Removal of Cu(II), Ni(II) and Co(II) ions from aqueous solutions by hazelnut husks carbon activated with phosphoric acid

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ABSTRACT

The purpose of this study was to examine phosphoric acid activated hazelnut husk carbon (HHPAAC) feasibility in removing Cu(II), Ni(II) and Co(II) ions from aqueous solutions. The effects of various parameters including, pH of the aqueous phase, contact time and initial metal ion concentration were studied in batch adsorption experiments. Adsorption of Cu(II), Ni(II) and Co(II) ions was found to be favorable at a pH of 6.0 and reached equilibrium at 600 min. Adsorption equilibrium of Cu(II), Ni(II) and Co(II) ions was found to be compatible with the Langmuir isotherm model. The maximum adsorption capacity of HHPAAC for Cu(II), Ni(II) and Co(II) ions were calculated to be 24.3, 16.3 and 17.3 mg g^{-1}, respectively, from the Langmuir equation. The kinetic behavior of Cu(II), Ni(II) and Co(II) adsorption was well expressed by the pseudo-second-order model. Adsorbed Cu(II), Ni(II) and Co(II) ions were quantitatively desorbed from the HHPAAC surface using 0.1 M nitric acid solution. HHPAAC exhibits green and cheap procedures for the treatment of wastewater including heavy metals such as Cu(II), Ni(II) and Co(II) ions.

Keywords: Adsorption; Hazelnut husk; Activated carbon; Removal; Cu(II); Ni(II); Co(II); Heavy metal ions

1. Introduction

Pollution of air, soil and water by heavy metals is an increasing environmental problem from the past to the present as a result of technological and industrial developments [1,2]. Among them, water pollution is very important due to the easy transfer of the metal ions from the waters to the food chain and then, to human beings and other living organisms. Accumulation of heavy metals in the human body by consumption of food and water can cause health deterioration such as lung fibrosis, kidney disease, irregularity in blood composition and some cardiovascular problems and also create nervous system damages and carcinogenic effects [3–6]. In fact, some metal ions such as zinc and copper at trace levels are necessary for human metabolisms, but some of them such as lead and mercury are highly toxic, even at trace levels [3,4]. However, high concentrations of all metal ions are toxic to humans. Hence, heavy metal contamination in the environment should be prevented to protect human and other living organisms' health via treating metal ion-containing wastewaters.

It is impossible to give up technological and industrial development, so new treatment alternatives should be proposed to cope with the industrial wastewaters polluted by heavy metals. There are many methods used to remove heavy metals from wastewaters. Some of them can be listed as follows; reverse osmosis [2], spray drying [7], precipitation [8,9], ion-exchange [10,11], electrocoagulation

[12] and adsorption [13–16]. Unfortunately, almost all of these methods have disadvantages such as high construction and operation costs, sludge formation and inability to remove metal ions at low concentrations, which limit their practical application. The features of the adsorption technique such as design simplicity, ease of application and sludge-free operation greatly reduce the disadvantages together with the cheapness, efficiency and reusability of the preferred adsorbent [17–19]. In developing countries where economical technologies are preferred, the adsorption technique for the treatment of wastewater polluted with heavy metals is a promising method that is widely applied with a wide range of adsorbents [18] such as silica and derivatives [20], agro-based materials [21], polymeric adsorbents [22], clays [23], zeolites [24], nanomaterials [18], bio-sorbents [25] and activated carbons (ACs) [26]. Commercially ACs are highly effective, although there are relatively inexpensive types, they are generally expensive, so they are not widely used in large quantities [26]. For this reason, researches have been increasing recently to produce new, cheap and effective adsorbents from natural agricultural wastes such as rice hulls [27], cherry stones [28], pomelo peel [29], date pits [30], apricot stone [31] and hazelnut husk [32].

Hazelnut husk (HH) is an agricultural waste material obtained after harvesting hazelnut. Its annual production is nearly approximately 1.4×10^5 t y^{-1} in Turkey [33]. HH is a real waste material since it is not used for any purpose. HH can be eliminated from the threshing field by burning in the open air. HH as a precursor has some important advantages for the production of activated carbon, for example, being suitable for long-term storage, being ready in the threshing field to bring to the storage area and having zero economic value. Thus, some ACs were prepared from HH using zinc chloride [34], potassium carbonate [35], sulfuric acid [36,37], potassium acetate [38] and phosphoric acid [39]. Effective adsorption of methylene blue [39] and Cd(II) ions [40] by phosphoric acid activated HH was canalized to investigate the adsorption of other metal ions such as Cu(II), Ni(II) and Co(II) ions from aqueous solutions. In our literature survey, there has not been any study about the adsorption of Cu(II), Ni(II) and Co(II) ions onto hazelnut husks carbon activated with phosphoric acid.

