



# Statistical analysis of Cu(II) and Co(II) sorption by apple pulp carbon using factorial design approach



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## ABSTRACT

Toxic metal bearing effluents can cause severe environmental contamination; thus metal removal by adsorption is a vital situation. In this study, apple pulp carbon was tested as low-cost adsorbent for the copper(II) and cobalt(II) adsorption studies. 2<sup>5</sup> full factorial experimental design was utilized to optimize the effects of pH, adsorbent dosage, initial metal ion concentration, contact time and temperature. ANOVA, F-test and Student's t-test showed that Cu(II) and Co(II) adsorption is slightly temperature and contact time dependent but markedly increases with solution pH and adsorbent dosage. Although the initial Cu(II) concentration had a negative effect on removal efficiency, the initial Co(II) concentration had a positive effect. The suggested optimum conditions for 90.49% Cu(II) and 65.11% Co(II) removal were: pH 5, the adsorbent dosage = 0.4 g/50 mL, the initial metal ion concentration = 10 and 20 mg/L, temperature = 40 and 20 °C, contact time = 60 and 120 min, respectively. pH was found as significant within a 95% confidence level for both Cu(II) and Co(II) removal. Additionally, main effects of *adsorbent dosage* and *initial concentration*, the interaction effect of *pH × initial concentration* were also found as significant for Cu(II) removal. In conclusion, apple pulp carbon could be successfully applied for the removal of heavy metals because of its low-cost and abundance.

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## Introduction

In recent years, rapid increases in world population, urbanization and industrial activities such as metal-plating facilities, mining operations, leather tanning, corrosion inhibitors, battery manufacturing processes, the production of paints and pigments, fertilizer manufacturing, the printing and photographic industries, the non-ferrous metal industry, wood pulp production, steel and automobile industries, the ceramic and glass industries are responsible to generate a large amount of hazardous heavy metal ions [1–8].

Heavy metal pollution causes a serious threat to the environment and human health because of its non-biodegradability, toxic

effects, accumulation in living tissues and food chain even at low concentrations [9–12]. Copper and cobalt are two widely used metals in our daily life. Small amounts of cobalt and copper are essential for human health. Cobalt is a part of vitamin B12; unfortunately, high dosage of cobalt has many toxic effects such as resulting paralysis, diarrhea, genotoxicity, low blood pressure, cardiomyopathy, lung irritations, bronchial asthma, carcinogenicity, and bone defects [2,5,6]. Additionally, high dosages intake of copper causes its deposit in liver, brain, skin, pancreas, and myocardium, generates gastrointestinal problems, inhalation of sprays including copper leads lung cancer [13–18]. Therefore, these hazardous effluents need to be treated and controlled before discharging into the environment [19]. Improvement of techniques for heavy metal treatment and rising the heavy metals levels to allowable limits in wastewaters have been gained a great concern globally to meet the altering environmental regulations [10,20]. Coagulation/flocculation process, evaporation, membrane filtration, ultra-filtration, biological systems, oxidation process, activated carbon adsorption, reverse osmosis, ion exchange, solvent extraction, electrolytic processes and adsorption are conventional physicochemical methods for removing metals from industrial effluents [5,11,16,21,22]. However, application of such technologies

**Abbreviations:** ANOVA, analysis of variance; AP, apple pulp; APC, apple pulp carbon; Co(II), cobalt(II) metal ion; Cu(II), copper(II) metal ion; FT-IR, Fourier transform infrared spectroscopy; pH<sub>ZPC</sub>, point of zero charge analysis; SEM, scanning electron microscope; XRF, X-ray fluorescence spectrometer.

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### Nomenclature

$A$	The solution pH
$a$	The number of levels
$B$	The adsorbent dosage (g/50 mL)
$C$	The initial metal concentration (mg/L)
$C_e$	The liquid phase concentrations of metal ion at equilibrium (mg/L)
$C_0$	The liquid phase concentrations of metal ion at initial (mg/L)
$D$	Temperature ( $^{\circ}\text{C}$ )
$E$	The contact time (min)
$k$	The number of factors
$P$	Probability level
$R\text{-}Sq$	Correlation coefficient
$S$	The standard error of the estimate
$X_0$	The global mean
$X_i$	The regression coefficient relating to the main factor effects and interactions
$Y$	The predicted response (removal efficiency(%))
$\eta$	The metal ion removal efficiency (%)

is constricted because of technical or economical limitations. All these methods have various limitations, especially the insufficient removal of traces of metal ions [23], expensive equipment [24], the high capital investment and energy consumption, low efficiency and the necessary disposal of residual sludge holding heavy metals [3,12,25]. Thus, development of novel separation technologies is focused on more efficient and low-cost methods for metal ion uptake. Among various water-treatment processes, adsorption is preferred for the removal of heavy metal ions due to its high efficiency, its easy handling, the availability of different adsorbents, and its cost-effectiveness [1,26]. The application of conventional adsorbents such as granular or powdered activated carbon is usually limited due to their high cost. Lately, various alternative adsorbents such as microbial biomass [15]; agricultural by-products including carrot olive mill residue [27], carrot residue [28], wheat shell [29,30], rice husk [31], pine bark [13,32], onion skins [33], sunflower stalks [34], corn cobs [11,35]; industrial waste such as waste rubber [36], fly ash [37], animal bones [38,39], sawdust [40]; and also clay [41], activated alumina [42], zeolite [43], chitosan [6,44], *Aspergillus niger* [45], graphene oxide nano-sheets [46,47], graphene oxide onto  $\text{TiO}_2$  [48], magnetite/graphene oxide composite [49], carbonaceous nanofibers [50], biochar [51], multi-walled carbon nanotubes [52] have been studied for conceivable use as low cost and effective sorbents in the treatment of heavy metal-containing water. Unfortunately, low-cost adsorbents have commonly low adsorption capacities and require great amounts of sorbents. Consequently, a requirement rises to find new, economical, abundant, and highly effective adsorbents [53].

