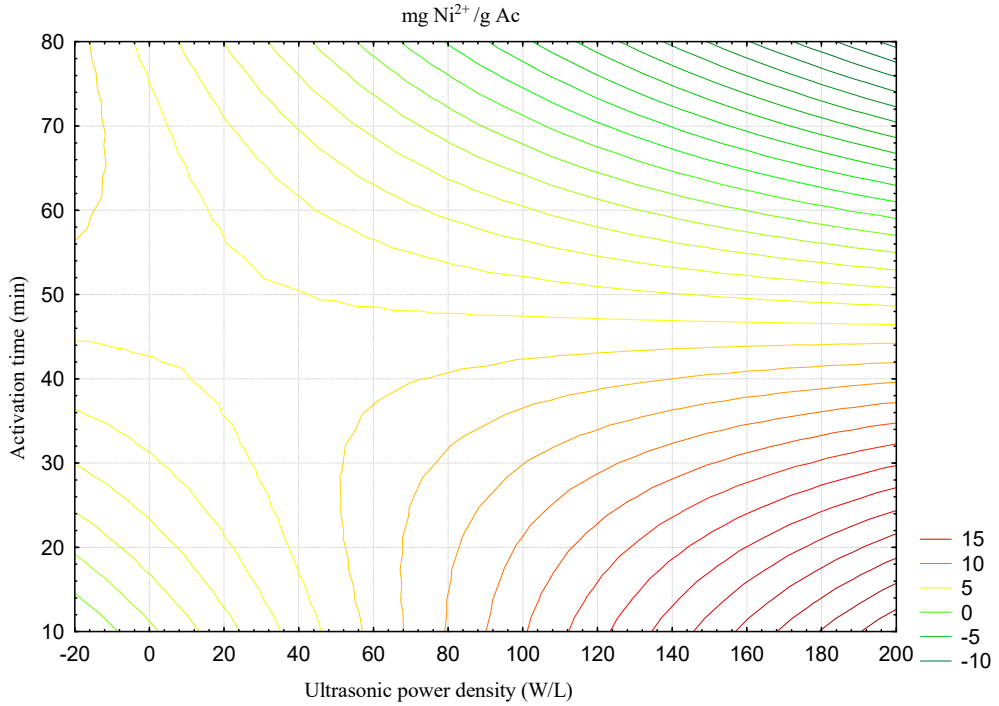

Figure 1.h. Response surface contour plots for the effects of activation time and ultrasonic power density