In this study, removal of Cu(II), Ni(II) and Co(II) ions from aqueous solutions by hazelnut husks carbon activated with phosphoric acid was investigated using a batch adsorption system. Effect of pH, contact time and initial concentration were studied batchwise. Desorption of Cu(II), Ni(II) and Co(II) ions from the phosphoric acid activated hazelnut husk carbon (HHPAAC) surface was examined using a nitric acid solution. Equilibrium and kinetic of Cu(II), Ni(II) and Co(II) adsorption onto HHPAAC were investigated.

2. Experimental

2.1. Instruments and chemicals

A flame atomic absorption spectrometer (Shimadzu AA-7000 F, Shimadzu Corporation, Kyoto, Japan) was utilized for the determination of Cu(II), Ni(II) and Co(II) concentrations. The pH of Cu(II), Ni(II) and Co(II) solutions was measured by a pH meter (Schott CG 840, Schott AG, Mainz, Germany). A temperature-controlled orbital shaker (KS4000i, IKA®-Werke GmbH & Co. KG, Staufen, Germany) was employed for shaking the suspension of HHPAAC and metal solutions.

Aqueous solutions of Cu(II), Ni(II) and Co(II) ions at 1,000 mg L^{-1} were prepared by dissolving the required amount of their nitrate salts (purchased from Merck KGaA, Darmstadt, Germany) in deionized water. Other chemicals used in the experiments were of analytical reagent grade. Distilled-deionized water was used throughout the study. The pH values of the Cu(II), Ni(II) and Co(II) solutions were adjusted by stepwise adding the required amount of 0.1 M HCl solutions to desired pH values ranged between 1.0 and 3.0. A diluted buffer solution (0.01 M acetic acid-sodium acetate solution) was used for pH values between 4.0 and 6.0.

Preparation of hazelnut husk (HH) carbon with H$_3$PO$_4$ used as an adsorbent for the removal of Cu(II), Ni(II) and Co(II) ions was given in the previous study [39]. Briefly, an equal amount of H$_3$PO$_4$ and HH were suspended in deionized water. After impregnation for 3 h at 60°C, the suspension was dried at 105°C. Then, it was carbonized and activated in a tubular reactor placed in a muffle furnace at 500°C under N$_2$ atm. Iodine number and Brunauer–Emmett–Teller surface area of the HHPAAC were reported to be 535 mg g^{-1} and 770 m^2 g^{-1}, respectively [39].

2.2. Adsorption experiments

Adsorption dynamics of Cu(II), Ni(II) and Co(II) ions onto HHPAAC were studied batchwise. The effect of parameters such as pH, initial concentration of Cu(II), Ni(II) and Co(II) ions and contact time were examined. The effect of pH was studied by adding 0.050 g of HHPAAC into 50 mL of individual adsorbate solutions at 50 mg L^{-1} at various pH values and then the suspension was shaken using the orbital shaker for 24 h at room temperature. For the investigation of contact time effects on the adsorption, the solutions of adsorbates (50 mL) at pH 6.0 were prepared and then, 0.050 g of HHPAAC was added to the solutions and the obtained suspensions were shaken for the time ranged from 10 to 1,440 min. To examine the effect of the initial metal ion concentrations on the adsorption, 50 mL of Cu(II), Ni(II) and Co(II) solutions at pH of 6.0 were prepared at several concentrations ranged between 10 and 100 mg L^{-1} and then, 0.050 g of HHPAAC was added in these solutions and the obtained suspensions were shaken for 1,440 min. At the end of the adsorption process, the suspensions were filtered off and the concentrations of Cu(II), Ni(II) and Co(II) ions in the filtrate were measured by flame atomic absorption spectrometer (FAAS). The adsorbed amount of Cu(II), Ni(II) and Co(II) ions per gram of HHPAAC (q_e) and the adsorption percentage of Cu(II), Ni(II) and Co(II) ions were calculated with Eqs. (1) and (2), respectively.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\text{Adsorption}, \% = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the concentrations of Cu(II), Ni(II) and Co(II) ions before and after adsorption (mg L^{-1}), V is the volume of the solution (L) and m is the mass of adsorbent (g) [35].

2.3. Desorption experiments

Desorption of Cu(II), Ni(II) and Co(II) ions from the HHPAAC surface was investigated. Firstly, the metal ions were loaded onto HHPAAC by adding 0.050 g of the adsorbent into 50 mL of individual solutions of Cu(II), Ni(II) and Co(II) ions at 50 mg L^{-1} and pH 6.0. The suspensions were shaken for 24 h. After equilibrium, the HHPAAC was separated by filtration. Cu(II), Ni(II) and Co(II) loaded HHPAACs were added into 20 mL of HNO$_3$ solutions (0.1, 0.5 and 1.0 M) for 60 min at room temperature. Then, the suspensions were filtered off and Cu(II), Ni(II) and Co(II) levels in HNO$_3$ solutions were measured by FAAS. Finally, the desorption percentages of Cu(II), Ni(II) and Co(II) ions were calculated.