Apples are classified as one of the most abundant fruits, with a world production of 76.4 million metric tons (Mt) in 2012 [54]. Apple is one of the soft-core fruit and has a significant role for Turkish trade since Turkey is in the third place for apple production (2.550 thousand tons in a year) in the world [55]. Although apples are mainly consumed as a fruit, about 12% of the harvesting is canalized to the fabrication of apple juice and cider. Consequently, pressing apples causes the solid residue (apple pulp) which indicates more than 12 wt.% of the fruit. Hence, taking a mean value of 60 Mt for the yearly world production, about 0.84 Mt of apple pulp are produced yearly worldwide. Although it is not as polluting as other vegetable by-products from the food industry, apple pulp

is an unadaptable material that is frequently spilled in an unrestrained way [56,57].

Determination of optimum physicochemical conditions such as medium pH, temperature and sorbent dosage, etc. is an essential stage in sorption processes. Factorial design technique can be used instead of the traditional one-variable-at-a-time experiments to diminish the number of experiments, time and overall research cost [9]. There is no information in the literature on optimization of adsorption parameters of copper(II) and cobalt(II) removal by using apple pulp residue via modeling  $2^5$  full factorial design. The apple pulp (AP) has a capability of being used as an alternative raw material to obtain carbonaceous material (APC); therefore the main objective of present study is to examine the feasibility of apple pulp carbon as an adsorbent to remove copper(II) and cobalt(II) metal ions from aqueous solutions. Analysis of variance (ANOVA) statistical approach and a five-factor full factorial design were used to figure out the significance of two level operating factors (pH, sorbent dosage, temperature, initial metal ion concentration and contact time). In the last stage, sorption isotherms and kinetics were analyzed.

### Material and methods

The preparation of adsorbent and deciding for operating conditions are crucial to remove metal ions; hence adsorbent characteristics should be determined, and experimental conditions should be optimized carefully.

#### Adsorbent preparation and characterization

Apple pulp was obtained from a fruit juice factory in Bursa (Turkey), and then it was air-dried, crushed and sieved to obtain mean sizes. Carbonization process was carried out at  $550^{\circ}\text{C}$  with a heating rate of  $10^{\circ}\text{C}/\text{min}$  to produce a carbonaceous product. Apple pulp (AP) and apple pulp carbon (APC) were stored in plastic bottles and used as sorbents. There were no other chemical or physical treatments for sorption studies.

Different characterization techniques such as structure and preliminary analysis, elemental analysis, FT-IR spectroscopy, scanning electron microscopy (SEM), X-ray fluorescence (XRF) spectrometry,  $\text{pH}_{\text{ZPC}}$  point analysis and particle size analysis of AP and APC were used to identify the properties of raw material and adsorbent. All of these characterization techniques were described, and results were given in detail in our previous study [57].

#### Aqueous metal ion solutions preparation

All reagents used in the preparation and sorption studies were of analytical grade from Merck (Germany) and were utilized without further purification. Metal solutions were prepared using distilled water to prevent and minimize possible interferences. The stock solution of copper(II) and cobalt(II) (1000 ppm) was prepared by dissolving the nitrate salts in distilled water and diluted to arrange different working concentrations. The pH adjustment of each solution to the desired value was done by adding 0.1 M NaOH or 0.1 M HCl, and pH was monitored by a digital pH meter Thermo Scientific Orion 3 Star.

#### Batch sorption procedure

The sorption of metal ions from aqueous solutions under different operating conditions was performed by batch experiments in the constant volume at 50 mL. In order to determine the factors that affect the copper(II) and cobalt(II) sorption by APC, and to examine the interaction effects of several parameters,  $2^5$  full factorial experimental design was implemented. pH, sorbent

**Table 1**  
Levels of independent process variables used in full factorial design.

Factors	Levels	
	Low level	High level
pH (A)	3	5
Adsorbent dosage, g/50 mL (B)	0.1	0.4
Initial concentration, mg/L (C)	10	20
Temperature, °C (D)	20	40
Contact time, min (E)	60	120

dosage, temperature, initial metal ion concentration and contact time were selected as experimental factors. The temperature of the solutions was set at desired values in an isothermal water bath shaker (THERMAL H11860) at 120 rpm. The suspensions were then filtered, and dye concentrations in the supernatant solutions were measured. Copper(II) and cobalt(II) ion concentrations were measured by using Atomic Absorption Spectrophotometer model GBC933AA using air-acetylene (8:2 L/min) flame under optimized conditions. Radiation sources were hollow cathode lamps of copper(II) and cobalt(II).

Sorbed metal concentrations were calculated by using the difference between initial and final metal ion concentrations in aqueous solutions. The removal efficiency of metal ion ( $\eta$ ) is defined as [58]:

$$\eta = [(C_0 - C_e)/C_0]100 \quad (1)$$

where  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium concentrations of copper(II) or cobalt(II) solutions, respectively.

#### The full factorial design of experiments

Factor-response relationship is analyzed in the factorial design of experiments to specify the optimal experimental conditions by reducing the number of required runs. The main priority of factorial design is to find an opportunity for evaluating both the individual parameters and interactions among factors when compared to traditional one-variable-at-a-time experiment [59]. If the number of levels is  $a$ , and the number of factors is  $k$ , the number of runs is shown as  $a^k = 2^5 = 32$  [60]. The  $2^5$  full factorial design for cobalt(II) and copper(II) sorption was applied to investigate the effects of factors and levels (Table 1). The solution pH, initial metal ion concentration, sorbent dosage, temperature and contact time were chosen as independent factors. The main effects and interaction effects, statistical parameters (coefficients and standard deviation of coefficients) and the statistical plots (Pareto chart and normal probability, main effects, and interaction plots) were analyzed by using MINITAB 14 statistical software.

## Results and discussion

In this section, statistical analyses of copper(II) and cobalt(II) ions were examined according to ANOVA results.

#### Factorial design adsorption experiments

In current method, the  $2^5$  full factorial design was employed to identify the important factors and their interactions in sorption process. Analysis of variance (ANOVA) was used to establish the interactions between independent factors; and also the main effects of metal ion adsorption were identified depend upon the  $P$ -value with >95% of confidence level. The probability value of  $P$ -value is used to determine the statistically significant effects in the model [61].  $P$ -value is the lowest level of significance leading to the rejection of the null hypothesis [62]. The factorial design matrix and the responses (removal efficiency(%)) of copper(II) and cobalt (II) metal ion uptake related with variables are given in Tables 2–4.

