



OPTIMIZATION OF SELECTIVE Cu^{2+} ADSORPTION WITHIN THE MULTI-ION SYSTEM BY USING ACTIVATED CARBON PREPARED BY ULTRASOUND

Berrak BAŞAR^{1,*}, Enes ŞAYAN¹

¹ Department of Chemical Engineering, Faculty of Engineering, Atatürk University, Erzurum, Turkey

ABSTRACT

In this study, optimization of the selective Cu^{2+} adsorption from multi-ion media containing Cu^{2+} , Zn^{2+} and Ni^{2+} on activated carbons (AC) prepared from ultrasound-assisted 10 % KOH impregnated hazelnut shells was investigated. For the suitable activated carbons production of selective adsorption of Cu^{2+} from multi-ion media, the effects of independent variables such as particle size, ultrasound power density, impregnation rate, impregnation time, activation temperature and activation time were investigated by experiments with partial factorial and central composite design. At the end of the adsorption experiments, activated carbons were evaluated by their adsorption capacities. Additionally, the results were statistically modelled and optimized by using a constrained optimization program via Matlab computer software. The results of the experiments revealed that activated carbon prepared by ultrasound method can be used for the selective Cu^{2+} adsorption from multi-ion system efficiently. The selectivity sequence based on the distribution coefficient (K_d) is generally $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ for the multi-ion system. Finally, maximum adsorption capacity was found as 82.9 mg Cu^{2+} /g Ac under optimum conditions such as particle size 1.7504 mm, ultrasound power/volume 2 W/L, impregnation ratio 0.0168 g/mL, impregnation time 132 min, activation temperature 661 °C and activation time 71.5 min.

Keywords: Activated carbon, Adsorption, Multi-ion system, Selectivity, Optimization

1. INTRODUCTION

Wastewater can be defined as water that is contaminated as a result of domestic, industrial, agricultural and other uses, or whose properties have changed partially or completely. Wastewater can be defined as water that is contaminated as a result of domestic, industrial, agricultural and other uses, or whose properties have changed partially or completely [1]. Water pollution is a physical, biological or chemical change in water quality that affects living organisms negatively [2]. Heavy metals which are important contaminant species especially in industrial wastewater cannot be broken down in biological processes. Since heavy metals can accumulate in living organisms they can threaten human life when exceed their limit values [3]. Environmental pollution by heavy metals poses a serious threat to human health due to hemotoxicity as toxic or carcinogenic [4].

Since drinking water is supplied from natural water sources, heavy metals should be removed from the environment [1]. Particularly developed countries have prepared National and International waste programs and charters with the help of various organizations such as the USPHS (American Health Organization), the WHO (world Health Organization) and the EPA (Environmental Protection Organization) [5, 6]. Since especially drinking water need to provide determined limit values in terms of human health, to removal of heavy metal ions from the waste water has become one of the important topics investigated and studied in the world [7]. Therefore, examination of the pollution process has become important in scientific research [8].

Heavy metals are regarded as one type of the most dangerous substances in the world due to their high toxicity to the ecosystem and they are classified into two classes, vital and non-vital according to their

*Corresponding Author: berrakbsr.25@gmail.com

Received: 25.01.2018 Accepted: 10.12.2018

degree of incorporation into biological processes. Heavy metals need to be present at a certain concentration in the structure of the organism, and these metals should be taken regularly by food or other means when participating in biological reactions. For example; iron prevents anemia, zinc is involved in more than 100 enzyme reactions, and copper is an indispensable part of red blood cells and it is present many oxidation and reduction processes in animals and in humans. Moreover, copper is found as a basic compound of some organs such as hair, skin, bone, and the lack of copper leads to important health problems in children [6, 9, 10]. Non-vital heavy metals can cause health problems by affecting psychological well-being even at very low concentrations. Heavy metals increase the acidity of the blood and the body draws more calcium from the bones to correct the body's acidity when it is necessary. Heavy metals also cause allergic reactions, mutation of genes, tissue damage, and death of beneficial bacteria as well as harmful bacteria [9, 11].

It has been observed that zinc, which is at the top of the list of environmental pollutants in the United States, causes disturbances in the gastrointestinal system when it reaches the high concentrations in human body [12]. It is well known that high nickel concentration causes stomach irritation, birth defects, vascular occlusion, headache, dizziness, nausea, chest pain, stress, increased respiratory rate, excessive weakness, lung cancer, and bone cancer in human [13, 15]. Even at very low concentrations, the accumulation of copper in the liver, which causes poisoning of organisms in the human body, causes gastrointestinal distress, liver and kidney failure [13, 14].

The treatment methods such as oxidation, reduction, liquid-liquid extraction, chemical precipitation, biological treatment, reverse osmosis, ultrafiltration, membrane processes, ion exchange and adsorption are applied in the removal of heavy metal from wastewaters [3, 4, 12, 13, 16, 17]. Removal of heavy metal ions by adsorption onto activated carbon prepared from agricultural wastes has high efficiency and at the same time it comes out as an economical method compared to the other processes with extremely high investment and operating costs. Parameters, such as pore size distribution and structure of adsorbents used in adsorption processes, production cost, removal capacity, surface properties and regeneration are important factors determining the applicability of the process [18]. Activated carbon, one of the most effective adsorbents, is a cheap and easily available material that effectively removes heavy metals from waste water [19]. Adsorption on activated carbon is generally used for taste and odor control especially in drinking water [20].

Activated carbon is one of the most commonly used adsorbents in environmental pollution control, bleaching, deodorization processes. It is obtained by improving the surface properties and pore volume by activating carbon content from high materials. Carbon materials reported to be the most effective adsorbents due to their textural and surface properties with various functional groups. All solid raw materials which contain sufficient amount of carbon in their structure, low cost and easy to obtain can be used for active carbon production. Commercial active carbons can be prepared from a variety of raw materials such as wood, lignite, coal, bone, petroleum residues, hazelnuts, coconut shells, and various polymer based synthetics. Active carbons are produced from a wide range of agricultural wastes such as almond, apricot, cherry and olive seeds, peanuts, nuts, walnuts and a variety of tree bark economically in recent years due to the high cost of commercial activated carbon [18, 21, 22].

