An Optimization Study on Removal of Zn^{2+} from Aqueous Solution by Ultrasound-Assisted Preparation of Activated Carbon from Alkaline Impregnated Hazelnut Shell

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Summary: Nowadays, ultrasound has gained importance in a wide variety of industrial fields especially in wastewater and sewage treatment. Ultrasound exhibits several beneficial effects in solid–liquid systems by means of the cavitations phenomenon by causing the formation of many microcracks on the solid surface; thus, it increases the surface area between the reactants and cleans solid reactant or catalyst particle surfaces. In this study, activated carbon adsorbent for removing heavy metal cations such as Zn^{2+} from aqueous solutions has been prepared. For this purpose, KOH solution was impregnated into hazelnut shells under ultrasonic irradiation. After filtration, hazelnut shells have been carbonized under inert N_2 atmosphere. The experiments were planned by statistical design methods. Finally, activated carbons were characterized by the evolution of their zinc adsorption capacity. Optimum preparation conditions were obtained by using constrained optimization program by means of the Matlab computer software. Activated carbon with the maximum adsorption capacity was further characterized by using scanning electron microscopy. The alkaline impregnation into hazelnut shells under ultrasonic irradiation was found to be beneficial for preparation of activated carbon for use as adsorbents to remove Zn^{2+} from aqueous solutions.

Keywords: Hazelnut shell, activated carbon, ultrasound, zinc adsorption, statistical modeling, optimization.

Introduction

The aqueous solutions are widely found in every industrial and laboratory scales. Hence, it is considered to contaminate a diverse range of organic, inorganic, metallic and biological effluents of all classes and properties, and cause serious disposal problems for environment. Pollution by heavy metals is one of the most serious environmental problems facing life of earth. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. For this reason, the concentration of heavy metals in waste water and drinking water as water used for agriculture must be reduced to the maximum permissible concentration [1]. There are many purification and separation methods (e.g. adsorption, chlorination, chemical oxidation and air stripping or aeration) to remove of pollutants from wastewater. Adsorption has gained an increasing importance as a purification and separation process on industrial applications recently [2]. One of the oldest methods for removal of pollutants from wastewater is using porous solid adsorbents. The properties of porous solids that render them useful for water treatment include high porosity and surface activity as well as the physical and chemical nature of the adsorptive surfaces. The ability of many porous substances to adsorb vapors in large quantities has been recognized since the 18th century [3], but application on an industrial scale has been more recently enhanced by the advancement in studies of adsorption fundamentals. Compared with the other purification and separation methods, adsorption has demonstrated efficiency and economic feasibility as a wastewater treatment operation. Adsorption still remains one of the more novel chemical engineering processes in water purification, separation, mineral beneficiation, soil conversation, and many other process areas even though the concept of appliying the adsorption process to treat wastewater and gases has been realized for many years.

Generally, granular activated carbon(GACs) were produced by activating either chemical activating or physical activating from various carbonaceous raw materials such as wood, peat, coal, lignite, and wastes of vegetable origin (e.g. grape seeds, palm-tree cobs, nutshells and fruit stones) as the two major resources [4-6]. Today, one promising approach for the production of cheap and highly efficient activated carbon is the use of cheaper and readily available non-classical materials such as hazelnut shell, coconut shell, olive-waste cakes and corn cob [5, 7-15]. The combination of the chemical and physical activation processes leads to the production of activated carbon with specific surface properties. The first step involves a chemical activation step where raw agricultural materials are

impregnated with a solution of dehydrating agent (for example $ZnCl_2$, H_2SO_4) to retard the formation of tars during the carbonization process. Furthermore in physical activation, they are washed, dried and carbonized in an inert atmosphere to produce the final activated carbon [4, 5, 9, 13, 16].

It is now widely accepted that ultrasound power has great potential for uses, in addition to conventional applications in cleaning and plastic welding, in a wide variety of industrial fields such as electrochemistry, food technology, nanotechnology, chemical synthesis, dissolution and extraction, dispersion of solids, phase separation, water and sewage treatment [17]. Ultrasound produces its mechanical and chemical effects through the formation and collapse of "cavitations" bubbles [18]. A significant amount of research has been published concerning with this "sonochemical effect", and collected in various recent books [19, 20]. Ultrasound exhibits also several beneficial mechanical effects in solid-liquid systems by means of the cavitations phenomenon by causing the formation of many microcracks on the solid surface, it increases the surface area between the reactants and cleans solid reactant or catalyst particle surfaces; thus, it enhances mass transfer rates [21].