**Table 2**  
Factorial design matrix of five variables along with copper(II) and cobalt(II) sorption.

Runs	Factors					Removal efficiency (%)	
	A	B	C	D	E	Copper(II)	Cobalt(II)
1	3	0.4	20	40	120	22.95	12.24
2	5	0.4	20	40	120	80.76	64.45
3	3	0.1	10	40	60	28.6	3.39
4	3	0.4	10	20	60	53.06	24.08
5	3	0.1	10	20	60	29.16	8.91
6	3	0.4	10	20	120	59.37	28.63
7	5	0.4	20	20	60	79.3	63.55
8	5	0.4	20	20	120	81.04	65.115
9	5	0.1	10	20	60	56.46	29.77
10	5	0.1	10	40	60	55.96	28.48
11	3	0.1	20	20	60	1.29	0.88
12	5	0.4	10	20	60	73.33	37.97
13	3	0.1	20	40	60	2.01	1.21
14	5	0.1	10	20	120	50.46	32.77
15	5	0.1	20	20	120	54.83	58.82
16	5	0.4	20	40	60	79.42	59.9
17	3	0.4	20	20	60	15.46	8.04
18	5	0.4	10	40	60	90.49	52.83
19	3	0.1	10	20	120	27.08	13.41
20	5	0.1	10	40	120	61.21	33.72
21	3	0.1	20	40	120	4.25	2.115
22	3	0.4	20	20	120	10.72	11.34
23	3	0.1	20	20	120	1.89	1.07
24	3	0.4	10	40	120	64.84	29.83
25	3	0.4	20	40	60	6.68	15.98
26	5	0.1	20	20	60	47.95	56.38
27	5	0.4	10	20	120	82.55	40.62
28	3	0.1	10	40	120	21.46	2.75
29	3	0.4	10	40	60	67.24	24.91
30	5	0.4	10	40	120	81.67	42.71
31	5	0.1	20	40	60	58.11	56.88
32	5	0.1	20	40	120	50.55	57.59

**Table 3**  
Statistical parameters for  $2^5$  design of copper(II) removal.

Term	Effect	Coef	SE Coef	T	P
Constant		46.880	0.6347	73.86	0.009
A	41.752	20.876	0.6347	32.89	0.019
B	24.851	12.425	0.6347	19.58	0.032
C	-19.108	-9.554	0.6347	-15.05	0.042
D	3.266	1.633	0.6347	2.57	0.236
E	0.694	0.347	0.6347	0.55	0.681
A × B	1.778	0.889	0.6347	1.40	0.395
A × C	16.587	8.293	0.6347	13.07	0.049
A × D	0.766	0.383	0.6347	0.60	0.654
A × E	-0.438	-0.219	0.6347	-0.35	0.788
B × C	-5.419	-2.710	0.6347	-4.27	0.146
B × D	1.637	0.818	0.6347	1.29	0.420
B × E	1.671	0.835	0.6347	1.32	0.414
C × D	-1.734	-0.867	0.6347	-1.37	0.402
C × E	1.402	0.701	0.6347	1.10	0.468
D × E	-0.797	-0.398	0.6347	-0.63	0.643
A × B × C	6.601	3.030	0.6347	4.77	0.131
A × B × D	-1.638	-0.819	0.6347	-1.29	0.420
A × B × E	-1.057	-0.528	0.6347	-0.83	0.558
A × C × D	-0.867	-0.433	0.6347	-0.68	0.619
A × C × E	-1.058	-0.529	0.6347	-0.83	0.558
A × D × E	-1.907	-0.953	0.6347	-1.50	0.374
B × C × D	-2.346	-1.173	0.6347	-1.85	0.316
B × C × E	-0.114	-0.057	0.6347	-0.09	0.943
B × D × E	0.029	0.015	0.6347	0.02	0.985
C × D × E	1.773	0.887	0.6347	1.40	0.396
A × B × C × D	0.837	0.418	0.6347	0.66	0.629
A × B × C × E	0.441	0.220	0.6347	0.35	0.787
A × B × D × E	-1.936	-0.968	0.6347	-1.52	0.370
A × C × D × E	-2.779	-1.390	0.6347	-2.19	0.273
B × C × D × E	4.147	2.073	0.6347	3.27	0.189

S = 3.59033, R-Sq = 99.95%, R-Sq(adj) = 98.41%.

**Table 4**  
Statistical parameters for 2<sup>5</sup> design of cobalt(II) removal.

Term	Effect	Coef	SE Coef	T	P
Constant		30.323	1.031	29.41	0.022
A	37.048	18.524	1.031	17.97	0.035
B	12.128	6.064	1.031	5.88	0.107
C	6.299	3.149	1.031	3.05	0.201
D	0.477	0.238	1.031	0.23	0.855
E	1.501	0.751	1.031	0.73	0.599
A × B	-3.036	-1.518	1.031	-1.47	0.380
A × C	16.678	8.339	1.031	8.09	0.078
A × D	0.969	0.484	1.031	0.47	0.720
A × E	-0.247	-0.123	1.031	-0.12	0.924
B × C	-3.919	-1.960	1.031	-1.90	0.308
B × D	2.461	1.231	1.031	1.19	0.444
B × E	-0.542	-0.271	1.031	-0.26	0.836
C × D	0.169	0.085	1.031	0.08	0.948
C × E	-0.261	-0.131	1.031	-0.13	0.920
D × E	-1.273	-0.637	1.031	-0.62	0.648
A × B × C	0.664	0.332	1.031	0.32	0.802
A × B × D	-0.748	-0.374	1.031	-0.36	0.778
A × B × E	-1.051	-0.526	1.031	-0.51	0.700
A × C × D	-2.876	-1.438	1.031	-1.39	0.396
A × C × E	1.323	0.662	1.031	0.64	0.637
A × D × E	0.114	0.057	1.031	0.06	0.965
B × C × D	-1.976	-0.988	1.031	-0.96	0.513
B × C × E	0.721	0.360	1.031	0.35	0.786
B × D × E	-0.784	-0.392	1.031	-0.38	0.769
C × D × E	0.639	0.320	1.031	0.31	0.809
A × B × C × D	-0.633	-0.317	1.031	-0.31	0.810
A × B × C × E	1.614	0.807	1.031	0.78	0.577
A × B × D × E	-0.503	-0.252	1.031	-0.24	0.848
A × C × D × E	0.834	0.417	1.031	0.40	0.755
B × C × D × E	0.404	0.202	1.031	0.20	0.877

S = 5.83186, R-Sq = 99.78%, R-Sq(adj) = 93.06%.