Many heavy metals, which are harmful to the environment in industrial wastewater, usually coexist in the same environment. However, most of the adsorption studies on environmental pollution prevention are for the removal of heavy metals in single-component systems; but this can be considered as a hypothetical situation. If different heavy metals are present in the adsorption medium, such adsorption is defined as competitive adsorption since heavy metals will be adsorbed on the same adsorbent surface [23]. As the heavy metals in waste water and drinking water, removal of impurities and impurities, extraction, decomposition and concentration of many compounds are actually carried out by a competitive adsorption mechanism, it is important to elucidate the competitive adsorption mechanism [24].

In systems containing more than one ion, the adsorption of heavy metal ions is not only dependent on the properties of the adsorbent and solution but also on the interaction between the ion species. There is a competition between different metal ions held on the adsorbent surface and the adsorption of each ion species changes the adsorption characteristics of the system [7].

The combined effects of metals on the adsorbent depend on the metals combination, metal concentration levels, metal addition order and adsorbent species [25]. The adsorbents affinity of metals in a competitive adsorption is a limiting factor. Metals with higher affinity are adsorbed more on the adsorbent. In the presence of multi metal ions, the total metal ion concentration increases, number and characteristic of the adsorbents play an important role for the binding sites [23].

In this study, the optimization of selective Cu^{+2} adsorption of on activated carbons prepared from ultrasound-assisted alkaline impregnated hazelnut shells from multi-ion media containing Cu^{+2} , Zn^{+2} and Ni^{+2} has been investigated. The aim of the work is to investigate suitable activated carbon production conditions for selective adsorption of Cu^{+2} from multi-ion containing aqueous solutions. Experiments were statistically designed. At the end of the experiments, among the parameters related to Cu^{+2} , Zn^{+2} and Ni^{+2} adsorption capacities, statistical models were established with the help of variance analysis and optimum process conditions were tried to be found by using restricted optimization technique.

2. MATERIAL AND METHOD

2.1. Material

Activated carbons prepared from ultrasound-assisted 10% KOH impregnated hazelnut shells produced in project number 2003/38 supported by Erzurum/Atatürk University Research Fund were used in the adsorption experiments [26]. The main characteristics of ACs were given in previous papers [26,27,31,32]. The compounds of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ produced by Merck were dissolved with distilled water to prepare a stock solution, each having an ion concentration of 1000 ppm metal. Adsorption experiments were carried out at a speed of 170 rpm in a TH15 brand shaker from Edmund Buhler GmbH. Cu^{+2} , Zn^{+2} and Ni^{+2} ion concentrations in the adsorbate solutions were determined by Shimadzu (AA-670) model atomic absorption spectrometry (AAS) before and after adsorption.

2.2. Planning of Experiments

Adsorption experiments investigating optimum adsorption conditions of Cu^{+2} in multi ion systems containing Cu^{+2} , Zn^{+2} and Ni^{+2} ions on active carbons prepared from ultrasound-assisted KOH impregnated hazelnut shells are planned with $\frac{1}{4} 2^6$ fractional factors and central composite designs [26]. In the planning and analysis of experiments, the coded values used instead of absolute values of the variables are given in Table 1. The relationship between coded value (X) and absolute value (Z) is as follows:

$$X = \frac{2(Z - Z_0)}{(Z_2 - Z_1)} \quad (1)$$

Where Z_1 is low level, Z_2 is high level and Z_0 is medium level of the variable.

Where; N: number of variables, F: number of first-order factorial experiments, m_0 : number of central replicates experiments;

$$N = F + 2n + m_0 \text{ (Total number of experiments)} \quad (5)$$

$$Q = [N^{1/2} - F^{1/2}]^2 \quad (6)$$

If the 2nd order model is defined as follows, it makes calculations easier:

$$y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} (x_i^2 - \bar{x}_i^2) + \sum_{i=1}^n \sum_{j>i}^n b_{ij} x_i x_j \quad (7)$$

Thus, 2n experiments are performed, where n is the number of variables. Experiments with a central replicate are also included in these experiments if it is necessary. The value of β is chosen by the researcher. There are different criteria for the determination of β value. The appropriate choice of β can make the design orthogonal. Where;

$$c = \bar{x}^2 = \frac{1}{N} \sum_{i=1}^N x_i^2 = \frac{(F + 2\beta^2)}{N} \quad (8)$$

2.3. Determination of Cu^{+2} , Zn^{+2} , and Ni^{+2} adsorption capacities

The batch mode adsorption experiments are preferred because they are suitable for processing small volumes. A 100 mg/L solution prepared from a 1000 mg/L stock solution containing heavy metals (Cu^{+2} , Zn^{+2} and Ni^{+2}) was contacted with 200 mg of Ac at 18 ° C for 6 hours in 250 mL flask. At the end of the experiments, the samples were filtered and heavy metals (Cu^{+2} , Zn^{+2} and Ni^{+2}) analysis were carried out by using Atomic Absorption / Flame Emission Spectrophotometer Shimadzu Model AA-670.

As a result of the analysis, heavy metals adsorption capacities of activated carbons were calculated by the following equations. Adsorption capacity;

$$q_{e, \text{Me}^{2+}} = \frac{(C_0 - C_e)V}{m} \quad (9)$$

In this equation,

$q_{e, \text{Me}^{2+}}$ is the mass of adsorbed heavy metal per unit weight of activated carbon (Cu^{2+} Zn^{2+} Ni^{2+}) / (mg Me^{2+} /g Ac),

C_0 is the concentration of heavy metal (Cu^{+2} , Zn^{+2} and Ni^{+2}) at the beginning (mg / L),

C_e is the concentration of heavy metal in equilibrium (Cu^{+2} , Zn^{+2} and Ni^{+2}) (mg / L),

V is the volume of solution (L) and m is the activated carbon dosage (g).