The emphasis of this paper is to prepare the activated carbon from hazelnut shells for use as adsorbents to remove Zn^{2+} from aqueous solution. Alkaline impregnation was used as pre-chemical activation and ultrasound irradiation was especially applied in this step to enhance the diffusion of KOH solution into the pores of the cellulosic material. After this step, hazelnut shells were washed, dried and carbonized under inert N_2 atmosphere. Activated carbons prepared in this way were characterized by their zinc adsorption capacity, scanning electron microscopy and BET surface examination method. The experiments were planned by using statistical design method. The particle size, ultrasound power, impregnation ratio and time, activation temperature and time were chosen as independent parameters. The regression models obtained by means of variance analysis were used in a constrained optimization to find optimum process conditions for maximum adsorption capacity.

Results and Discussion

A series of activated carbon suitable for use as adsorbents to remove Zn^{2+} from aqueous solutions were prepared for experiments. The production method, characterization and methodology of experimental design were described below.

Experimental Design Method

In generally, the orthogonal central composite design was widely applied for fitting a second-order model. By using this method, modeling is possible and it requires only a minimum number of experiments. It is not necessary in the modeling procedure to know the detailed reaction mechanism since the mathematical model is empirical. Each variable runs at two levels [22]. These designs consist 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) [22, 30]. Meanwhile, as the number of factors, n, increases, the number of runs for a complete replicate of the design increases rapidly. In this case, main effects and interactions may be estimated by fractional factorial designs running only a minimum number of experiments. Individual second-order effects can not be estimated separately by 2^n factorial designs. Therefore, the central composite design was employed in this study using expressions as described in detailed in previous experimental studies [31-33]. The responses and the corresponding parameters were modelled and optimized using Matlab and statistical computer software by means of response surface methods.

Response Analysis and Modeling

In the light of pre-experiments, six parameters, namely, particle size (X_1), ultrasound power (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 Zn^{2+} adsorption from aqueous solutions by ultrasound-assisted preparation of activated carbon from alkaline impregnated hazelnut shell. The parameter levels with coded values were shown in Table-1. Initially, the ¼ 2^6 orthogonal fractional factorial design were applied to estimate both main effects and interaction effects. Furthermore, three central replicates were also employed to calculate pure experimental error. As usual, the experiments were carried out in a random order to minimize the effect of systematic error. The analysis of variance reveals that quadratic terms were effective on production of activated carbon from hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solution, the orthogonal central composite design was planned to estimate quadratic terms separately because central composite design may be 'built up' from the first-order design (2^n) by adding the axial points and perhaps several points [22]. The experimental design matrix and the corresponding experimental parameters and response

value were shown in Table-2. The experimental results were analyzed by using the Matlab computer software. The full second order model relating process response to process parameters obtained by regression analysis is as follows.

Table-1: Parameter levels (coded values) used in the experimental design.

Parameter		+β	+1	0	-1	-β
Particle size (mm)	X_1	1.85	1.55	1.29	0.93	0.78
Ultrasound power (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

*some variable levels were rounded based on the sensitivity of the equipment

$$\mathbf{Y}_{Zn^{2+}} = 17.5423 - 0.6963X_1 + 1.2339X_2 - 0.5237X_3 - 0.345X_4 - 1.6023X_5 + 0.5021X_6 - 0.8872X_1^2 - 0.6719X_2^2 + 0.1381X_3^2 - 2.3224X_4^2 + 0.7824X_5^2 + 0.0504X_6^2 + 0.6287X_1X_2 - 0.1112X_1X_3 - 0.6475X_1X_4 - 1.1375X_1X_5 - 1.9025X_1X_6 - 1.1375X_2X_3 - 0.1888X_2X_4 - 0.1112X_2X_5 - 3.2687X_2X_6 - 3.2687X_3X_4 + 0.6287X_3X_5 - 0.1888X_3X_6 - 1.9025X_4X_5 - 1.1375X_4X_6 - 0.6475X_5X_6 \quad (1)$$

This full second-order model with 27 factors fits the experimental results very well and the correlation coefficient (r^2) of model obtained in this case is 0.9999. However, a simpler model with fewer factors and with a high r^2 value may also be found by means of analysis of variance. For this purpose, the model established with effective parameters obtained by variance analysis tested at 90% confidence level was given as follows. The correlation coefficient (r^2) of model obtained in this case is 0,9933.

$$\mathbf{Y}_{Zn^{2+}} = 17.7571 + 1.2339X_2 - 1.6023X_5 - 0.8872X_1^2 - 2.3224X_4^2 - 1.1375X_1X_5 - 1.9025X_1X_6 - 1.1375X_2X_3 - 3.2687X_2X_6 - 3.2687X_3X_4 - 1.9025X_4X_5 - 1.1375X_4X_6 \quad (2)$$

This simpler model with 11 factors was as adequate as full second-order model to estimate responses in all experiments. In this model as a simpler model with fewer factors for a well-established, systematic errors are absent, and normalized residuals result from experimental errors which exhibit a normal distribution according to a widely accepted statistical convention.