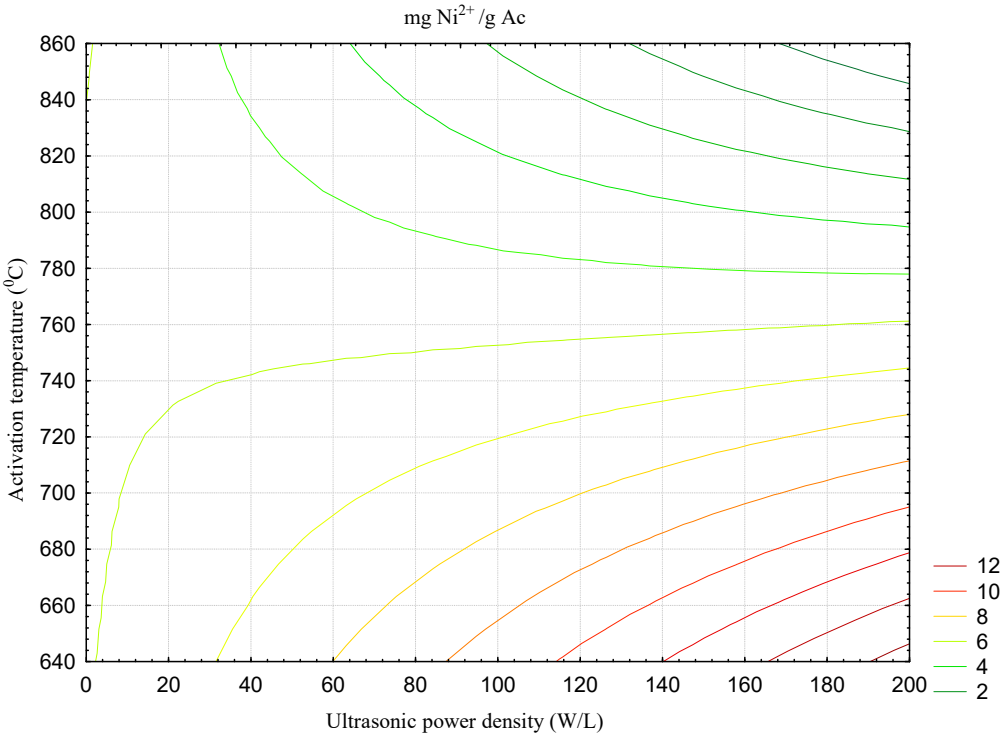

Figure 1.i. Response surface contour plots for the effects of activation temperature and ultrasonic power density

In Figure 1.a., it is seen that the increase of ultrasonic irradiation in the alkaline impregnation step to prepare activated carbon from hazelnut shell (especially 1,55 mm-1,85 mm particle size) increased the amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions. In Figure 1.b., the amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the decrease of alkaline impregnation ratio for chemical activation of hazelnut shells (1,29 mm–1,85 mm particle size). The amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the increase in impregnation time (80 min–160 min) and particle size (1,29 mm–1,85 mm) as shown in Figure 1.c. In Figure 1.d., the amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the decrease in impregnation time and increased with the increase in ultrasonic power density. The amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the increase in ultrasonic power density and increased with increase in impregnation time especially between 80 min and 140 min as shown in Figure 1.e. The amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the increase in impregnation time and increased with the decrease in impregnation ratio as shown in Figure 1.f. This behavior could be attributed to the ratio of alkaline impregnation to hazelnut shell which is important in sonication. The diffusion of KOH solution into the pores entails an opening and enlargement pores, which enhance the adsorption of $^{2+}$ from aqueous solutions. In Figure 1.g., the amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the increase in activation time (especially between10 min and 50 min) and increased with the decrease in activation temperature especially between 640 0C and 720 ^{0}C. The amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the increase in ultrasonic power density (especially between 60W/L and 190W/L) and increased with the decrease in activation time especially between 10 min and 40 min, as shown in Figure 1.h. In Figure 1.i., the amount of adsorbed mg Ni^{2+}/g Ac from aqueous solutions increased with the increase in ultrasonic power density especially above 100 W/L and increased with the decrease in activation temperature especially under 700 ^{0}C.

The enhancement of adsorption mg Ni^{2+}/g Ac from aqueous solutions on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell was attributed to higher diffusion of KOH solution into the pores of the hazelnut shells, higher surface area with the formation of many micro-cracks on the hazelnut shells surface and cleaner solid particle surfaces produced by cavitation process under ultrasound irradiation [18].

3.2. Surface Characterization of the activated carbon

Figure 10 shows the SEM micrographs of the activated carbon. Figure 10.a shows the surface of the raw hazelnut shell, whilst Figure 10.b shows the surface of activated carbon adsorbed Ni^{2+} from aqueous solution. It can be seen from the micrographs that the external surface of this carbon is full of cavities because of mechanical effects of ultrasound. It seems that the cavities on the surface resulted from the evaporation of KOH during carbonization, leaving the space previously occupied by KOH. It seems that the cavities on the surface are occupied full of nickel. BET surface areas of the raw and activated carbon from hazelnut shell were calculated to be 0.188 and 8 m^2/g, respectively. Considering BET surface areas, the surface area of the activated carbon is approximately 43 times greater than raw hazelnut shell surface area. In conclusion, it is considered that the surface area and adsorption capacity can be increased for activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for heavy metal removal from aqueous solutions.