3. RESULTS AND DISCUSSION

3.1. Response Analysis, Modeling and Interpretation

The experimental design matrix for Cu^{+2} , Zn^{+2} and Ni^{+2} adsorption on prepared activated carbons and the results are presented in Table 3. The data obtained from the experiments were evaluated by Matlab program and the following model equations (10-12). The main and second order terms in eqn. 10-12

were developed at 90% confidence level for the adsorption of Cu^{2+} , Zn^{2+} and Ni^{2+} on prepared active carbon. Statistical test graphs of the models developed are given in Figure 1. The correlation coefficients of the obtained models were 0.9802, 0.9855 and 0.9983, respectively. As a result of the statistical test graphs and analysis of the obtained model, it shows that the model is appropriate, has a good estimation of experimental data and does not contain any systematic error.

$$\begin{aligned}
 Y_{\text{Cu}^{2+}} = & 28.70189 + 2.7236 X_1 - 1.2955 X_2 - 1.3038 X_3 - 0.7008 X_4 - 2.5436 X_5 \\
 & + 1.5174 X_6 + 0.1662 X_1 X_1 + 3.3286 X_2 X_2 + 0.7072 X_3 X_3 - 1.7851 X_4 X_4 \\
 & + 0.9704 X_5 X_5 - 0.4174 X_6 X_6 + 0.9157 X_1 X_2 - 2.0364 X_1 X_3 + 1.4241 X_1 X_4 \\
 & - 1.3234 X_1 X_5 + 2.1762 X_1 X_6 - 1.3234 X_2 X_3 - 2.2122 X_2 X_4 - 2.0364 X_2 X_5 \\
 & - 3.1228 X_2 X_6 - 3.1228 X_3 X_4 + 0.9157 X_3 X_5 - 2.2122 X_3 X_6 + 2.1762 X_4 X_5 \\
 & - 1.3234 X_4 X_6 + 1.4241 X_5 X_6
 \end{aligned} \tag{10}$$

$$\begin{aligned}
 Y_{\text{Zn}^{2+}} = & 7.79586 - 0.1399 X_1 - 1.2727 X_2 + 0.1662 X_3 + 0.9598 X_4 - 0.1276 X_5 \\
 & + 0.1989 X_6 - 0.2900 X_1 X_1 + 2.5060 X_2 X_2 + 0.2937 X_3 X_3 - 1.1965 X_4 X_4 \\
 & + 0.1062 X_5 X_5 - 0.1802 X_6 X_6 - 1.4111 X_1 X_2 + 0.3661 X_1 X_3 + 0.7949 X_1 X_4 \\
 & + 0.5487 X_1 X_5 + 0.6627 X_1 X_6 + 0.5487 X_2 X_3 - 0.5845 X_2 X_4 + 0.3661 X_2 X_5 \\
 & - 0.7575 X_2 X_6 - 0.7575 X_3 X_4 - 1.4111 X_3 X_5 - 0.5845 X_3 X_6 + 0.6627 X_4 X_5 \\
 & + 0.5487 X_4 X_6 + 0.7949 X_5 X_6
 \end{aligned} \tag{11}$$

$$\begin{aligned}
 Y_{\text{Ni}^{2+}} = & 6.183246 - 0.1321 X_1 - 0.0394 X_2 - 0.0949 X_3 + 0.0426 X_4 - 0.4278 X_5 \\
 & + 0.2826 X_6 - 0.0491 X_1 X_1 - 0.2227 X_2 X_2 + 0.1509 X_3 X_3 - 0.0553 X_4 X_4 \\
 & + 0.5537 X_5 X_5 - 0.3919 X_6 X_6 - 0.2683 X_1 X_2 - 0.1347 X_1 X_3 + 0.1296 X_1 X_4 \\
 & - 0.3978 X_1 X_5 + 0.5944 X_1 X_6 - 0.3978 X_2 X_3 - 0.2118 X_2 X_4 - 0.1347 X_2 X_5 \\
 & - 0.2337 X_2 X_6 - 0.2337 X_3 X_4 - 0.2683 X_3 X_5 - 0.2118 X_3 X_6 + 0.5944 X_4 X_5 \\
 & - 0.3978 X_4 X_6 + 0.1296 X_5 X_6
 \end{aligned} \tag{12}$$

Adsorption in multiple ion systems is quite complicated due to ion-ion competition and ion-surface interaction. In such systems, parameters such as ion radius, electronegativity, active sites in the solid surface play an important role on a competitive adsorption. If the electronegativity is high, the adsorption on the solid surface is high as well. The most important parameter showing the adsorption of metals on the adsorbent in multi-ion systems is the affinity of metals to solid surfaces. Affinity depends on some parameters such as the ion radius of metals, atomic weight, electronegativity, hydrolysis constant and softness. A metal with a large hydrolysis constant has a small affinity, a large ionic radius, a large atomic weight, a large electronegativity and a great softness of metal has a great affinity. The metal properties and the affinity sequences of Cu^{2+} , Zn^{2+} and Ni^{2+} ions are given in Table 2.