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 Zn^{2+} from aqueous solution by ultrasound-assisted preparation of activated carbon from alkaline impregnated hazelnut shell under experimental conditions in response surface contour plots of Figs. 1–7. In Fig. 1, it is seen that the increase of ultrasound irradiation in the alkaline impregnation step to prepare activated carbon from hazelnut shell (1,29 mm–1,55 mm particle size) increased the amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions. In Fig. 2, The amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the decrease of alkaline impregnation ratio for chemical activation of hazelnut shells (0,93 mm–1,29 mm particle size). The amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the increase in impregnation time (80 min–100 min) and particle size (0,93 mm–1,29 mm) as shown in Fig. 3. In Fig. 4, the amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the decrease in impregnation time and increased with the increase in ultrasound power. The amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the increase in ultrasound power and increased with increase in impregnation time especially between 80 min and 100 min as shown in Fig. 5. The amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the increase in impregnation time and increased with the decrease in impregnation ratio as shown in Fig. 6. In Fig. 7, the amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the increase in activation time and increased with the decrease in activation temperature especially between 660 ^{0}C and 680 ^{0}C.

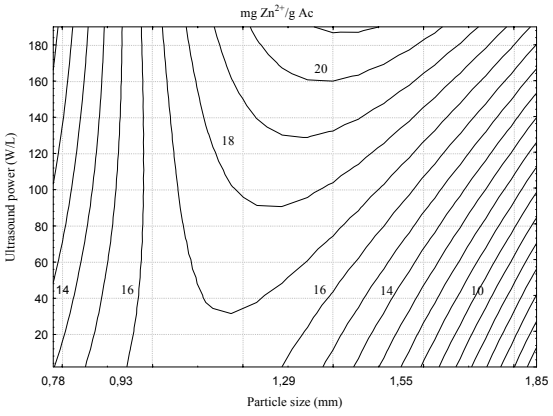

Fig.1: Response surface contour plots for the effects of ultrasound power and particle size on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

Table-2: Experimental design matrix and response value.

Exp. no	Particle size (mm)	Ultrasound power (W/L)	Impregnation ratio (g/mL)	Impregnation time (min)	Activation temperature (^{0}C)	Activation time (min)	Adsorbed mg Zn^{2+}/g Ac
3	-1	1	-1	-1	1	1	16.32
4	1	1	-1	-1	-1	1	13.53
15	-1	1	1	1	-1	1	16.77
10	1	-1	-1	1	1	1	13.08
8	1	1	1	-1	1	-1	17.16
6	1	-1	1	-1	-1	1	20.16
11	-1	1	-1	1	1	-1	12.42
5	-1	-1	1	-1	1	1	17.97
16	1	1	1	1	1	1	6.36
9	-1	-1	-1	1	-1	1	21.75
1	-1	-1	-1	-1	-1	-1	8.52
13	-1	-1	1	1	1	-1	9.69
14	1	-1	1	1	-1	-1	8.96
2	1	-1	-1	-1	1	-1	6.24
12	1	1	-1	1	-1	-1	22.59
7	-1	1	1	-1	-1	-1	13.56
31	-1.7707	0	0	0	0	0	18.06
23	1.7707	0	0	0	0	0	14.34
22	0	-1.7707	0	0	0	0	12.6
21	0	1.7707	0	0	0	0	21.15
28	0	0	-1.7707	0	0	0	21.63
25	0	0	1.7707	0	0	0	17.2
29	0	0	0	-1.7707	0	0	13.35
27	0	0	0	1.7707	0	0	10.05
24	0	0	0	0	-1.7707	0	24
26	0	0	0	0	1.7707	0	18.87
30	0	0	0	0	0	-1.7707	23.55
20	0	0	0	0	0	1.7707	14.73
1^0	0	0	0	0	0	0	15.66
2^0	0	0	0	0	0	0	15.43
3^0	0	0	0	0	0	0	13.29
Raw	hazelnut	shell					2.4