3. Results and discussions

3.1. Effect of pH

pH has an important role in the adsorption process because protonation and deprotonation of the adsorbent surface and competition between adsorbate and hydronium ions are directly related to the solution pH [41]. Fig. 1 displays the effect of pH on the adsorption of Cu(II), Ni(II) and Co(II) ions by HHPAAC. As seen, the adsorbed amount of the metal ions increased with raising pH from 1.0 to 6.0, slowly at the beginning (up to pH 3.0) but quickly after that point. The pH at point of zero charge (pH$_{PZC}$) of HHPAAC was reported to be 4.5 [39]. Low adsorption of the metal ions at pH ≤ 3.0 may be due to the protonation of the HHPAAC surface functional groups. So, the positively charged HHPAAC surface repulse positively charged metal ions via electrostatic repulsion and hinder their adsorption on the HHPAAC surface. However, by the increasing pH, adsorption of metal ions becomes favorable on the negatively charged surface by disappeared competition between H$_3$O$^+$ ions and the metal ions and so, electrostatic attraction occurs between HHPAAC surface and the metal ions [42]. The HHPAAC surface is negatively charged when the pH of the solution is higher than 4.5 and the adsorbed amount of Cu(II), Ni(II) and Co(II) ions increased due to electrostatic attraction [43].

3.2. Effect of contact time

The contact time effect on the adsorption of heavy metal ions by HHPAAC is a key factor to specify the equilibrium time and kinetic characteristics of the process. The changes in the adsorbed amount of Cu(II), Ni(II) and Co(II) ions per gram of HHPAAC (q_e, mg g^{-1}) depending on the contact time are illustrated in Fig. 2. By increasing the contact time from 10 to 600 min, the adsorbed amount
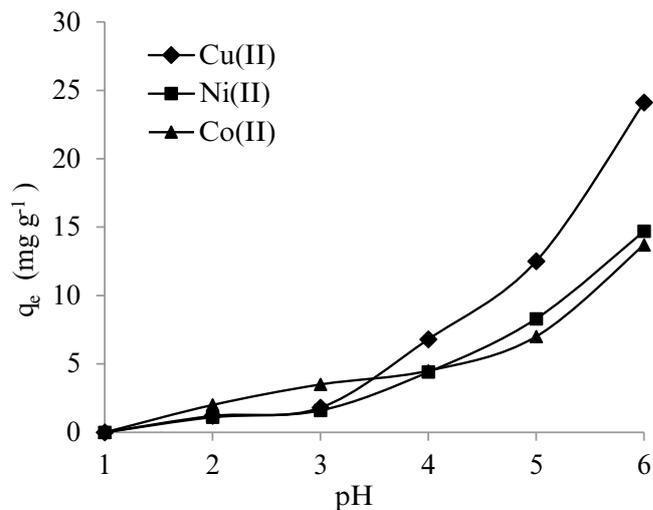
Fig. 1. Effect of pH on adsorption of Cu(II), Ni(II) and Co(II) by HHPAAC (initial adsorbate concentration: 50 mg L^{-1}; amount of HHPAAC: 50 mg; solution volume: 50 mL; contact time: 24 h).
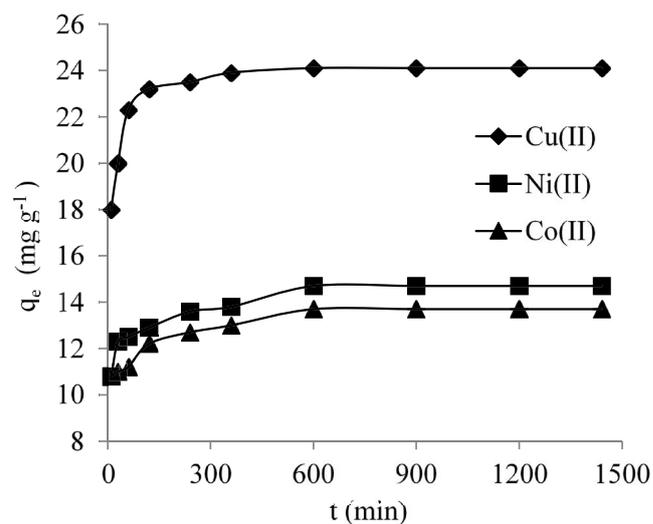
Fig. 2. Effect of contact time on adsorption of Cu(II), Ni(II) and Co(II) by HHPAAC (pH of solution: 6.0; initial adsorbate concentration: 50 mg L^{-1}; amount of HHPAAC: 50 mg; solution volume: 50 mL).

of the metal ions on HHPAAC increased from 18.0, 10.8 and 10.8 mg g^{-1} to 24.1, 14.7 and 13.7 mg g^{-1} for Cu(II), Ni(II) and Co(II) ions, respectively. However, a further increase of the contact time (up to 1,440 min) did not cause an increase in the adsorption of Cu(II), Ni(II) and Co(II) ions. Hence, the equilibrium time for the adsorption of Cu(II), Ni(II) and Co(II) ions with HHPAAC was 600 min.