In Table 3, when the adsorption of Cu^{2+} , Zn^{2+} and Ni^{2+} in the multi-component media was compared with the adsorption of the single ion medium obtained from our previous studies, it was observed that the adsorption of Cu increased, the adsorption of Zn decreased and the adsorption of Ni decreased partially [26,31,32]. The combined effect of the ternary system of Cu^{2+} , Zn^{2+} and Ni^{2+} seems to be synergistic for Cu^{2+} . It has been reported by [33] that the adsorption capacity of Cu^{2+} increases in relation to the increase of Cu^{2+} equilibrium concentration in single component and multi component (Cu-Cd-Ni-Pb) systems. Similar synergistic effect was reported by [34] during Cu^{2+} adsorption from the four-ion solution Cu^{2+} , Zn^{2+} , Pb^{2+} and Ni^{2+} by onto chitosan-montmorillonite composite beads. The presence of Zn^{2+} and Ni^{2+} may be to have a positive effect on the copper adsorption. This can be explained by the adsorbent and adsorbate properties of the adsorption of heavy metal ions and also the interaction between the ions in the solution with the multiple ions. There may be a requirement to attach to the various bonding sites which increase the adsorption capacity of the copper in the working

concentrations. In such systems, there is a race to attach to the surface between metal ions, which changes the adsorption characteristic [7]. The results obtained from this study and adsorption selectivity sequences are consistent with the literature [34].

Table 2. Metal properties and affinity sequences of Cu^{+2} , Zn^{+2} and Ni^{+2} ions

Parameters	Cu^{2+}	Zn^{2+}	Ni^{2+}	Affinity series
Ion radius (Å)	0.70	0.74	0.69	Zn> Cu> Ni
Atom weight (g/mol)	63.54	65.38	58.7	Zn> Cu> Ni
Electronegativity (Ec)	1.9	1.6	1.8	Cu> Ni >Zn
Hydrolysis constant	8.0	9.0	9.9	Cu> Zn> Ni
Softness	2.89	2.34	2.82	Cu> Ni >Zn

Table 3. Experimental design matrix and adsorption capacities

Exp. no	P. Size (mm)	Ult. Power density (W/L)	Imp. Ratio (g/mL)	Imp. Time (min)	Act. Temp. (°C)	Act. Time (min)	Ads. mg Cu^{+2} /g Ac	Ads. mg Zn^{+2} /g Ac	Ads. mg Ni^{+2} /g Ac
3	-1	1	-1	-1	1	1	23.1830	9.41331	5.47723
4	1	1	-1	-1	-1	1	42.1040	3.892349	7.56895
15	-1	1	1	1	-1	1	15.1680	8.748481	4.87444
10	1	-1	-1	1	1	1	35.9120	14.50816	7.53089
8	1	1	1	-1	1	-1	22.7469	6.633021	3.92393
6	1	-1	1	-1	-1	1	36.28	9.8	7.038
11	-1	1	-1	1	1	-1	25.7786	10.73311	7.27359
5	-1	-1	1	-1	1	1	33.7413	5.658199	7.03695
16	1	1	1	1	1	1	33.2391	10.28719	5.76506
9	-1	-1	-1	1	-1	1	37.8252	10.13746	6.19293
1	-1	-1	-1	-1	-1	-1	20.3940	6.945813	5.46551
13	-1	-1	1	1	1	-1	28.1206	8.839907	6.12065
14	1	-1	1	1	-1	-1	32.2248	10.95694	6.88756
2	1	-1	-1	-1	1	-1	28.5476	6.833996	5.07206
12	1	1	-1	1	-1	-1	37.1177	8.294717	8.88090
7	-1	1	1	-1	-1	-1	43.5444	12.27295	7.09376
31	-1.771	0	0	0	0	0	25.2336	7.427447	6.69454
23	1.771	0	0	0	0	0	36.6651	6.539	5.52312
22	0	-1.771	0	0	0	0	46.1424	22.79	4.5455
21	0	1.771	0	0	0	0	35.5877	8.707865	6.58383
28	0	0	-1.771	0	0	0	39.2084	8.456244	7.12881
25	0	0	1.771	0	0	0	26.0829	9.170507	6.34331
29	0	0	0	-1.771	0	0	27.7823	4.050736	6.06178
27	0	0	0	1.771	0	0	21.8793	4.230949	6.11734
24	0	0	0	0	-1.771	0	40.0385	9.552454	10.1804
26	0	0	0	0	1.771	0	26.9031	6.898789	5.81747
30	0	0	0	0	0	-1.771	24.9359	6.340734	4.60290
20	0	0	0	0	0	1.771	33.3027	8.314246	5.46495
1 ⁰	0	0	0	0	0	0	23.3432	6.948566	6.39465
2 ⁰	0	0	0	0	0	0	23.5239	8.02583	6.13238
3 ⁰	0	0	0	0	0	0	26.3508	7.859649	5.56666
Raw	hazelnut	shell					2	2.4	4.27