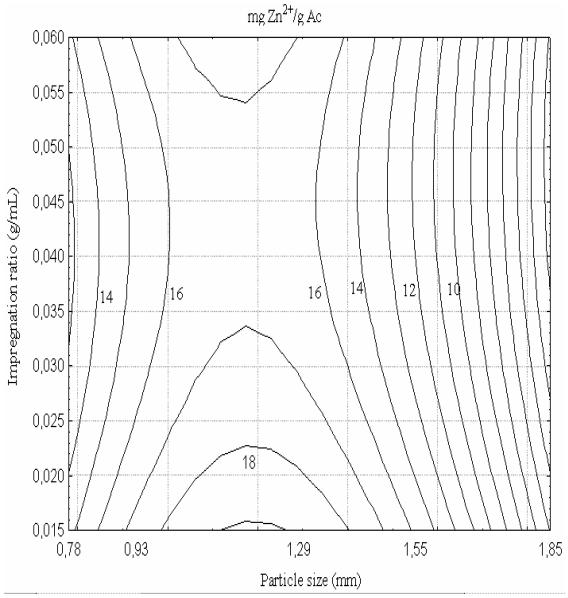

Fig. 2: Response surface contour plots for the effects of impregnation ratio and particle size on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions

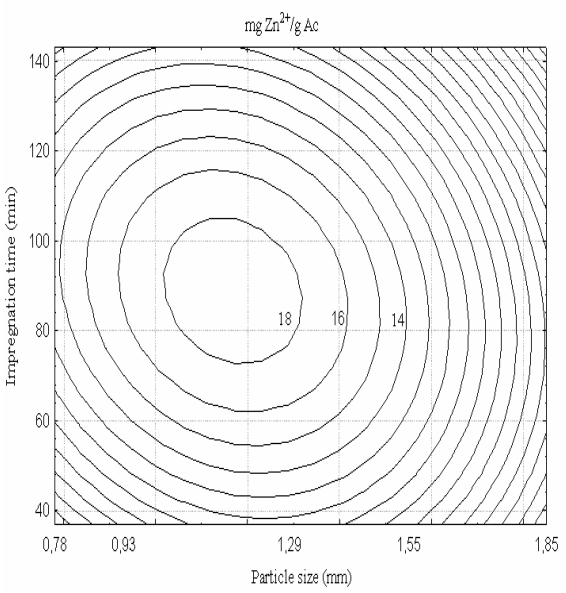

Fig. 3: Response surface contour plots for the effects of impregnation time and particle size on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

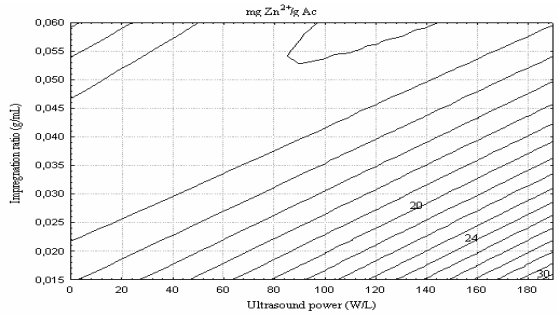

Fig. 4: Response surface contour plots for the effects of impregnation ratio and ultrasound power on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

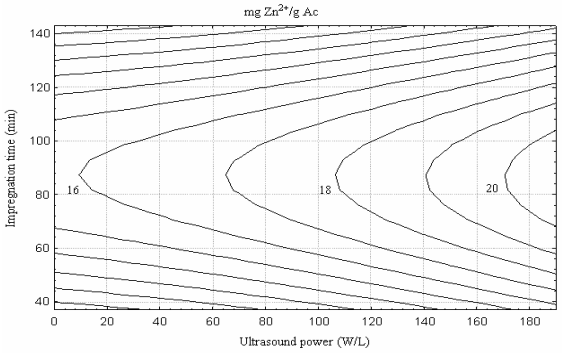

Fig. 5: Response surface contour plots for the effects of impregnation time and ultrasound power on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

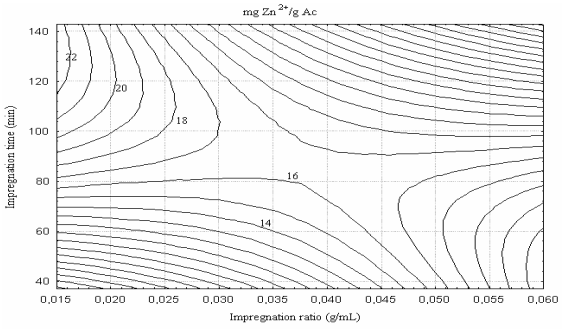

Fig. 6: Response surface contour plots for the effects of impregnation time and impregnation ratio on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