3.3. Effect of initial concentration

The effect of the initial concentration of Cu(II), Ni(II) and Co(II) ions on the adsorption by HHPAAC is shown in Fig. 3. The adsorbed amount of Cu(II), Ni(II) and Co(II) ions onto HHPAAC fairly increased by increasing of initial

concentrations of the adsorbates until 40 mg L^{-1} and then slowly increased until saturation of adsorption zones onto HHPAAC surface by the adsorbates at the initial concentrations of 75 mg L^{-1}. At the low initial concentration of Cu(II), Ni(II) and Co(II) ions, there were available empty adsorption zones onto the HHPAAC surface and hence increasing the Cu(II), Ni(II) and Co(II) concentrations caused an increase in the adsorbed amounts of the metal ions per gram of HHPAAC. But after full loading of adsorption zones on HHPAAC surface by the metal ions, there were no longer available zones for the adsorption and so adsorption of Cu(II), Ni(II) and Co(II) ions not practically increased after their initial concentrations of 75 mg L^{-1}. Similar trends were observed for the adsorption of Cd(II) ions by agro-based adsorbents [21] and Pb(II) ions by pine cone biochar [44].

It was also found that the adsorption percentage of Cu(II), Ni(II) and Co(II) ions on HHPAAC decreased with the increasing initial concentration of Cu(II), Ni(II) and Co(II) ions. At low concentrations of the adsorbates, there were available sufficient adsorption zones for the adsorption and so, the percent of adsorption was high. At high concentrations of the metal ions, the amount of metal ions was higher than the amount of adsorption zones where the adsorbates could be adsorbed, and therefore not all of the metal ions

could be adsorbed. Thus, at high concentrations of metal ions, their adsorption percentages were found to be low.

3.4. Cu(II), Ni(II) and Co(II) adsorption kinetics onto HHPAAC

Cu(II), Ni(II) and Co(II) adsorption kinetics were studied by shaking a suspension of 0.050 g of HHPAAC in 50 mL of the individual metals solutions at pH 6.0 for times ranged between 10 and 1,440 min. The adsorption kinetics of Cu(II), Ni(II) and Co(II) ions onto HHPAAC were examined by pseudo-first-order [45] and pseudo-second-order [46] kinetic models using Eqs. (3) and (4), respectively.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_1 (min^{-1}) and k_2 (mg g^{-1} min^{-1}) are the kinetic rate constants which can be obtained by the slope of the linear plots drawn $\ln(q_e - q_t)$ vs. t and t/q_t vs. t, respectively.

The calculated kinetic parameters and correlation coefficients for adsorption Cu(II), Ni(II) and Co(II) ions on HHPAAC are summarized in Table 1. The correlation coefficients obtained by pseudo-second-order equation for adsorption of Cu(II), Ni(II) and Co(II) ions on HHPAAC was higher than pseudo-first-order and also closer to the unity. When $q_{e,\text{cal}}$ values predicted by pseudo-first-order and pseudo-second-order equation were compared, it can be seen from the table that $q_{e,\text{cal}}$ values provided by pseudo-second-order are closer to the experimental ones for the adsorption of Cu(II), Ni(II) and Co(II) ions onto HHPAAC. Hence, it was concluded that the adsorption kinetics of Cu(II), Ni(II) and Co(II) ions onto HHPAAC were expressed by the pseudo-second-order kinetic model. Similar trends were reported in the literature for adsorption of Pb(II), As(III), Cd(II) ions on sultone-modified magnetic activated carbon [47] and removal of Pb(II), Cd(II) ions by hollow mesoporous MgO spheres [7].

3.5. Adsorption isotherms Cu(II), Ni(II) and Co(II) by HHPAAC

The adsorption equilibrium of Cu(II), Ni(II) and Co(II) ions by HHPAAC was analyzed by Langmuir [48] and Freundlich [49] isotherm models.