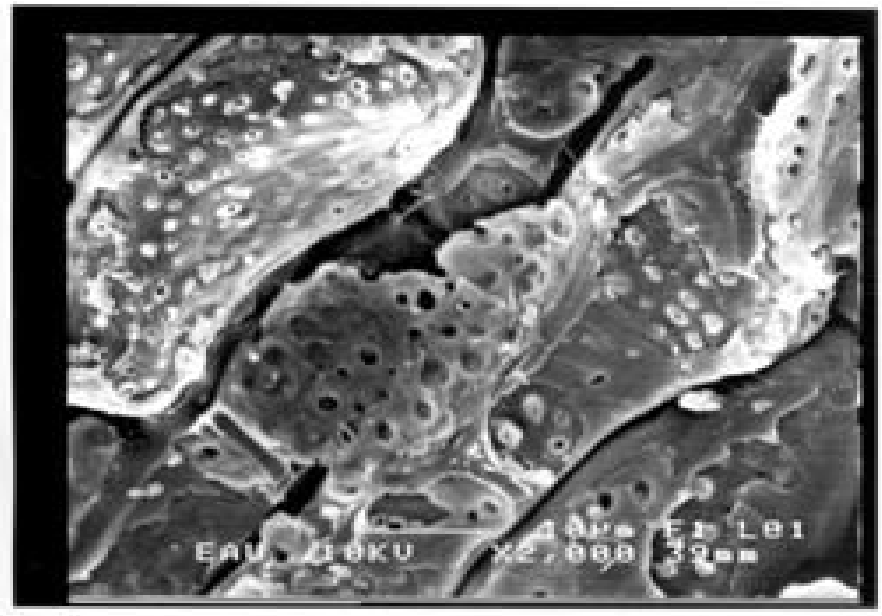

Figure 10 a. The SEM micrographs (2000X) of the raw hazelnut shell surface

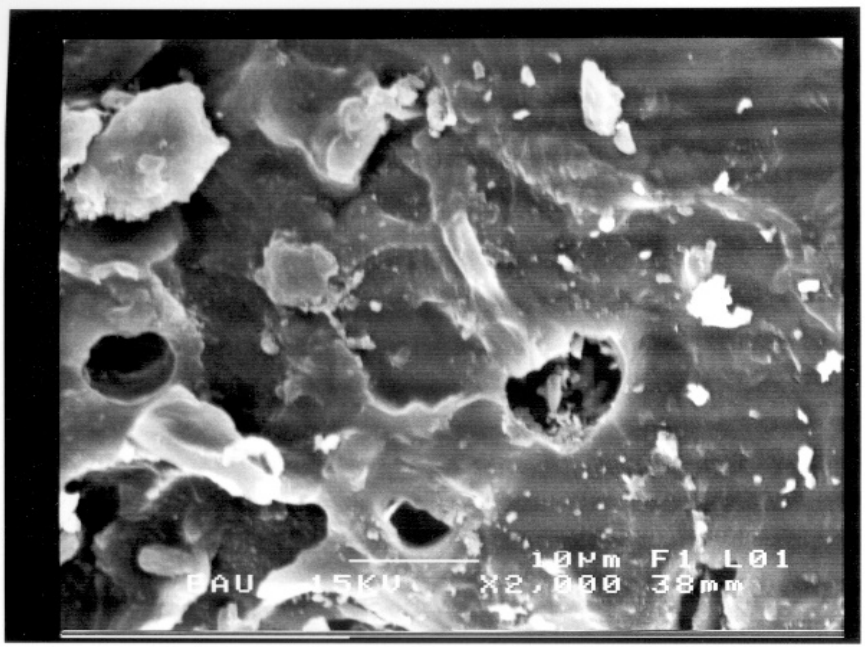

Figure 10 b. The SEM micrographs (2000X) of activated carbon with maximum adsorption capacity

3.3. Optimization Results

The main objective of this study is to determine the optimum process conditions to remove Ni^{2+} from aqueous solutions. Firstly, it was to set up the response value from the models obtained experimentally. Then, using the above mentioned methodology for experimental design, the ranges of the parameters required to obtain this optimum activated carbon were determined. Amount of the adsorbed mg Ni^{2+}/g Ac from aqueous solutions were chosen as the objective function in this optimization study.