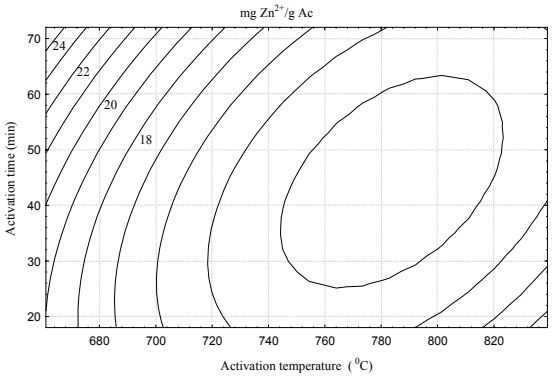

Fig. 7: Response surface contour plots for the effects of activation time and activation temperature on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

The enhancement of adsorption mg Zn^{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 [21]. The amount of adsorbed mg Zn^{2+}/g Ac from aqueous solutions increased with the increase in impregnation time and increased with the decrease in impregnation ratio. 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 Zn^{2+} from aqueous solutions.

Fig. 8 illustrates the graphical representation of 'size effect' of significant main, second order and interaction terms on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell as adsorbents to remove Zn^{2+} from aqueous solutions. From Fig. 8, it can be seen that ultrasound power (W/L) (X_2) has a positive effect, while activation temperature (X_5) has a negative effect on response, in the way of amount of the adsorbed mg Zn^{2+}/g Ac from aqueous solutions. The second order term and interaction terms in Eq. (2) affect to process at various ratios. The activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for maximum adsorption of Zn^{2+} from aqueous solutions was obtained at high ultrasound power, low activation temperature and medium level concerning

the other parameters as shown in above mentioned Figures.

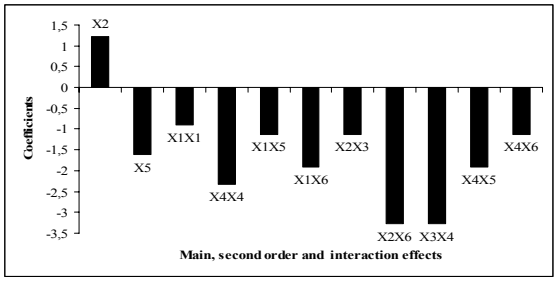

Fig. 8: The size effect of significant main, second order and interaction terms on the activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solutions.

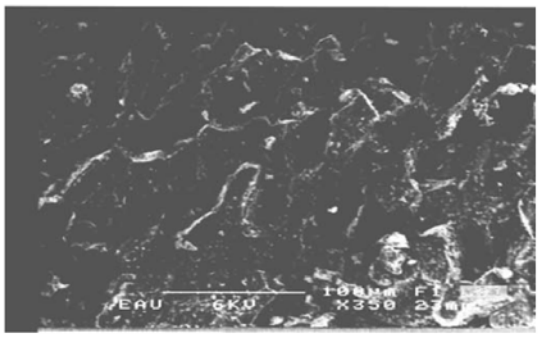

Fig. 9: a. The surface of the raw hazelnut shell.

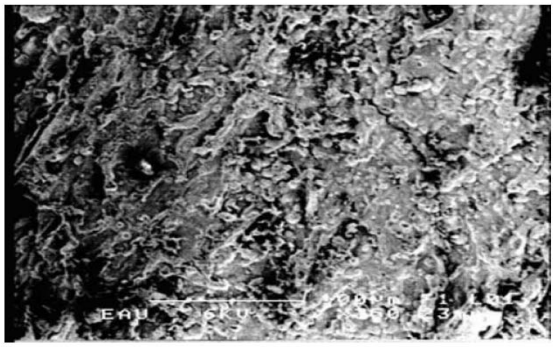

Fig. 9: (b). The surface of activated carbon adsorbed Zn^{2+} from aqueous solution.

Optimization Results

The main objective of this optimization study is to determine the optimum process conditions required to prepare activated carbon from hazelnut shell, suitable for their efficient employment as adsorbents to remove Zn^{2+} from aqueous solutions. The first step was to set up the response value from the models obtained experimentally. Then, using 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 Zn^{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 which ensure them to be more realistic. Because the model is an empirical one, high and low levels of the process parameters used in the experimental design were considered, inevitably, as explicit constraints, in order to avoid extrapolation in this optimization study.