The linear forms of Langmuir and Freundlich isotherms equations are expressed by Eqs. (5) and (6), respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \tag{5}$$
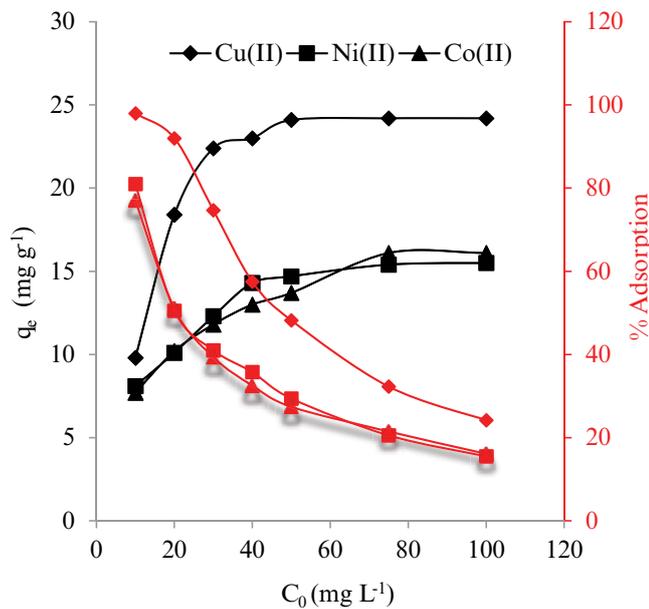
Fig. 3. Effect of initial concentration of Cu(II), Ni(II) and Co(II) on their adsorption by HHPAAC (pH of solution: 6.0; contact time: 24 h; amount of HHPAAC: 50 mg; solution volume: 50 mL).

Table 1
Parameters of pseudo-first-order and pseudo-second-order kinetic models for Cu(II), Ni(II) and Co(II) adsorption onto HHPAAC

Adsorbate	$q_{e,\text{exp}}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		$k_1 \times 10^2$ (min^{-1})	$q_{e,\text{cal}}$ (mg g^{-1})	R^2	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	$q_{e,\text{cal}}$ (mg g^{-1})	R^2
Cu(II)	24.2	0.58	2.5	0.8572	0.80	24.2	1.0000
Ni(II)	14.7	0.58	3.1	0.8593	0.51	14.9	0.9996
Co(II)	13.7	0.57	2.8	0.8653	0.56	13.9	0.9997

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \tag{6}$$

where q_e is the adsorbed amount of the metal ions at equilibrium time (mg g^{-1}), C_e is the equilibrium concentration of the metal ions in the solution after adsorption (mg L^{-1}), q_{max} and K_L are the Langmuir constants related to the maximum adsorption capacity (mg g^{-1}) and binding site affinity (L mg^{-1}), respectively [50], K_F and n are Freundlich constants concerned to adsorption capacity and adsorption consistency, respectively [51].