Furthermore, optimum conditions were calculated in the presence of some constraints on the parameters X_i (–β and +β values) given in Table 1. Thus, the optimization problem is defined as follows;

- Maximize Y_{Ni}^{2+} (3)

- Constraints on the parameters X_i;

$$-\beta_i < Xi < +\beta_i \qquad i = 1....6 \tag{4}$$

The optimization problem in Equation (3) was solved using constrained optimization program supplied in the Matlab optimization toolbox. These results show that the higher (+β) bound particle size, ultrasonic power density, impregnation time and the lower (-β) bound carbonization temperature, carbonization time and impregnation ratio are sufficient for optimum activated carbon from hazelnut shell for use as adsorbents to remove Ni^{2+} from aqueous solution. The optimum process conditions are given in Table 2 by taking into account the model established with effective parameters obtained by variance analysis tested at 90% confidence level. Maximum adsorption capacity of activated carbon from alkaline impregnated hazelnut shell under ultrasound was 27 mg Ni^{2+}/g Ac, whereas maximum adsorption capacity of raw hazelnut shell and activated carbon from alkaline impregnated hazelnut shell under the same process conditions (Table 2) without ultrasound application was found as 4 and 21 mg Ni^{2+}/g Ac, respectively. According to these results, the adsorption capacity of the activated carbon from alkaline impregnated hazelnut shell under ultrasound is approximately 7 times greater than raw hazelnut shell and thirty percent greater than that of the adsorption capacity of activated carbon from alkaline impregnated hazelnut shell without ultrasound. In conclusion, the application of ultrasonic irradiation in the impregnation step was found to be beneficial to prepare with high adsorption capacity activated carbon for use as adsorbent to remove Ni^{2+} from aqueous solutions.

Table 2. The optimum process conditions to prepare activated carbon from hazelnut shell for use as adsorbents to remove Ni^{2+} from aqueous solution

Particle size (mm)	Ultrasonic power density (W/L)	Impregnation ratio (g/ml)	Impregnation time (min)	Activation temperature (^{0}C)	Activation time (min)	Adsorbed mg Ni^{2+}/g Ac
1.75	120	0.0168	143	661	18	27

For the sake of comparison, Table 3 presents comparative values of nickel adsorption capacity for some adsorbents [26-30]. The comparison of the experimental adsorption capacity obtained in this study with the data in the literature for various adsorbents shows that activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell is an effective adsorbent of Ni^{+2} from aqueous solutions.

Table 3. The Nickel adsorption capacities of some adsorbents from the aqueous solutions

Adsorbent	**Adsorption capacity (mg/g)**	**Reference**
Carbon anode dust	8.64	[26]
Fly ash	0.99	[27]
Magnetite	18.43	[28]
Activated slag	30	[29]
Calcined phosphate	15.53	[30]
Red mud	13.69	[30]
Clarified sludge	14.30	[30]
Activated carbon	27.08	This work

4. CONCLUSION

In this paper, the adsorption of nickel ions on activated carbons prepared from ultrasound-assisted KOH-impregnated hazelnut shell was studied in a batch equilibrium conditions. For this goal, the experimental parameters, particle size, ultrasound power, impregnation ratio, impregnation time, activation temperature and activation time have been explored by statistically designed experiments. The 2^{6-2} orthogonal fractional factorial design and central composite design were used to found second order model relating amount of the adsorbed mg Ni^{2+}/g Ac from aqueous solutions. Furthermore, optimum conditions required to prepare activated carbon suitable for use as adsorbents to remove Ni^{2+} from aqueous solutions were calculated in the presence of some constraints on the parameters. Optimum process conditions were obtained as follows: particle size 1.75 mm, ultrasonic power density 120 W/L, impregnation ratio 0.0168 g/mL, impregnation time 143 min, activation temperature 661 ^{o}C and activation time 18 min, following with maximum adsorption capacity was found as 27 mg Ni^{2+}/g Ac. Based on the results, particle size, ultrasonic power density and impregnation time have a positive effect, while impregnation ratio, activation temperature and activation time have a negative effect on the Ni^{2+} adsorption of prepared activated carbon. In conclusion, it show that the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell is an effective adsorbent for removal of Ni^{+2} from aqueous solutions when the optimization results compared to literature.

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