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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. 2^5 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.

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_{ZPC}, 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 (°C)
E	The contact time (min)
k	The number of factors
P	Probability level
R-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(%))
η	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 nanosheets [46,47], graphene oxide onto 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 °C with a heating rate of 10 °C/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, pH_{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