Experimental, Langmuir and Freundlich curves obtained from the experimental and predicted data from Eqs. (5) and (6) for adsorption of Cu(II), Ni(II) and Co(II) ions on HHPAAC are depicted in Fig. 4. The predicted curves by the Freundlich model was better correlated with experimental data at a low equilibrium concentration of all metal ions, while the Langmuir model was fitted well with the experimental data at their high concentration and so, the experimental maximum adsorption capacity of HHPAAC for Cu(II), Ni(II) and Co(II) ions were more accurately predicted by the Langmuir equation. Freundlich and Langmuir isotherms constants and correlation coefficients (R^2) for adsorption of Cu(II), Ni(II) and Co(II) ions with HHPAAC are listed in Table 2. The R^2 values obtained with the Langmuir equation for adsorption of Cu(II) and Ni(II) ions with HHPAAC is higher and closer to unity than those obtained by the Freundlich equation. So, adsorption of Cu(II) and Ni(II) on HHPAAC is compatible with the Langmuir equation. In the case of Co(II) adsorption on HHPAAC, the R^2 value of Freundlich isotherm was very close to that of Langmuir. The Co(II) isotherm line predicted by the Freundlich equation was more fitted with the experimental values than that of Langmuir. The maximum Co(II) adsorption capacity of HHPAAC estimated by the Langmuir isotherm, was very close to the experimentally
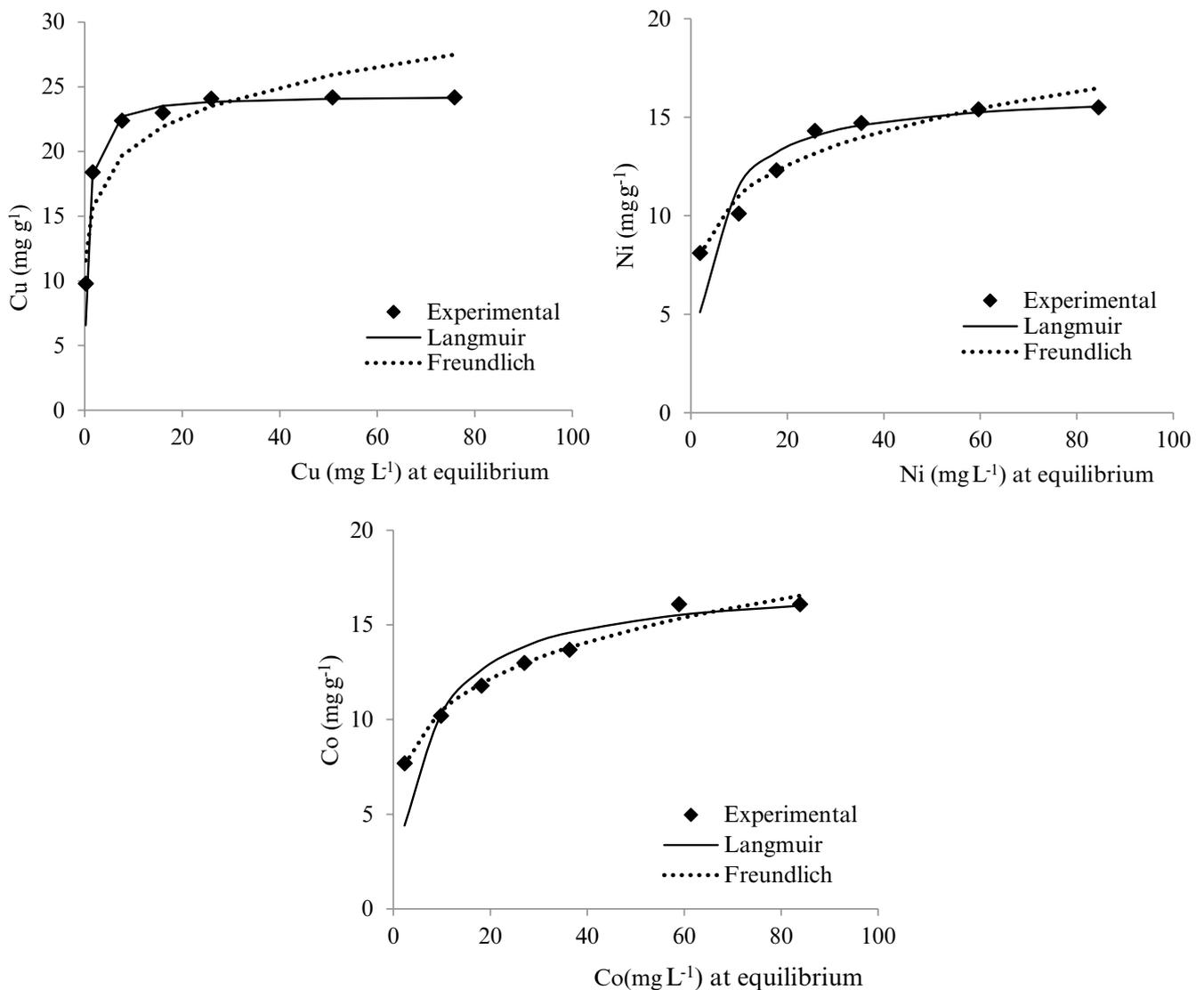
Fig. 4. Experimental, Langmuir and Freundlich curves obtained from experimental and predicted data from their equation for adsorption of (a) Cu(II), (b) Ni(II) and (c) Co(II) ions with HHPAAC.

found capacity of HHPAAC. Hence, it was concluded that Co(II) adsorption equilibrium with HHPAAC was fitted with both Langmuir and Freundlich isotherm models. Similar trends were reported in the literature for Cr(VI) adsorption on cephalosporin residue and derived chars [52], cobalt radionuclides adsorption on montmorillonite [53] and [134]Cs and ^{60}Co radioisotopes adsorption on synthetic nanocopper ferrocyanide-SiO$_2$ materials [54].

The adsorption capacity of HHPAAC for Cu(II), Ni(II) and Co(II) ions with some other adsorbents reported in the literature was compared. As seen in Table 3, Cu(II) adsorption capacities of the adsorbents were ranged between 4.5 mg g^{-1} with beech sawdust [57] and 117.6 mg g^{-1} with polyamine-polyurea polymer [63], while 24.3 mg g^{-1} with HHPAAC. Ni(II) adsorption capacities of adsorbents were ranged between 4.0 mg g^{-1} with beech sawdust [57] and 137.0 mg g^{-1} with polyamine-polyurea polymer [63], while 16.3 mg g^{-1} with HHPAAC. Co(II) adsorption capacities of adsorbents were ranged between 4.0 mg g^{-1} with zeolite [61] and 45.5 mg g^{-1} with cashew nutshell [59], while 17.3 mg g^{-1} with HHPAAC. It could be concluded that HHPAAC has a moderate adsorption capacity for Cu(II), Ni(II) and Co(II) ions.