**Table 5**  
Analysis of variance (ANOVA) for copper(II) removal.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
A	1	13945.75	13945.75	13945.75	1081.86	0.019
B	1	4940.43	4940.43	4940.43	383.26	0.032
C	1	2920.96	2920.96	2920.96	226.60	0.042
D	1	85.31	85.31	85.31	6.62	0.236
E	1	3.86	3.86	3.86	0.30	0.681
A × B	1	25.29	25.29	25.29	1.96	0.395
A × C	1	2201.00	2201.00	2201.00	170.75	0.049
A × D	1	4.69	4.69	4.69	0.36	0.654
A × E	1	1.54	1.54	1.54	0.12	0.788
B × C	1	234.96	234.96	234.96	18.23	0.146
B × D	1	21.43	21.43	21.43	1.66	0.420
B × E	1	22.33	22.33	22.33	1.73	0.414
C × D	1	24.06	24.06	24.06	1.87	0.402
C × E	1	15.72	15.72	15.72	1.22	0.468
D × E	1	5.08	5.08	5.08	0.39	0.643
A × B × C	1	293.85	293.85	293.85	22.80	0.131
A × B × D	1	21.47	21.47	21.47	1.67	0.420
A × B × E	1	8.94	8.94	8.94	0.69	0.558
A × C × D	1	6.01	6.01	6.01	0.47	0.619
A × C × E	1	8.96	8.96	8.96	0.69	0.558
A × D × E	1	29.09	29.09	29.09	2.26	0.374
B × C × D	1	44.02	44.02	44.02	3.41	0.316
B × C × E	1	0.10	0.10	0.10	0.01	0.943
B × D × E	1	0.01	0.01	0.01	0.00	0.985
C × D × E	1	25.15	25.15	25.15	1.95	0.396
A × B × C × D	1	5.60	5.60	5.60	0.43	0.629
A × B × C × E	1	1.55	1.55	1.55	0.12	0.787
A × B × D × E	1	29.97	29.97	29.97	2.33	0.370
A × C × D × E	1	61.80	61.80	61.80	4.79	0.273
B × C × D × E	1	137.57	137.57	137.57	10.67	0.189
Error	1	12.89	12.89	12.89		
Total	31	25139.40				
Main effects	5	21896.3	21896.3	4379.26	339.73	0.041
2-way interaction	10	2556.1	2556.1	255.61	19.83	0.173
3-way interaction	10	437.6	437.6	43.76	3.39	0.401
4-way interaction	5	236.5	236.5	47.30	3.67	0.376
Residual error	1	12.9	12.9	12.89		
Total	31	25139.4				

S = 3.59033, R-Sq = 99.95%, R-Sq(adj) = 98.41%.

Main and interaction effects, coefficients of the model, standard errors of each coefficient and T values are also shown in Tables 3 and 4. The coded equation in Eq. (6) was used to clarify the 2<sup>5</sup> factorial designs of metal ions removal by adsorption:

$$\begin{aligned}
 Y = & X_0 + X_1A + X_2B + X_3C + X_4D + X_5E + X_6AB + X_7AC + X_8AD \\
 & + X_9AE + X_{10}BC + X_{11}BD + X_{12}BE + X_{13}CD + X_{14}CE + X_{15}DE \\
 & + X_{16}ABC + X_{17}ABD + X_{18}ABE + X_{19}ACD + X_{20}ACE + X_{21}ADE \\
 & + X_{22}BCD + X_{23}BCE + X_{24}BDE + X_{25}CDE + X_{26}ABCD \\
 & + X_{27}ABCE + X_{28}ABDE + X_{29}ACDE + X_{30}BCDE
 \end{aligned} \quad (6)$$

where Y is the predicted response (removal efficiency(%)), X<sub>0</sub> is the global mean, X<sub>i</sub> value (i = 1, 2, 3, ... 30) represents the regression coefficient relating to the main factor effects and interactions, A is the solution pH, B is the adsorbent dosage (g/50 mL), C is the initial metal ion concentration (mg/L), D is the temperature (°C) and E is the contact time (min).

Two model equations obtained for copper(II) and cobalt(II) removal efficiency were given in Eqs. (7) and (8). Following equations were attained by substituting the coefficients X<sub>i</sub> in Eq. (6) by their values from Tables 3 and 4, respectively.

$$\begin{aligned}
 Y_{Cu^{2+}} = & 46.880 + 20.876A + 12.425B - 9.554C + 1.633D \\
 & + 0.347E + 0.889AB + 8.293AC + 0.0219AE - 2.710BC \\
 & + 0.818BD + 0.835BE - 0.867CD + 0.701CE - 0.398DE \\
 & + 3.030ABC - 0.819ABD - 0.528ABE - 0.433ACD \\
 & - 0.529ACE - 0.953ADE - 1.173BCD - 0.057BCE \\
 & + 0.015BDE + 0.887CDE + 0.418ABCD + 0.220ABCE \\
 & - 0.968ABDE - 1.390ACDE + 2.073BCDE
 \end{aligned} \quad (7)$$