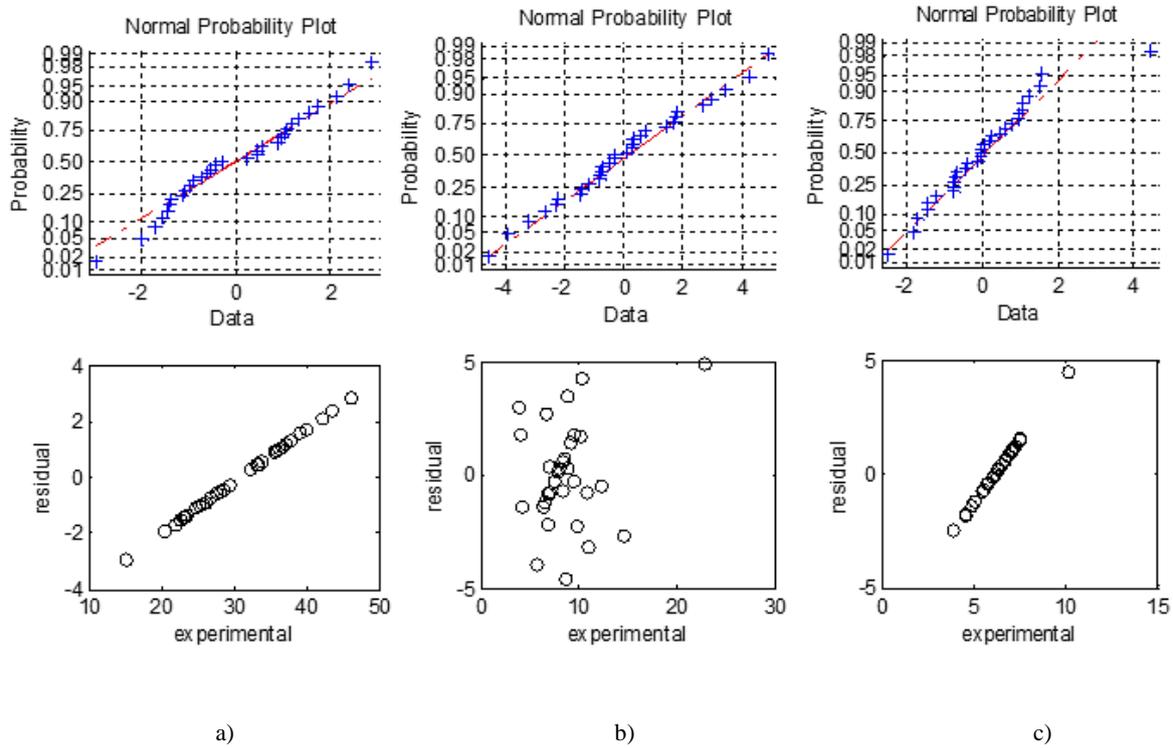


Figure 1. Statistical graphs that test the validity of established models

In order to compare with the literature results, the adsorption capacity of Cu^{+2} on some adsorbents in multi-ion systems from aqueous solutions is given in table 4.

Table 4. Cu adsorption capacity of some adsorbents in multi-ion systems

Adsorbent	Adsorption capacity (mg/g)	Reference
Chitosan-Montmorillonite Composite Beads	13.17	[35]
Crosslinked Chitosan-Montmorillonite Composite Beads	12.89	[35]
Bentonite	3.96	[5]
Chlorella kessleri	90.3	[36]
Chlorella kessleri	57.3	[36]
Eucalyptus black liquor lignin	43.81	[37]
Bagasse carbon	29.11	[37]
Peat	14.29	[37]
Coal (leonardite)	19.06	[37]
Activated carbon	82.91	This study

In adsorption study, the distribution coefficient (K_d) is a useful index for comparing the adsorption capacities of different adsorbent materials under the same experimental conditions. In multi-ion systems, the distribution coefficient (K_d) is used to determine the selectivity sequences in the adsorption. The selectivity of the metal with the larger distribution coefficient is greater. The distribution coefficient (K_d) is calculated as follows [38].

$$K_d = \frac{\text{Concentration of adsorbed metal on adsorbent } (q_e)}{\text{Metal concentration in equilibrium solution } (C_e)} = \frac{(C_o - C_e) \times V}{C_{eM}} \quad (13)$$

Table 5 gives the distribution coefficients and selectivity sequences. The selectivity sequence based on the distribution coefficient (K_d) depends on atomic number and weight, electronic configuration,

coordination number, hardness-softness behavior, ionic radius and potential. The selectivity sequence of the metal adsorption on activated carbon is generally $\text{Cu}^{+2} > \text{Zn}^{+2} > \text{Ni}^{+2}$ for the multi-ion system. The highest K_d values of Cu^{+2} show that Cu^{+2} is the most strongly adsorbed metal by ACs compared to Ni^{+2} and Zn^{+2}

Table 5. Distribution coefficients and selectivity sequences.

Exp. no	P. Size (mm)	Ult. Power density (W/L)	Imp. Ratio (g/mL)	Imp. Time (min)	Act. Temp. (°C)	Act. Time (min)	$K_{d,Cu^{+2}}$	$K_{d,Zn^{+2}}$	$K_{d,Ni^{+2}}$	Selectivity sequences
3	-1	1	-1	-1	1	1	0.492731	0.119915	0.062604	Cu>Zn>Ni
4	1	1	-1	-1	-1	1	7.869924	0.042656	0.091209	Cu>Ni>Zn
15	-1	1	1	1	-1	1	0.242495	0.111588	0.055413	Cu>Zn>Ni
10	1	-1	-1	1	1	1	1.313053	0.205353	0.088844	Cu>Zn>Ni
8	1	1	1	-1	1	-1	0.616448	0.081287	0.044032	Cu>Zn>Ni
6	1	-1	1	-1	-1	1	3.901075	0.129801	0.085407	Cu>Zn>Ni
11	-1	1	-1	1	1	-1	0.557979	0.138313	0.085753	Cu>Zn>Ni
5	-1	-1	1	-1	1	1	1.251998	0.064481	0.083017	Cu>Ni>Zn
16	1	1	1	1	1	1	1.130584	0.131634	0.065695	Cu>Zn>Ni
9	-1	-1	-1	1	-1	1	1.648158	0.127756	0.070869	Cu>Zn>Ni
1	-1	-1	-1	-1	-1	-1	0.348022	0.080859	0.061476	Cu>Zn>Ni
13	-1	-1	1	1	1	-1	0.713722	0.109202	0.070506	Cu>Zn>Ni
14	1	-1	1	1	-1	-1	0.986979	0.142113	0.080457	Cu>Zn>Ni
2	1	-1	-1	-1	1	-1	0.671062	0.079235	0.056485	Cu>Zn>Ni
12	1	1	-1	1	-1	-1	1.865211	0.101032	0.109865	Cu>Ni>Zn
7	-1	1	1	-1	-1	-1	3.853489	0.163639	0.08292	Cu>Zn>Ni
31	-1.771	0	0	0	0	0	0.518145	0.087485	0.077492	Cu>Zn>Ni
23	1.771	0	0	0	0	0	1.705354	0.076035	0.062638	Cu>Zn>Ni
22	0	-1.771	0	0	0	0	6.88693	0.422991	0.05011	Cu>Zn>Ni
21	0	1.771	0	0	0	0	2.016302	0.109053	0.077672	Cu>Zn>Ni
28	0	0	-1.771	0	0	0	1.93622	0.102129	0.083378	Cu>Zn>Ni
25	0	0	1.771	0	0	0	0.60099	0.114488	0.073559	Cu>Zn>Ni
29	0	0	0	-1.771	0	0	0.865493	0.044958	0.07116	Cu>Zn>Ni
27	0	0	0	1.771	0	0	0.411267	0.04652	0.070383	Cu>Ni>Zn
24	0	0	0	0	-1.771	0	2.383244	0.119182	0.12912	Cu>Ni>Zn
26	0	0	0	0	1.771	0	0.711723	0.08208	0.067215	Cu>Zn>Ni
30	0	0	0	0	0	-1.771	0.599422	0.074465	0.05159	Cu>Zn>Ni
20	0	0	0	0	0	1.771	1.219883	0.101579	0.062052	Cu>Zn>Ni
1 ⁰	0	0	0	0	0	0	0.442107	0.080844	0.073443	Cu>Zn>Ni
2 ⁰	0	0	0	0	0	0	0.480081	0.097165	0.070727	Cu>Zn>Ni
3 ⁰	0	0	0	0	0	0	1.058268	0.101284	0.066164	Cu>Zn>Ni