3.6. Desorption studies

Because of the importance to evaluate regeneration of adsorbents for subsequent uses, desorption of Cu(II), Ni(II) and Co(II) ions from the HHPAAC surface were studied and results are shown in Fig. 5. The desorption of Cu(II), Ni(II) and Co(II) ions from the HHPAAC surface was found to be quantitative (100% ± 5%) using HNO$_3$ solutions at concentrations ranged between 0.1 and 1.0 M. The ease desorption of Cu(II), Ni(II) and Co(II) ions from the HHPAAC surface using the dilute nitric acid solution (0.1 M) is the advantage of HHPAAC.

3.7. Single-stage batch adsorber design for removal of Cu(II), Ni(II) and Co(II) by HHPAAC

Typically, in the single-stage batch adsorber treatment system, wastewater to be treated and adsorbent are added to adsorber. After adsorption of metal ions, treated water and spent (or metal loaded) adsorbents are discharged from the adsorber. Scheme of single-stage batch adsorber for the treatment of individual solutions of Cu(II), Ni(II) and Co(II) at 10 mg L^{-1} using HHPAAC are shown in Fig. 6.

The decreased amount of the metal ions in the aqueous waste solution must be equal to the adsorbed amount of the metal ions onto HHPAAC. So, the following mass balance Eq. (7) can be written as:

$$V\left(C_0 - C_e\right) = W\left(q_e - q_0\right) \tag{7}$$

Table 2
Parameters of Langmuir and Freundlich isotherms for Cu(II), Ni(II) and Co(II) adsorption onto HHPAAC

Adsorbates	Langmuir constants			Freundlich constants		
	q_{max} (mg g^{-1})	K_L (mg g^{-1})	R^2	K_F	n	R^2
Cu(II)	24.3	1.85	0.9999	14.6	6.9	0.8559
Ni(II)	16.3	0.24	0.9976	7.1	5.3	0.9445
Co(II)	17.3	0.15	0.9928	6.4	4.6	0.9908

Table 3
Comparison of adsorption capacity of HHPAAC towards ions with some other adsorbents reported in the literature

Adsorbent	Adsorption capacity (mg g^{-1})			Literature
	Cu(II)	Ni(II)	Co(II)	
Banana peel	49.5			[55]
Natural neem sawdust	48.3	31.5		[56]
Acid treated sawdust	286	74.1		[56]
Beech sawdust	4.5	4.0		[57]
Alkali treated lemon peel			35.7	[58]
Cashew nut shell			45.5	[59]
Chelating resin		4.76	9.3	[60]
Zeolite			9.1	[61]
Willow wood	11.3	9.3		[62]
Polyamine-polyurea polymer	117.6	137.0	–	[63]
ZnCl$_2$ activated hazelnut husk carbon	6.6	–	–	[33]
Heteropoly acid prepared sorbent	–	–	33.5	[64]
HHPAAC	24.3	16.3	17.3	This study
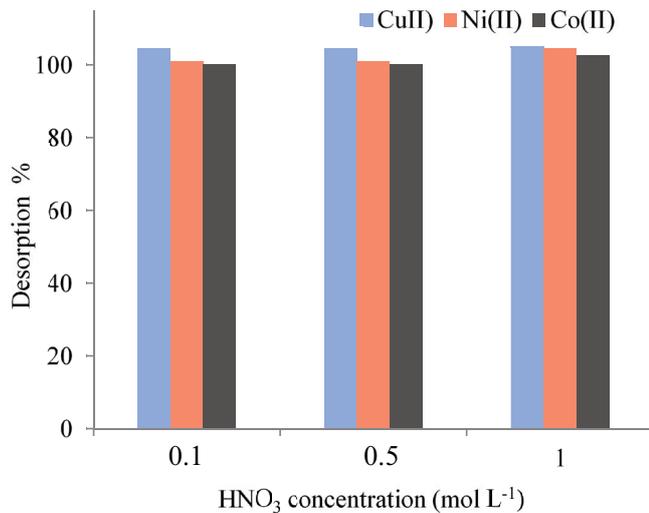
Fig. 5. Effect of HNO_3 concentrations on the desorption of Cu(II), Ni(II) and Co(II) ions from HHPAAC surface (adsorption conditions: pH of solution: 6.0; initial adsorbate concentration: 50 mg L^{-1}; amount of HHPAAC: 50 mg; solution volume: 50 mL; desorption conditions; 20 mL HNO_3 solutions; contact time: 60 min).
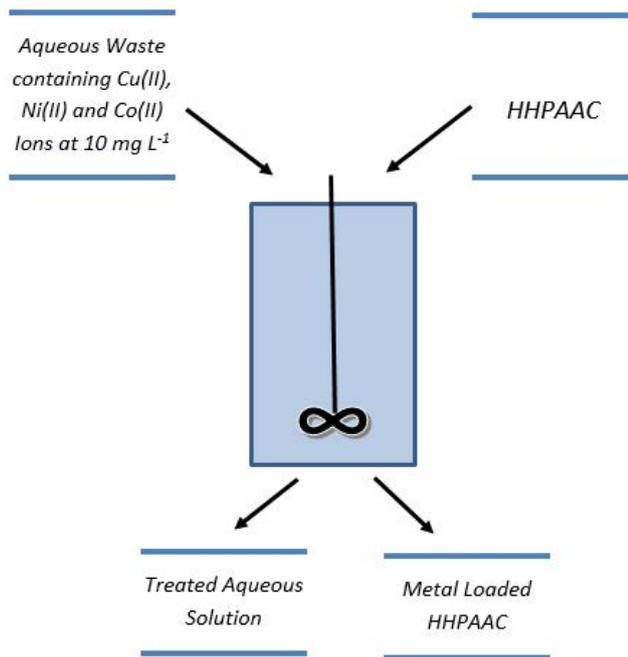
Fig. 6. Scheme of single stage batch adsorber for the treatment aqueous waste containing Cu(II), Ni(II) and Co(II) at 10 mg L^{-1} using HHPAAC.

