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Adsorption of Cu^{2+}, Ni^{2+} And Zn^{2+} from Aqueous Solutions on Activated Carbons Prepared from Ultrasound-Assisted KOH-Impregnated Hazelnut Shell in Multi-Ion System

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Abstract

The adsorption of three toxic heavy metals (Cu^{2+}, Zn^{2+} and Ni^{2+}) from aqueous solutions on activated carbon prepared from ultrasound-assisted KOH-impregnated hazelnut shells has been studied as a function of particle size, ultrasonic power density, impregnation ratio, impregnation time, activation temperature and activation time. In this study, batch equilibrium adsorption was employed to optimize of adsorption data of Cu^{2+}, Ni^{2+} and Zn^{2+} in multi-ion system. The order of the percentage removal via activated carbon is found as $Cu^{2+} > Zn^{2+} > Ni^{2+}$.

Keywords: Hazelnut shell, activated carbon, heavy metal adsorption, adsorption capacity

INTRODUCTION

Industrial waste waters contain of organic, inorganic, metallic and biological pollutant, and they cause serious disposal problems for environment. Heavy metals are stable and persistent environmental contaminants since they cannot be destroyed. For this reason, the concentration of heavy metals in waste water must be reduced to the maximum permissible concentration [1]. There are many purification and separation methods such as adsorption, chlorination, chemical oxidation and air stripping to remove of pollutants from wastewater. Compared with the other purification and separation methods, adsorption has demonstrated efficiency and economic feasibility as a wastewater treatment operation.. Adsorption has gained an increasing importance as a purification and separation process on industrial applications recently [2]. 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 [3,4,5].

The aim of this study is to prepare the activated carbon from hazelnut shells for use as adsorbents to remove Cu^{2+}, Ni^{2+} and Zn^{2+} from aqueous solution.

MATERIALS and METHODS

The orthogonal central composite design was applied for fitting a second-order model in this study as described in detailed in our previous experimental studies [6-8]. 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 [9]. 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 m0 center points (0, 0, 0, . . .,0) [9, 10]. 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 cannot be estimated separately by 2n factorial designs. The response and the corresponding parameters were modelled and optimized using Matlab and statistical computer software by means of response surface methods.

Activated carbon used in the adsorption experiments were supplied from project number 2003/38 supported by Atatürk University Research Foundation, Erzurum/Turkey [11].

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 [12]. Ten percent of KOH solution was used in all the experiments [13,14]. 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/cm²) at desired carbonization temperature and time for final activated carbon.

Batch mode adsorption experiments for determination of the nickel ions were carried out in a shaker Thermolyne Rosi 1000TM (Reciprocating/Orbital Shaking Incubator) Model. Hundred millgram per liter solutions of Cu^{2+}, Ni^{2+} and Zn^{2+} were prepared by dissolving the solid of the heavy metal salts in distilled water. Samples of 200 mg of activated carbon was added to 100 mL solution of Cu^{2+}, Ni^{2+} and Zn^{2+} of varying initial concentrations (between 100 mg/L and 300mg/L) in 250 mL Erlenmeyer flasks and shaked at 18 ◦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. Shimadzu Model AA-670. The amount of Cu^{2+}, Ni^{2+} and Zn^{2+} adsorbed was calculated as follows: At the end of the experiments, the solutions of Cu^{2+}, Ni^{2+} and Zn^{2+} were separated from the samples activated carbons by filtering and filtrates were analyzed by using an Atomic

Absorption/Flame Emission Spectrophotometer.

$$Y_{HM} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

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

RESULTS and DISCUSSION

Particle size (X1), ultrasound power (X2), impregnation ratio (X3), impregnation time (X4), activation temperature (X5) and activation time (X6) were chosen as the independent parameters for response analysis and modeling of Cu^{2+}, Ni^{2+} and Zn^{2+} adsorption from aqueous solutions on activated carbon prepared from ultrasound-assisted alkaline impregnated hazelnut shell in the light of pre-experiments. The parameter levels with coded values were shown in Table 1. The experimental design matrix and the corresponding experimental parameters and response value were shown in Table 2.

Table 1. The parameter levels with coded values

Parameter	**+ß**	**+1**	**0**	**-1**	**-ß**
Particle size (mm) X1	1.85	1.55	1.29	0.93	0.78
Ultrasonic power density (W/L) X2	190	76	19	6	2
Impregnation ratio (g/mL) X3	0.06	0.05	0.038	0.025	0.015
Impregnation time (min) X4	143	120	90	60	37
Activation temperature (0C) X5	839	800	750	700	661
Activation time (min) X6	72	60	45	30	18

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 Cu^{2+}, Ni^{2+} and Zn^{2+} from aqueous solutions. The order of the percentage removal via activated carbon is found as $Cu^{2+} > Zn^{2+} > Ni^{2+}$. However, detailed optimization researches along with cost analysis are needed to assess the profitability of the method. It is expected that the optimization results presented in this paper may provide background information for a detailed process improvement research.