**Table 6**  
Analysis of variance (ANOVA) for cobalt(II) removal.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
A	1	10980.51	10980.51	10980.51	322.86	0.035
B	1	1176.73	1176.73	1176.73	34.60	0.107
C	1	317.39	317.39	317.39	9.33	0.201
D	1	1.82	1.82	1.82	0.05	0.855
E	1	18.03	18.03	18.03	0.53	0.599
A × B	1	73.75	73.75	73.75	2.17	0.380
A × C	1	2225.28	2225.28	2225.28	65.43	0.078
A × D	1	7.51	7.51	7.51	0.22	0.720
A × E	1	0.49	0.49	0.49	0.01	0.924
B × C	1	122.89	122.89	122.89	3.61	0.146
B × D	1	48.46	48.46	48.46	1.42	0.308
B × E	1	2.35	2.35	2.35	0.07	0.444
C × D	1	0.23	0.23	0.23	0.01	0.836
C × E	1	0.55	0.55	0.55	0.02	0.948
D × E	1	12.97	12.97	12.97	0.38	0.920
A × B × C	1	3.52	3.52	3.52	0.10	0.648
A × B × D	1	4.48	4.48	4.48	0.13	0.802
A × B × E	1	8.84	8.84	8.84	0.26	0.700
A × C × D	1	66.18	66.18	66.18	1.95	0.396
A × C × E	1	14.01	14.01	14.01	0.41	0.637
B × C × D	1	31.24	31.24	31.24	0.09	0.810
B × C × E	1	4.15	4.15	4.15	0.61	0.577
B × D × E	1	4.91	4.91	4.91	0.06	0.848
C × D × E	1	3.27	3.27	3.27	0.10	0.809
A × B × C × D	1	3.21	3.21	3.21	0.09	0.810
A × B × C × E	1	20.83	20.83	20.83	0.61	0.577
A × B × D × E	1	2.03	2.03	2.03	0.06	0.848
A × C × D × E	1	5.56	5.56	5.56	0.16	0.755
B × C × D × E	1	1.30	1.30	1.30	0.04	0.877
Error	1	34.01	34.01	34.01		
Total	31	15196.61				
Main effects	5	12494.5	12494.5	2498.90	73.47	0.088
2-way interaction	10	2494.5	2494.5	249.45	7.33	0.280
3-way interaction	10	140.7	140.7	14.07	0.41	0.849
4-way interaction	5	32.9	32.9	6.59	0.19	0.928
Residual error	1	34.0	34.0	34.01		
Total	31	15196.6				

S = 5.83186, R-Sq = 99.78%, R-Sq(adj) = 93.06%.

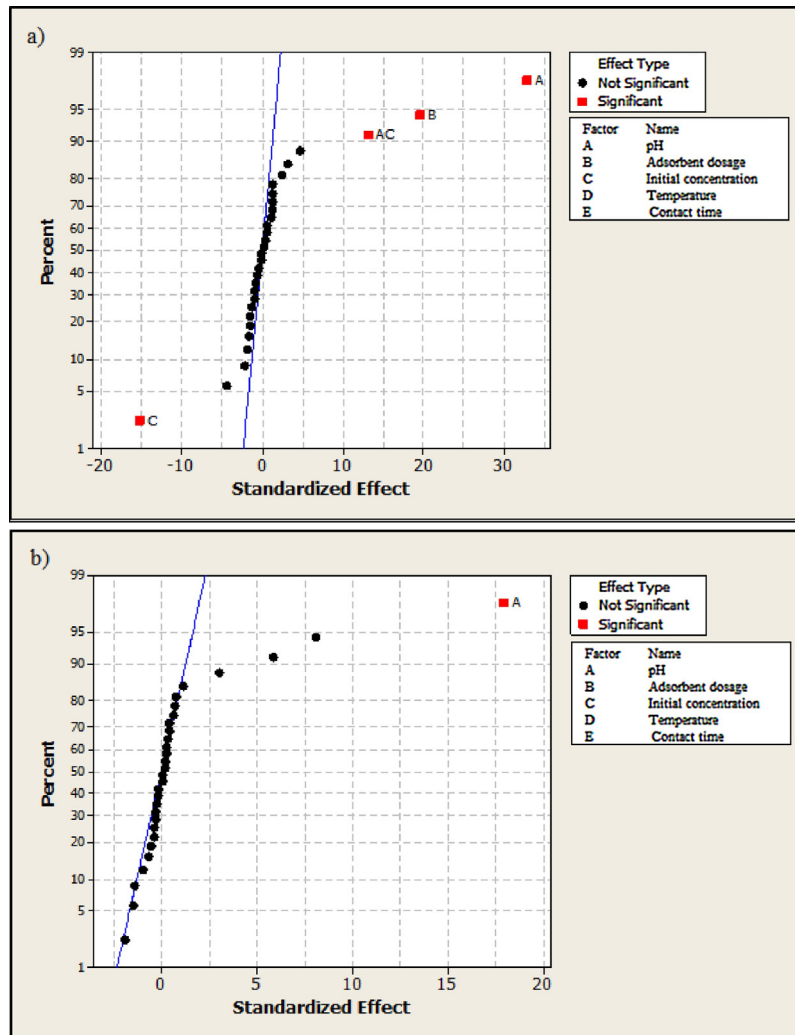


Fig. 1. Normal probability plot of standardized effects for (a) copper(II) and (b) cobalt(II) removal efficiency(%).

$$\begin{aligned}
 Y_{\text{Co}^{2+}} = & 30.323 + 18.524A + 6.064B + 3.149C + 0.238D + \\
 & 0.751E - 1.518AB + 8.339AC + 0.484AD - 0.123AE - \\
 & 1.960BC + 1.231BD - 0.271BE + 0.085CD - 0.131CE - \\
 & 0.637DE + 0.332ABC - 0.374ABD - 0.526ABE - 1.438ACD + \\
 & 0.662ACE + 0.057ADE - 0.988BCD + 0.360BCE - 0.392BDE + \\
 & 0.320CDE - 0.317ABCD + 0.807ABCE - 0.252ABDE + 0.417ACDE + \\
 & 0.202BCDE \quad (8)
 \end{aligned}$$

The removal efficiency increases via changing the factor from low to high levels when the effect of a factor is positive [1]. On the contrary, the negative effect causes a reduction in removal efficiency, when the same factor is altered from low to the high level [63]. According to Eq. (7), initial metal ion concentration had a negative effect on removal efficiency of copper(II) ion, while pH, adsorbent dosage, temperature and contact time had a positive effect.

#### Analysis of variance (ANOVA)

The statistical method of ANOVA is used to subdivide the total variation into its component parts each of which is correlated with a different source of variation [53]. A variance analysis (ANOVA) is applied to perform a test for the significance of regression; thus the suitability of the model can be confirmed. The interaction effects are easily determined and tested by utilizing the usual ANOVA. The

ANOVA results of main effects, 2-way, 3-way and 4-way interactions are shown in Tables 5 and 6. The sum of the squares used to estimate factors effect, Fisher's F-ratios and P-values were also represented. The preciousness of a factor in the model estimated by its sum of squares (SS). In such a way that significance of the factor in the process increases when SS value rises.