Thus, the optimization problem is defined as follows;

- Maximize $Y_{Zn}{}^{2+}$ (3)

- Constraints on the parameters X_i;

$$-\beta_i < Xi < +\beta_i \quad i = 1\ldots.. 6 \qquad (4)$$

Constraints on the parameters X_i ($-\beta$ and $+\beta$ values) are given in Table-1. The optimization problem in Eq. (3) was solved using constrained optimization program supplied in the Matlab optimization toolbox. These results show that average (medium level) particle size, impregnation ratio, impregnation time and carbonization time are sufficient for optimum activated carbon from hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solution, whereas ultrasound power and carbonization temperature have more strong impacts on the optimum conditions for the production of activated carbon from hazelnut shell. The optimum process conditions are given in Table-3 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 26 mg Zn^{2+}/g Ac, whereas maximum adsorption capacity of activated carbon from alkaline impregnated hazelnut shell under the same process conditions (Table-3) without ultrasound application was found as 20 mg Zn^{2+}/g Ac. According to these results, the adsorption capacity of the activated carbon from alkaline impregnated hazelnut shell under ultrasound is approximately thirty percent greater than that of the adsorption capacity of activated carbon from alkaline impregnated hazelnut shell without ultrasound. In conclusion, the application of ultrasound irradiation in the impregnation step was found to be beneficial to prepare with high adsorption capacity activated

carbon for use as adsorbent to remove Zn^{2+} from aqueous solutions.

The comparison of the experimental adsorption capacity obtained in this study with the data in the literature for various adsorbents shows that activated carbon from ultrasound-assisted KOH-impregnated hazelnut shell is an effective adsorbent of Zn^{+2} from aqueous solutions. For the sake of comparison, Table-4 presents comparative values of zinc adsorption capacity for some adsorbents [23-29].

Surface Characterization of The Optimally Prepared Activated Carbon

The SEM photographs of the surface appearances of the activated carbon are shown in Fig. 9.a-b. Fig. 9.a shows the surface of the raw hazelnut shell, whilst Figure 9.b shows the surface of activated carbon which adsorbed Zn^{2+} from aqueous solution. It seems that the cavities on the surface are occupied full of zinc. BET surface areas of the raw and activated carbon from hazelnut shell were calculated to be 0.188 and 5 m^2/g, respectively. Considering BET surface areas, the surface area of the activated carbon is approximately 27 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.

Experimental

Material and Methods

Hazelnut shells supplied from the Black Sea Region in Turkey were first dried, crushed and sieved to obtain a particle size between 0,78 mm and 1,85 mm. The experimental set-up consisted of an ultrasonic power generator (Meinhardt ultraschalltechnic, K 80-5, 140W, 850 kHz), a jacketed glass reactor equipped with a titan probe (E/805/T/solo ultrasonic transducer) which is connected to the bottom of the reactor and fitted with a reflux condenser. A typical impregnation experiment (chemical activation) was carried out as follows: specified particle size and amounts of hazelnut shells and 10% KOH were loaded into the glass reactor and chemical activation process maintained the desired impregnation time. Ultrasound power (continuous mode) was adjusted using the relationship between the intensity setting of the generator, and ultrasound power absorbed by the reaction medium measured by the calorimetric method [34]. Ten percent of KOH solution was used in all the experiments [10, 16]. A constant impregnation temperature of 50 ^{0}C was applied by means of a constant temperature circulator. At the end of the impregnation experiment, the sample was immediately filtered, washed with hot distilled water for removal of its alkalinity, the basic and water-soluble components and dried. The impregnated sample was carbonized in a furnace (Carbolıte, CWF 1300) under N_2 atmosphere (1 kg/cm^2) at desired carbonization temperature and time for final activated carbon. The surface area of the activated carbon samples were investigated by using JEOL (JSM) 6400 scanning electron microscopy and the BET surface area method by a Quantachrome QS–17 model apparatus.