3.2. Optimization

In this study, the adsorption of Cu^{+2} on activated carbons prepared from ultrasound-assisted alkaline impregnated hazelnut shells from the multi-ion system containing Cu^{+2} , Zn^{+2} and Ni^{+2} was chosen as the optimization criterion. Selectivity is another criterion which can be considered as a secondary optimization criterion. Selectivity is also calculated as follows:

$$\text{Selectivity} = (\text{the adsorption capacity of } \text{Cu}^{+2} / \text{the adsorption capacities of } \text{Zn}^{2+} + \text{Ni}^{2+})$$

Furthermore, optimum conditions which ensure to be more realistic are often calculated in the presence of some constraints. Secondary process responses (Zn^{2+} and Ni^{2+} adsorption capacities) are also considered constraints. The lower and the upper limit values of the process variables also form natural constraints. Second-order model equations (10-12) are used in the optimization. Thus, the optimization problem is defined as;

$$\text{maximize } Y_{\text{Cu}^{2+}} \quad (14)$$

- Constraints on the variables X_i

$$-\beta_i < X_i < +\beta_i, i= 1, \dots, 6 \quad (15)$$

- Constraints on the secondary responses

$$\% 0.3 < \text{Zn}^{2+} \text{ and Ni}^{2+} \text{ adsorption capacities} < \% 25 \quad (16)$$

β values are given in Table 1. These constraints are necessary to avoid extrapolation out of the region of experimentation. The optimization problem given in Eq. (14) is solved using constrained optimization program supplied in the Matlab optimization toolbox. The optimum results are given in Table 6.

Table 6. Optimum conditions for selective adsorption of Cu^{+2}

P. Size (mm)	Ult. Power density (W/L)	Imp. Ratio (g/mL)	Imp. Time (min)	Act. Temp. ($^{\circ}\text{C}$)	Act. Time (min)	Ads. mg Cu^{2+} / g Ac	Ads. mg Zn^{2+} / g Ac	Ads. mg Ni^{2+} / g Ac	Selectivity
1.7504	2	0.0168	132	661	71.5	82.9131	25.5527	9.3273	2.3771

Among the optimum results; particle size, ultrasound power density, impregnation rate, impregnation time, activation temperature, and activation time appear to be constitute active constraints. Zn^{+2} and Ni^{+2} adsorption capacities which are secondary process responses determine the value of selectivity.

The graph of Cu^{+2} adsorption versus the secondary process responses Zn^{+2} and Ni^{+2} adsorption is given in Figure 2. In the graph, high Zn^{+2} and Ni^{+2} adsorption have been observed against high Cu^{+2} adsorption. However, this is not true when selectivity is considered as the secondary optimization criteria. High selectivity values correspond especially to low Ni^{+2} adsorption capacity values. As a result, realistic optimum conditions should be determined by taking into account both the adsorption capacity and selectivity.

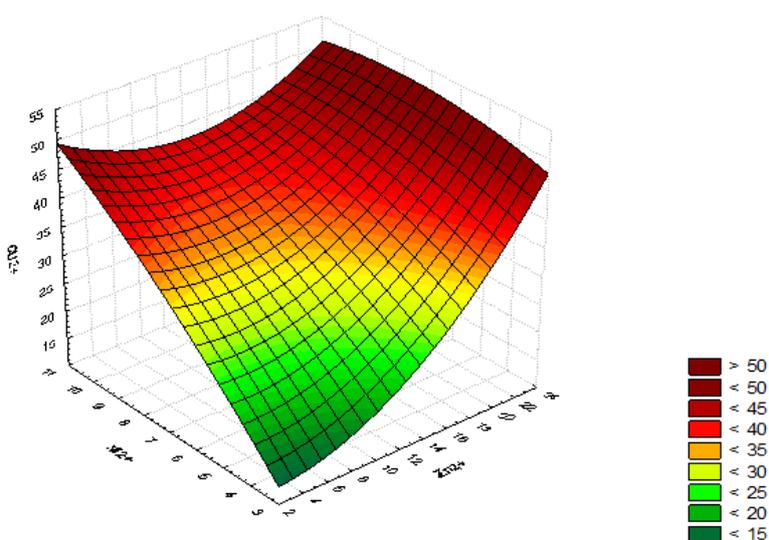


Figure 2. Cu^{+2} adsorption versus the secondary process responses of Zn^{+2} and Ni^{+2} adsorption

4. CONCLUSIONS

In this study, it was aimed to investigate suitable activated carbon production conditions for selective adsorption of Cu^{+2} from multiple ion systems containing more than one ion. Adsorption experiments were statistically designed and statistical models were established by using variance analysis among the experimental parameters related to Cu^{+2} , Zn^{+2} and Ni^{+2} adsorption capacities and optimum process conditions were found using a constrained optimization program supplied in the Matlab optimization toolbox.