ANOVA estimated that the main factors (A, B and C) and the interactions (A × C) were highly significant ( $P < 0.05$ ) and the model was applicable very well for copper(II) removal. Only pH effect (A) was significant at a 5% of probability level for cobalt(II) removal. Besides, the fit models presented square correlation coefficients ( $R^2$ ) of 99.95% and 99.78% fitted very well to the statistical model for copper(II) and cobalt(II) removal, respectively.

#### Normal probability plot of standardized effect and the Pareto chart

The normal probability plot is applied to judge the normality of data as "real" or "chance" [60,62,64,65]. Each point on the plot is referred to one effect. Fig. 1 shows the normal probability plot of standardized effects for copper(II) and cobalt(II) removal. The graph was separated into two regions: the factors and interactions with negative coefficients were located below 50%, and factors with positive coefficients were lied in the upper region. The non-significant effects symbolized by a circle are close to a fitted line, and "real" factor effects represented as a square were situated away from the line [9,62,66]. Student's *t*-test was implemented to

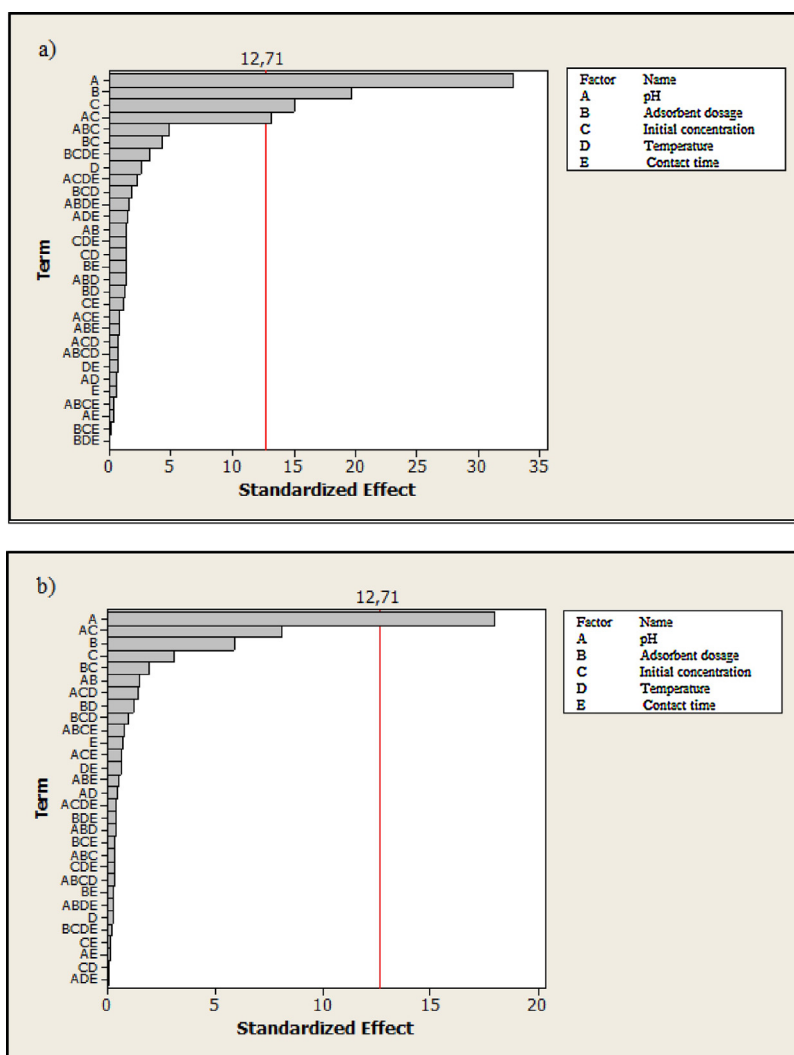


Fig. 2. Pareto charts for (a) copper(II) and (b) cobalt(II) removal.

determine the significance of the regression coefficients. Results obtained from normal probability plots are also proved by Pareto charts in Fig. 2. All the values located at the right of the vertical line were significant, the line implied the minimum statistically significant effect magnitude for 95% confidence level [63,66]. It can be concluded that pH of the solution was the most important variable of both sorption processes. Higher pH value improved the metal ion removal from the solutions; this result was compatible with the literature. Copper(II) ions could precipitate soon after the pH value of 6; thus the highest pH of the solutions was chosen as 5 [67,68]. The second important factor for copper(II) removal was adsorbent dosage (B). The third important factor was the initial metal ion concentration (C), the highest removal efficiency was accomplished by using lower initial metal ion concentration. The last important factor for copper(II) removal optimization was  $A \times C$  interaction with positive coefficient value. A small increase in the solution pH conjunction with a slight increase in the initial dye concentration could lead to an unexplained increase in removal efficiency; this synergistic effect could not be noticed with the univariate design of the system.

#### Main effects and interaction effects of the factors

The main effects of the process parameters (A, B, C, D, and E) for copper(II) and cobalt(II) ions removal are shown in Fig. 3a and b, respectively. The change in response generated by the shift in the

level of a factor is called as main effect [53]. The length of the vertical line is directly associated with the statistical significance of a factor, and the slope of the effect implies the sign of the main effect [57,60]. The larger the change in removal efficiency(%) when it is changing from low to high levels due to the information above. Also, removal efficiency(%) increases as the factor alters from level 1 to level 2 if the effect of a factor is positive [62,69]. The effect of pH had a positive effect on the response in such a way that the increase in the pH led to a remarkable increase of metal ion removal. The sorption medium had more available surface area and active sites with rising adsorbent dosage; thus the greater removal of metal ions attained at higher dosages. Copper(II) and cobalt(II) removal The effect of initial metal ion concentration had a negative effect on the response of copper(II) removal efficiency, which also led to decreasing line direction. This behavior can be based on the saturation of active sites of sorbents at higher concentrations [57,70]. The contact time needed to reach the equilibrium is influenced by the characteristics of sorbents and their available sorption sites. As seen in main effects plot, the removal efficiencies slightly increased with rising contact time. Increasing the temperature is a trade-off such as the adsorptive forces between sorbent and sorbate become powerless at higher temperatures; thus metal ions sorbed on the adsorbent surface desorb into the solution. Despite this, the total pore volume and porosity of the