Determination of the Zinc Adsorption Capacity and Adsorption Isotherm

The shapes of adsorption isotherms can provide qualitative information on the adsorption process and the extent of the surface area available to the adsorbate. It is also important to apply the modes of contacting the activated carbon and waste water when applying the adsorption system to treatment process. Batch-type processes are usually suitable for the treatment of small volumes of effluent [2]. Therefore, batch mode adsorption experiments for determination of the zinc adsorption capacity and adsorption isotherm were carried out in a shaker Thermolyne Rosi 1000^{TM} (Reciprocating/Orbital Shaking Incubator) Model. Hundred millgram per liter solutions of Zn^{2+} were prepared by dissolving the solid $ZnSO_4.7H_2O$ in distilled water. Samples of 200 mg of activated carbon was added to 100 mL solution of Zn^{2+} of varying initial concentrations (between 100 mg/L and 300mg/L) in 250 mL erlenmayer flasks and shook at 18 $^{\circ}$C, 170 rpm for a contact time of 6 h which was found sufficient to obtain a nearly constant adsorption capacity in the light of pre-experiments. At the end of the experiments, the solutions of Zn^{2+} were separated from the samples activated carbons by filtering and filtrates were analyzed by using a Atomic Absorption/Flame Emission Spectrophotometer Shimadzu Model AA-670.The amount of Zn^{2+} adsorbed was calculated as follows:

$$Y_{Zn^{2+}} = \frac{(C_0 - C_e)V}{m} \qquad (5)$$

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

Table-3: The optimum process conditions to prepare activated carbon from hazelnut shell.

Particle size (mm)	Ultrasound power (W/L)	Impregnation ratio (g/mL)	Impregnation time (min)	Activation temperature (^{0}C)	Activation time (min)	Adsorbed mg Cu^{2+}/g Ac
1.29	120	0.0375	90	661	45	26

Table-4: Comparative values of zinc adsorption capacity for some adsorbent from aqueous solutions.

Adsorbent	Adsorption capacity (mg/g)	Reference
The leonardite	27.2	28
Sand	8.342	29
Zeolite	9.43	30
Aspergillus niger	24.6	31
Cellulosic sorbent (Maize Stalk Meal)	4.3	32
Activated carbons (from agricultural by-products)	3.2-6.5	33
Blast furnace sludge	4.26	34
Activated carbon (from ultrasound-assisted KOH-impregnated hazelnut shell)	26	This work

The Langmuir and Freundlich isotherms constants were calculated for adsorption of Zn^{2+} from in different initial concentrations of aqueous solutions. The Langmuir and Freundlich isotherms constants are listed in Table-5. Error estimation of the Langmuir and Freundlich isotherms show that Freundlich isotherms is more accurate to describe the Zn^{2+} adsorption isotherm than Langmuir isotherms.

Table-5: Langmuir and freundlich constants for the Zn^{2+} adsorption.

Langmuir Constant		Freundlich Constant		Equilibrium range (ppm)
Q_{max} (mg/g)	b (l/mg)	K_F ($mg^{1-n}L\ g^{-1}$)	n	
26.5	0.0634	11.897	7.35	20–257

Conclusion

From the view of industrial use, the properties of activated carbon, optimum production conditions, adsorption capacity and isotherm are important. As mentioned in the experimental section, the combined chemical and physical activation process was attempted to prepare activated carbon from ultrasound-assisted KOH-impregnated hazelnut shell for heavy metal removal from aqueous solutions. 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 ¼ 2^6 orthogonal fractional factorial design and central composite design were used to found second order model relating amount of the adsorbed mg Zn^{2+}/g Ac from aqueous solutions to experimental parameters and the optimal experimental conditions required to prepare activated carbon suitable for use as adsorbents to remove Zn^{2+} from aqueous solutions.

According to the results of this study, 'waste hazelnut shell' can be effectively used as a raw material for the preparation of activated carbon, and high amount of the adsorbed mg Zn^{2+}/g Ac from aqueous solutions may be obtained under suitable process conditions. These results show that average (medium level) particle size, impregnation ratio, impregnation time and carbonization time are sufficient for optimum activated carbon from hazelnut shell for use as adsorbents to remove Zn^{2+} from aqueous solution, whereas ultrasound power and carbonization temperature have more strong impacts on the optimum conditions for the production of activated carbon from hazelnut shell. In conclusion, the application of ultrasound irradiation in the impregnation step is found quite beneficial to increase adsorption capacity of activated carbon for use as adsorbent to remove Zn^{2+} from aqueous solutions. However, detailed optimization researches along with cost analysis are needed to decide on the profitability of using ultrasound. Such information (e.g. the optimization results presented in this paper) in turn leads to the development of new and higher qualities of activated carbon and insight on how such qualities will be affected by the processes and conditions of manufacture of the activated carbon.It is expected that the optimization results presented in this paper may provide background information for a detailed process improvement research.