The significant conclusions of the study are listed as;

- As a result of the adsorption experiments, the statistical analysis of the models was made and the correlation coefficients were obtained as 0.9802, 0.9855 and 0.9983, respectively. It was observed that the models which have a good fit with the experimental data were sufficient and systematic errors were not found.
- On the basis of the distribution coefficient (K_d), the adsorption selectivity sequence on ACs is generally $\text{Cu}^{+2} > \text{Zn}^{+2} > \text{Ni}^{+2}$ for multi-ion systems.
- Compared with Cu^{+2} , Zn^{+2} and Ni^{+2} adsorption capacities in multi- and single component media, the adsorption capacity of Cu^{+2} increased and the adsorption capacities of Zn^{+2} and Ni^{+2} were partially reduced. It can be considered as the synergistic effect of Cu^{+2} , Zn^{+2} and Ni^{+2} ternary system for Cu^{+2} .

As a result, activated carbons prepared from ultrasound-assisted 10 % KOH impregnated hazelnut shells can be effectively used for selective adsorption of Cu^{+2} from multiple ion systems containing Cu^{+2} , Zn^{+2} and Ni^{+2} ions. Obtained models and optimum operating conditions constitute an important source of information in terms of being able to carry out detailed researches in larger dimensions and to be able to determine the appropriate process conditions that can be created by feasibility studies and starting points for industrial applications.

ACKNOWLEDGEMENTS

Financial support by Atatürk University research foundation through 2003/38 project is gratefully acknowledged.

REFERENCES

- [1] Erguvenerler, F., Removal of Toxic Metal from Water Using Natural Waste Adsorbents. (Master Thesis), Celal Bayar University Institute of Science, Department of Chemistry, 2015.
- [2] Odabaş, N., Synthesis of Alginate Containing Composites and Using in Removal of Organic Pollutants. (Master Thesis), Istanbul University Institute of Graduate Studies in Science and Engineering, Department of Chemical Engineering, Istanbul, 2018.
- [3] Mutlu, S., Adsorption of Active Carbon and Lead Ions Produced from Hazelnut Shell and Grape Hulls. (Master Thesis), Istanbul Technical University Institute of Science, Department of Chemistry Engineering, Istanbul, 2009.
- [4] Krstic V., Urosevic T., Pesovski B., A review on adsorbents for treatment of water and wastewaters containing copper ions. *Chemical Engineering Science*, 192, 273–287, 2018.

- [5] Gözübüyük, Ö., Lead, Copper and Nickel Removal by Adsorptive Method from Aqueous Solutions Using Oltu Stone. (Master Thesis), Ataturk University Institute of Science, Department of Chemistry Engineering, Erzurum, 2012.
- [6] İnci, A., Investigation of Some Heavy Metal Levels in Cow Milks Produced in Aydın City. (Master Thesis), Adnan Menderes University Institute of Health Sciences, Department of Biochemistry, Aydın, 2015.
- [7] Baylan, N., Investigation of Adsorption Properties of Bentonite and Grape Kernel Active Carbon in Single and Multiple Ion Systems. (Master Thesis), Istanbul Technical University Institute of Science, Department of Chemistry Engineering, Istanbul, 2013.
- [8] Ghorbel-Abid, I. and Trabelsi-Ayadi, M., Competitive Adsorption of Metals on Local Landfill Clay. *Arabian Journal of Chemistry*, 8, 25-31, 2015.
- [9] Alkan, E., Investigation of Adsorption Kinetic and Removal of Heavy Metal from Aqueous Solution Using a Baffler Cylinder. (Master Thesis), Yuzuncu Yıl University Institute of Science, Department of Chemistry, Van, 2008.
- [10] Parlak, M., Removal of Heavy Metals from Modified Killers. (Master Thesis), Yıldız Technical University Institute of Science, Analytical Chemistry, Istanbul, 2009.
- [11] Gönen, T., Adsorption of Copper and Nickel Ions from Solution of Clay Mineral. (Master Thesis), Kahramanmaraş Sutcu Imam University Institute of Sciences, Dept. of Soil Science, Kahramanmaraş, 2009.
- [12] Eloussaief, M., Hamza, W., Kallel, N. and Benzina M., Waste waters Decontamination: Mechanisms of Pb, Zn and Cd Competitive Adsorption on Tunisian Smectite in Single and Multi-Solute Systems. *Environmental Progress and Sustainable Energy*, 32(2), 229-238, 2013.
- [13] Coskun, S. and Soykan, C., Preparation of Amidoximated Polyester Fiber and Competitive Adsorption of Some Heavy Metal Ions from Aqueous Solution onto This Fiber. *Journal of Applied Polymer Science*, 112, 1798-1807, 2009.
- [14] Futralan, C., Kan, C., Dalida, M., Hsien, K., Pascua, C., Wan, M., Comparative and Competitive Adsorption of Copper, Lead and Nicel Using Chitosan Immobilized on Bentonite. *Carbohydrate Polymers*, 83, 528-536, 2011.
- [15] Kavand, M., Kaghazchi, T. AndSoleimani, M., Optimization of Parameters for Competitive Adsorption of Heavy Metal Ions (Pb, Ni, Cd) onto Activated Carbon. *Korean J. Chem. Eng.*, 31(4), 692-700, 2014.
- [16] Kampalanonwat, P. and Supaphol, P., The Study of Competitive Adsorption of Heavy Metal Ions from Aqueous Solution by Aminated Polyacrylonitrile Nanofiber Mats. *Energy Procedia*, 56, 142-151, 2014.
- [17] Yang, J., Wei, W., Pi, S., Ma, F., Li, A., Wu, D. and Xing, J., Competitive Adsorption of Heavy Metals by Extracellular Polymeric Substances Extracted from *Klebsiella* sp. J1. *Bioresource Technology*, 196, 533-539, 2015.
- [18] Sen, N., Obtaining and Characterization of Active Carbon from Hazelnut Shells. (Master Thesis), Firat University, Faculty of Science, Department of Chemical Engineering, Elazığ, 2009.