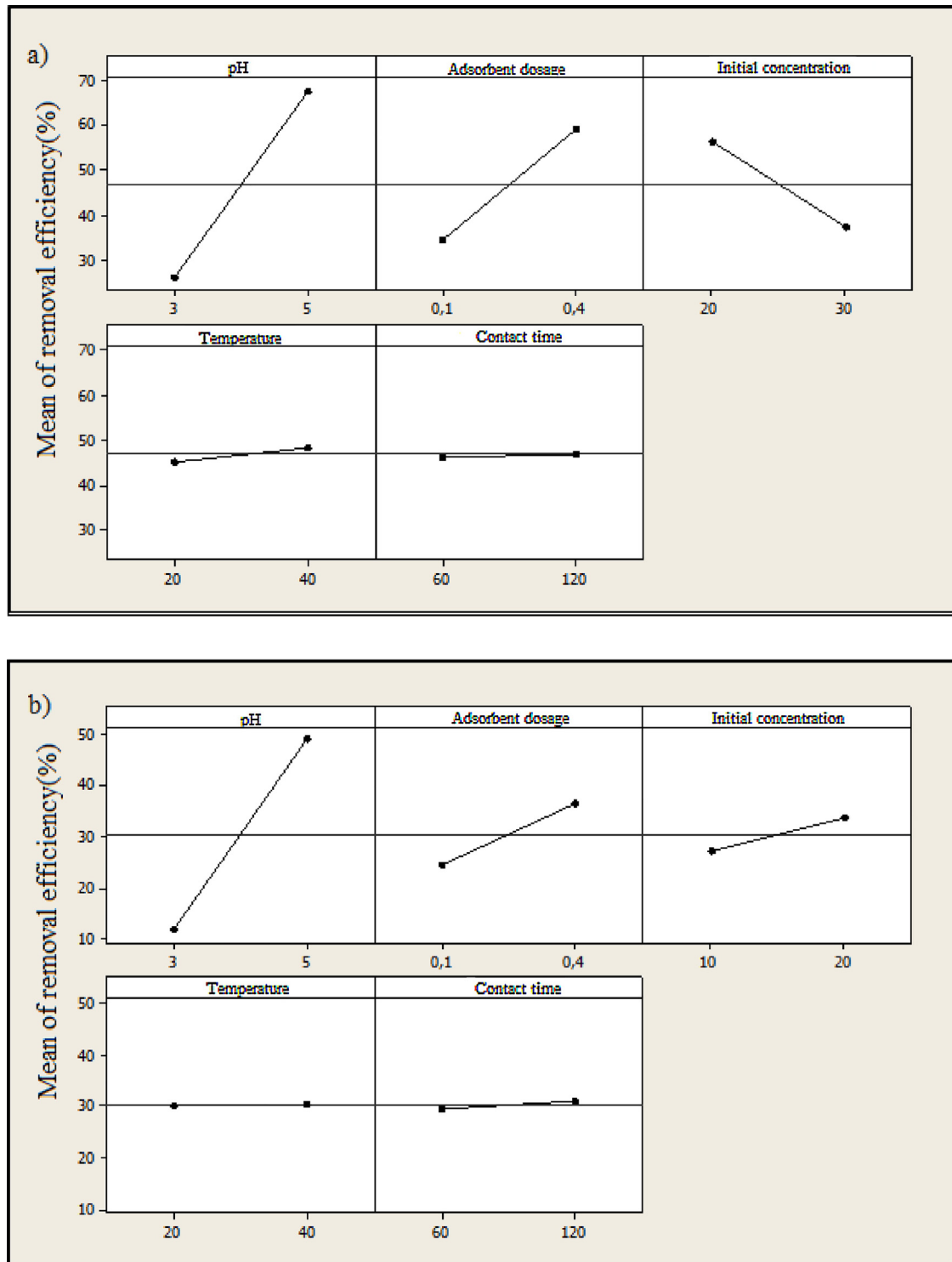


Fig. 3. Main effects plots of (a) copper(II) and (b) cobalt(II) removal efficiency(%).

sorbent can be increased by the temperature. Consequently, copper(II) and cobalt(II) uptakes were merely affected by the temperature because of neutralizing these effects to each other's [9]. The ABCDE effect, seemed insignificant compared to other effects, was neglected. The maximum cobalt(II) and copper(II) removal efficiencies(%) were obtained as 65.12% and 90.49%, respectively. Almond green hull was used to uptake cobalt ion with high removal efficiency of 97.22% [71]. Besides, only 60% cobalt(II) removal was performed by using watermelon rind as sorbent [72].

Copper(II) removal was performed by various sorbents with high removal efficiency, such as Lawsonia Inermis Plant Leaf (85.6%) [73], hydrochloric acid treated tomato factory waste (92.08%) [58], *Pinus sylvestris* L. (67%) [74], *Thuja orientalis* (98%) [75].

The interaction effect plots are important when two factors are added to each other by changing from lower level to higher level without representing non-parallel lines [61,76]. Despite that the main effects gave a clear idea, the interaction between those parameters would favor a superior expression of the process.