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References

1. F. Banat, S. Al-Asheh and L. Abu-Aitah, *Adsorption Science and Technology,* **20**, 107 (2002).
2. G. McKay, *Use of Adsorbents for the Removal of Pollutants from Wastewater, Tokyo* (1996).
3. J. W. Mcbain, *The sorption of Gases and Vapours by Solids. Routlrdge, London* (1932).
4. N. R. Khalili, M. Campbell, G. Sandi and J. Golas, *Carbon,* **38**, 1905 (2000).
5. G. H. Oh and C. R. Park, *Fuel,* **81**, 327 (2002).
6. J. Guo and A. C. Lua, *Carbon,* **38**, 1985 (2000).
7. C. Namasivayam and K. Kadirvelu, *Bioresource Technology,* **62**, 123 (1997).
8. J. Rivera-Utrilla and C. Moreno-Castilla, *Carbon*, **39**, 425 (2001).

9. W. T. Tsai, C. Y. Chang, S. Y. Wang, C. F. Chang, S. F. Chien and H. F. Sun, *Bioresource Technology*, **78**, 203 (2001).
10. S. J. Park and W. Y. Jung, *Carbon,* **40**, 2021 (2002).
11. B. S. Girgis and M. F. Ihsak, *Materials Letters,* **39**, 107 (1999).
12. J. Guo and A. C. Lua, *Carbon*, **38**, 1985 (2000).
13. M. Yalcin and A. I. Arol, *Hydrometallurgy,* **63**, 201 (2002).
14. E. Demirbaş, M. Kobya, S. Öncel and S. Şencan, *Bioresource Technology*, **84**, 291 (2002).
15. K. J. Hu, J. L. Hu, K. P. Ho and K. W. Yeung, *Carbohydrate Polymers*, **58**, 45 (2004).
16. J. Guo and A. C. Lua, *Microporous and Mesoporous Materials,* **32**, 111 (1999).
17. T. J. Mason, *Ultrasonics Sonochemistry*, **10**, 175 (2003).
18. J. G. Price, *Current trends in sonochemistry, The royal society of chemistry*, Cambridge, (1992).
19. L. A. Crum, T. J. Mason, J. L. Reisse, K. S. Suslick, *Sonochemistry and sonoluminescence*, Kluwer Academic press. Dardrecht (1990).
20. R. V. Eldik and C. D. Hubbard, *Chemistry under extreme or non-classical conditions, John-Wiley and sons,* New York, (1997).
21. L. H. Thompson and L. K. Doraiswamy, *Industrial and Engineering Chemistry Research,* **38**, 1215 (1999).
22. D. C. Montgomery, *Design and Analysis of Experiments, John Wiley and Sons,* New York (1976).
23. M. Solé, J. M. Casas and Conxita Lao, *Water, Air, and Soil Pollution*, **144**, 57 (2003).
24. M. M. Aslam, I. Hassan and M. Malik, *Electronic Journal of Environmental Agricultural and Food Chemistry*, **3**, 792 (2004).
25. A. Buasri, P. Yongbut, N. Chaiyut and K. Phattarasirichot, *Chiang Mai Journal of Science,* **35**, 56 (2008).
26. L. Yun-guo, F. Ting, Z. Guang-ming, L. Xin, T. Qing, Y.Fei, Z. Ming, X.Wei-hua and H. Yu-e, *Transactions of Nonferrous Metals Society of China,* **16**, 681 (2006).
27. E. U. Ikhuoria and F. E. Okieimen, *International Journal of Environmental Studies*, **57**, 401 (2000).
28. M. A. Ferro-García, J. Rivera-Utrilla, J. Rodriguez-Gordillo and I. Bautista-Toledo, *Carbon*. **26**, 363 (1988).
29. A. López-Delgado, C. Pérez and F. A. López, *Water Research,* **32**, 989 (1998).
30. R. H. Myers, *Response Surface Methodology, Allyn and Bacon*, New York, p. 126 (1971).
31. E. Şayan and M. Bayramoğlu, *Hydrometallurgy,* **57**, 181 (2000).
32. E. Şayan and M. Bayramoğlu, *Institution of Chemical Engineers, Trans IChemE* B, **79**, 291 (2001).
33. E. Şayan and M. Bayramoğlu, *Hydrometallurgy,* **71**, 397 (2004).
34. T. Kimura, T. Sakamoto, J. Leveque, H. Sohmiya, M. Fujita, S. Ikeda and T. Ando, *Ultrasonics Sonochemistry*, **3**, 157 (1996).