where q_0 is the adsorbent amount of the metal ions at the beginning stage. q_0 will be equal to 0 ($q_0 = 0$) at the beginning stage and so Eq. (8) can be written;

$$\frac{W}{V} = \frac{(C_0 - C_e)}{q_e} \tag{8}$$
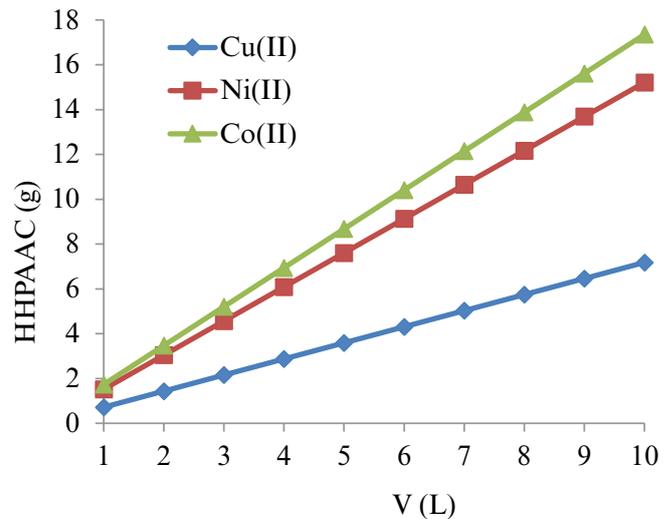
Fig. 7. HHPAAC (g) vs. volume (L) of aqueous waste containing Cu(II), Ni(II) and Co(II) at 10 mg L^{-1} for single-stage batch adsorber.

q_e value is best estimated by Freundlich isotherm for Cu(II), Ni(II) and Co(II) ions at low equilibrium concentrations of the metal ions, so Eq. (9) can be written [65–67].

$$\frac{W}{V} = \frac{(C_0 - C_e)}{K_F C_e^{1/n}} \tag{9}$$

To reduce the concentrations of individual Cu(II), Ni(II) and Co(II) ions from 10 to 0.5 mg L^{-1} using HHPAAC in various volumes of the solutions, the calculated data are illustrated in Fig. 7.

4. Conclusions

In this study, it is revealed that Cu(II), Ni(II) and Co(II) ions could be effectively removed from aqueous solutions with H_3PO_4 activated hazelnut husk. Adsorption of Cu(II), Ni(II) and Co(II) ions on HHPAAC was found to be affected by pH, contact time and initial metal ion concentration. Optimum pH value and contact time were found to be 6.0 and 600 min for Cu(II), Ni(II) and Co(II) ions. The adsorbed amounts of metal ions increased with increasing the metal ion concentrations until the filling capacity of HHPAAC. The Langmuir isotherm model was more suitable than the Freundlich isotherm to explain the adsorption equilibrium data of Cu(II) and Ni(II), while the adsorption of Co(II) was suitable for both Langmuir and Freundlich isotherms. Adsorption kinetics of Cu(II), Ni(II) and Co(II) ions with HHPAAC was well expressed by the pseudo-second-order model. The quantitative desorption of Cu(II), Ni(II) and Co(II) ions from the HHPAAC surface was obtained using 0.1 M HNO_3 solution.

As a result, this study showed that the activated carbon produced from hazelnut husk with H_3PO_4 activation has a good adsorption performance for heavy metal ions such as Cu(II), Ni(II) and Co(II) ions and thus it would be very promising to convert hazelnut husk wastes to economically

valuable material as AC and to eliminate hazelnut husk from the threshing field via environmentally friendly manner.

Acknowledgments

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