Table 2. Experimental design matrix and response value

Exp. N.	Particle size (mm)	Ultrasonic power density (W/L)	Impregnation ratio (g/mL)	Impregnation time (min)	Activation temperature (°C)	Activation time (min)	Adsorbed mg Cu^{+2} /g Ac	Adsorbed mg Zn^{2+} /g Ac	Adsorbed mg Ni^{2+} /g Ac
3	-1	1	-1	-1	1	1	23,18301	9,41331	5,477233
4	1	1	-1	-1	-1	1	42,10409	3,892349	7,56895
15	-1	1	1	1	-1	1	15,16808	8,748481	4,874443
10	1	-1	-1	1	1	1	35,91201	14,50816	7,530895
8	1	1	1	-1	1	-1	22,74694	6,633021	3,923937
6	1	-1	1	-1	-1	1	36,28	9,8	7,038
11	-1	1	-1	1	1	-1	25,77863	10,73311	7,273598
5	-1	-1	1	-1	1	1	33,74134	5,658199	7,036952
16	1	1	1	1	1	1	33,23917	10,28719	5,765066
9	-1	-1	-1	1	-1	1	37,82523	10,13746	6,192931
1	-1	-1	-1	-1	-1	-1	20,39409	6,945813	5,465517
13	-1	-1	1	1	1	-1	28,12065	8,839907	6,12065
14	1	-1	1	1	-1	-1	32,22488	10,95694	6,88756
2	1	-1	-1	-1	1	-1	0,54672	6,833996	5,072068
12	1	1	-1	1	-1	-1	37,1177	8,294717	8,880908
7	-1	1	1	-1	-1	-1	43,54443	12,27295	7,093765
31	-1.771	0	0	0	0	0	25,23364	7,427447	6,69454
23	1.771	0	0	0	0	0	36,66511	6,539	5,52312
22	0	-1.771	0	0	0	0	46,14243	34,79228	45,455
21	0	1.771	0	0	0	0	35,58773	8,707865	6,583838
28	0	0	-1.771	0	0	0	39,20846	8,456244	7,12881
25	0	0	1.771	0	0	0	26,08295	9,170507	6,343318
29	0	0	0	-1.771	0	0	27,78232	4,050736	6,061784
27	0	0	0	1.771	0	0	21,87938	4,230949	6,117345

24	0	0	0	0	-1.771	0	40,0385	9,552454	10,18046
26	0	0	0	0	1.771	0	26,90311	6,898789	5,817474
30	0	0	0	0	0	-1.771	24,93595	6,340734	4,602904
20	0	0	0	0	0	1.771	33,30279	8,314246	5,464956
10	0	0	0	0	0	0	23,34322	6,948566	6,394659
20	0	0	0	0	0	0	23,52399	8,02583	6,13238
30	0	0	0	0	0	0	26,35088	7,859649	5,566667
Raw hazelnut shell							2	2.4	4.27

REFERENCES

[1] F. Banat, S. Al-Asheh, L. Abu-Aitah, Adsorption Science and Technology, 20 (2), 107 (2002).

[2] G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewater, Tokyo, (1996).

[3] N. R. Khalili, M. Campbell, G. Sandi, J. Golas, Carbon, 38, 1905 (2000).

[4] G. H. Oh, C. R. Park, Fuel, 81, 327 (2002).

[5] J. Guo, A. C. Lua, Carbon, 38, 1985 (2000).

[6] E. Şayan, M. Bayramoğlu, Hydrometallurgy, 57, 181 (2000).

[7] E. Şayan, M. Bayramoğlu, Institution of Chemical Engineers, Trans IChemE B, 79, 291(2001).

[8] E. Şayan, M. Bayramoğlu, Hydrometallurgy, 71, 397 (2004).

[9] D.C. Montgomery, Design and Analysis of Experiments, John Wiley and Sons, New York, (1976).

[10] R.H. Myers, Response Surface Methodology, Allyn and Bacon, New York, p. 126 (1971).

[11] Şayan, E., 2006. Chemical Engineering Journal, 115, 213–218.

[12] T. Kimura, T. Sakamoto, J. Leveque, H. Sohmiya, M. Fujita, S. Ikeda, T. Ando, Ultrasonics Sonochemistry, 3, 157 (1996).

[13] S. J. Park, W. Y. Jung, Carbon, 40, 2021, (2002).

[14] J. Guo, A. C. Lua, Microporous and Mesoporous Materials, 32, 111 (1999).