- [19] Makeswari, M. and Santhi, T., Optimization of Preparation of Activated Carbon from *Ricinus communis* Leaves by Microwave-Assisted Zinc Chloride Chemical Activation: Competitive Adsorption of Ni Ions from Aqueous Solution. Hindawi Publishing Corporation Journal of Chemistry, (314790), 1-12, 2013.
- [20] Nas, B., Dolu, T., Ateş, H., Argun, M., Yel, E., Treatment Alternatives for Micropollutant Removal in Wastewater, Selcuk University, Engineering Faculty, Department of Environmental Engineering, Konya, 2017.
- [21] Liu, S., Tang, W., Yang, Y., Adsorption of nicotine in aqueous solution by a defective graphene oxide, *Science of the Total Environment*, 643, 507–515, 2018.
- [22] Akbulut, M., Activated Carbon Production and Characterization from Lignite and Biomass Mixture. (Master Thesis), Ankara University Institute of Science, Department of Chemistry Engineering, Ankara, 2015.
- [23] Ozturk, D., Investigation of lead adsorption on pumice samples collected from Ağrı Mountains and Optimization of ambient conditions by Response surface methods. (Master Thesis), Yuzuncu Yıl University Institute of Science, Department of Chemistry, Van, 2013.
- [24] Dogan, D., Spectroscopic Analysis of Organic Compounds in Competitive Adsorbent Similar Structures and Adsorption Modeling in Chemistry. (Doctorate thesis), Inonu University Institute of Science, Department of Chemistry, Malatya, 2008.
- [25] Alp, T., Comparative Study of Growth Kinetics of Various Kinds of Yeast and Mold Mushrooms and Biocorrosion of Cells in Metal Wastewater Containing Heavy Metal Pollution. (Master Thesis), Cumhuriyet University, Institute of Science and Technology, Department of Chemical Engineering, 2007.
- [26] Sayan, E., Ultrasound-assisted preparation of activated carbon from alkaline impregnated hazelnut shell: An optimization study on removal of Cu^{2+} from aqueous solution, *Chemical Engineering Journal*, 115, 213–218, 2006.
- [27] Sayan E, İngeç A., Modeling and optimization of surface areas of activated carbon prepared from by ultrasound-assisted alkaline impregnated hazelnut shell. *Anadolu University Journal of Science and Technology–A applied Sciences and Engineering*, 16 (2): 229-238, 2015.
- [28] Sayan, E., Bayramoğlu, M., Statistical modeling of sulfuric acid leaching of TiO_2 , Fe_2O_3 and Al_2O_3 from red mud. *I. Chem. E. Symp. Ser., Trans. IChemE 79 (B)*, 291–296, 2001.
- [29] Myers, R.H., *Response Surface Methodology*. Allyn and Bacon, N. York. 126 pp, 1971.
- [30] McKay, G., *Use of Adsorbents for the Removal of Pollutants from Wastewater*, Tokyo, 1996.
- [31] Ingeç, A., Modeling and optimization of Ni^{2+} adsorption from aqueous solutions with activated carbons prepared by alkali impregnation with ultrasound. (Master Thesis), Ataturk University Institute of Science, Engineering Faculty Chemistry Eng. Dear Mist, Erzurum, 2013.
- [32] Sayan, E., An Optimization Study on Removal of Zn^{2+} from Aqueous Solution by Ultrasound-Assisted Preparation of Activated Carbon from Alkaline Impregnated Hazelnut Shell. *J. Chem. Soc. Pak.*, 36, 28-36, 2014.
- [33] Bourliva A., Michailidis K., Filippidis A., Sikalidis C., Betsiou M., Bantsis G., Copper removal from single and multi-component systems by natural bentonite from milos island, Greece, 8th

Panhellenic Scientific Conference on Chemical Engineering, Thessaloniki, Greece, 26-28/05/2011, Proceedings, 8p, 2011.

- [34] Buscano, S.I., Lourdes, M., Dalida, P., Kan, C., Selectivity sequence and mechanism of adsorption of Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} onto chitosan-montmorillonite composite beads. Conference: 5th Cross-Straits Drinking Water Symposium, At Macao, China, 2009.
- [35] Wan, M., Kan, C., Buscano, S. I., Lourdes, M., Dalida, P., Comparative Adsorption of Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} in Aqueous Medium onto Chitosan-Montmorillonite Composite Beads. Conference:5th Cross-Straits Drinking Water Symposium, At Macao, China, 2009.
- [36] Kaduková, J., Horváthová, H., Biosorption of copper, zinc and nickel from multi-ion solutions. *Nova Biotechnologica et Chimica* 11-2, 125-132, 2012.
- [37] Mohan, D., Pittman Jr., C. U., Steele, P. H., Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent. *Journal of Colloid and Interface Science* 297, 489–504, 2006.
- [38] Alloway, B.J., Soil processes and the behaviour of metals. In: Alloway, B.J. (Ed.), *Heavy metals in Soils*. Blackie Academic&Professional, London, pp.11-37, 1995.