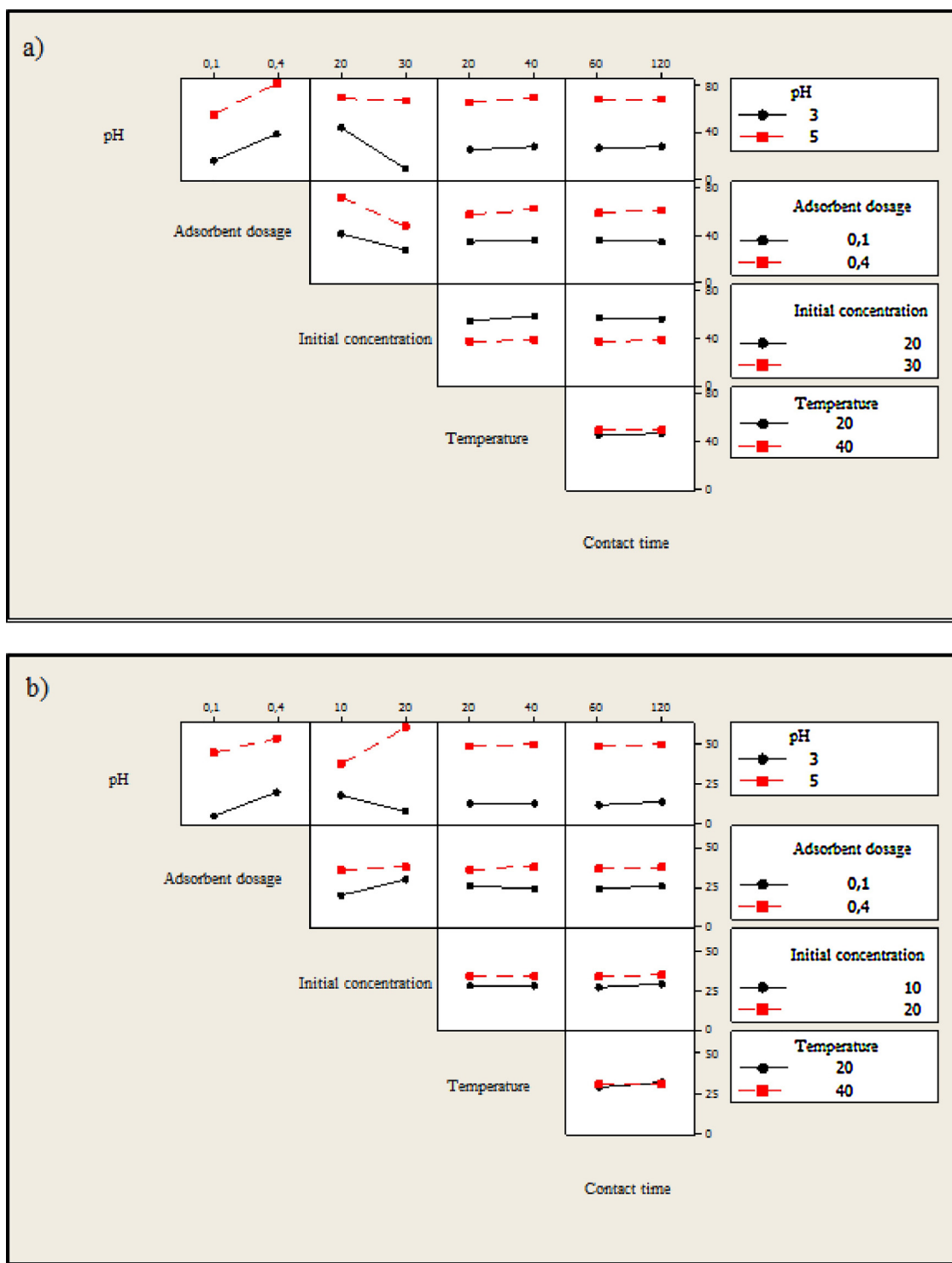


Fig. 4. Interaction effects plots of (a) copper(II) and (b) cobalt(II) removal efficiency(%).

Fig. 4a and b show the interaction effects plots between two factors (AB, AC, AD, AE, BC, BD, BE, CD, CE, and DE) for copper(II) and cobalt(II) uptake. The interactions between pH and initial concentration (AC) for both metal ions were more stronger than between adsorbent dosage and initial concentration (BC). These interactions were more significant than the temperature and contact time factors. It was observed that the effect of pH was more noticeable when the initial metal ion concentration was high; however, at lower initial dye concentration, the effect of pH was not quite high. In the case of copper(II) removal at lower initial concentrations

(10 mg/L), removal efficiency(%) was 64.84 and 81.67% at 3 and 5 pH levels, respectively. On the other hand, at higher initial concentrations (20 mg/L), removal efficiency(%) increased from 22.95 to 80.76% with increasing pH. Due to interaction effects plots (Fig. 4a and b) and coefficients of each factor (Tables 3 and 4), there were positive interactions between pH and initial concentration (AC), pH and temperature (AD), adsorbent dosage and temperature (BD) for both metal ions. Besides, pH and adsorbent dosage (AB), adsorbent dosage and contact time (BE), initial concentration and contact time (CE) interactions for copper removal with initial

concentration and temperature (CD) interactions for cobalt removal were detected. Other interactions had negative effects on removal efficiency(%).

## Conclusions

Copper(II) and cobalt(II) removal from aqueous solution by using APC were optimized through 2<sup>5</sup> full factorial experimental design. The effects of solution pH (3 and 5), adsorbent dosage (0.1 and 0.4 g/50 mL), initial concentration (10 and 20 mg/L), temperature (20 and 40 °C) and contact time (60 and 120 min) and their interactions on removal efficiency(%) were specified.

- Both cobalt(II) and copper(II) removals were mostly pH-dependent with the proper confidence level (95%). The increasing solution pH, adsorbent dosage, temperature and contact time had a positive effect while increasing initial metal ion concentration had a negative effect on copper(II) uptake. On the other hand, all of the main parameters had a positive effect on cobalt(II) removal.
- ANOVA, T-test and F-test results indicated that only solution pH (A) was significant for cobalt(II) removal. However, the main factors of solution pH (A), adsorbent dosage (B), initial concentration (C) and the interactions (A × C) were highly significant ( $P < 0.05$ ) for copper(II) uptake.
- Optimization results showed that the best sorption conditions for copper(II) removal were: pH 5, adsorbent dosage = 0.4 g/50 mL, initial concentration = 10 mg/L, temperature = 40 °C and contact time = 60 min to obtain 90.49% removal efficiency.
- Besides, 65.12% removal efficiency was obtained for cobalt(II) uptake under sorption conditions that adjusted as pH 5, adsorbent dosage = 0.4 g/50 mL, initial concentration = 20 mg/L, temperature = 20 °C and contact time = 120 min.

Apple pulp carbon was implemented as adsorbent, and full factorial design was applied for the first time in the literature to remove cobalt(II) and copper(II) metal ions. So that apple pulp was a potential low-cost and abundant material, operating with APC could be an efficient, promising and cost effective for the removal of metal ions from aqueous solutions.

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