

Peanut Shell Activated Carbon: Adsorption Capacities for Copper(II), Zinc(II), Nickel(II) and Chromium(VI) Ions from Aqueous Solutions

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ABSTRACT: The adsorption of copper(II), zinc(II), nickel(II) and chromium (VI) ions from aqueous solutions onto an activated carbon produced from peanut shell was studied as a function of the concentrations of the ions and the pH value of the solution. For that purpose, adsorption isotherms data were collected at different pH values. The amounts of Cu(II), Zn(II) and Ni(II) ions adsorbed increased with increasing equilibrium pH of the solution, while the uptake of Cr(VI) ions decreased. For Cr(VI) ions, maximum uptakes were found at a pH below the point of zero charge of the adsorbent (pH_{pzc}). The amount of metal cation adsorbed at a given equilibrium concentration increased in the order Ni(II) < Zn(II) < Cu(II). This metal ion uptake order may be explained from a consideration of the combined effects of the electronegativity of the metal ion and the first stability constant of the corresponding metal hydroxide. The activated carbon produced from peanut shell was an effective and economic adsorbent for the removal of metal cations at $pH \geq pH_{pzc}$ and anions at $pH \leq pH_{pzc}$.

INTRODUCTION

Heavy metals are among the most important pollutants in surface and groundwater. They are toxic elements that can seriously affect plants and animals. Treatments such as chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption have been suggested for the removal of heavy metals from wastewater. Among these methods, carbon adsorption is the most attractive because of its simplicity and economical feasibility. It has also been shown that adsorption is one of the most effective approaches for the removal of metal ions (Gabaldon *et al.* 1996; Chen and Lin 2001; Ricordel *et al.* 2001). Recently, Romero *et al.* (2003) demonstrated that activated carbon with a high surface area and porosity may be obtained using peanut shell as the precursor, and activated in the presence of air and phosphoric acid at moderate temperatures. Activated carbon obtained by this procedure was shown to have a high capacity towards the removal of metal ions from aqueous solutions compared to that of commercial materials (Dastgheib and Rockstraw 2001). This large capacity was associated with the existence of oxygen

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and oxygen/phosphorus functional groups on the surface. It is well known that most common functional groups on the carbon surface are carboxyl, lactone, carbonyl, phenolic and phosphorus-containing acidic groups (Dastgheib and Rockstraw 2001; Boehm 1966). However, for an understanding of the behaviour of carbon as a metal ion adsorbent, a more important aspect than the specific identification of surface groups is the point of zero charge (pH_{pzc}) of the active carbon. The adsorption of cations is favoured at $\text{pH} > \text{pH}_{\text{pzc}}$, while the adsorption of anions is favoured at pH values below the pH_{pzc} . The pH at the point of zero charge is a convenient reference for predicting how the charge of an activated carbon depends on the pH value

The main objective of the present study was an investigation of the adsorption characteristics of four heavy metal ions, i.e. Cu(II), Zn(II), Ni(II) and Cr(VI), onto peanut shell activated carbon. The effect of important factors such as the pH, the metal ion concentration of the solution and the surface charge of the adsorbent on the equilibrium adsorption capacity are discussed in this paper. All these data made a contribution towards improving information already available.

MATERIALS AND METHODS

Adsorbent

Activated carbon produced from peanut shells by phosphoric acid activation at moderate temperature was used in this work. A detailed discussion of their synthesis and characterization has been published previously (Romero *et al.* 2003). The physical properties and pore-size distribution of the activated carbon employed are given in Table 1.

Through the use of the mass titration method (Haghsersht *et al.* 2003), the pH of the carbon at the point of zero charge (pH_{pzc}) was determined by placing various amounts of carbon in 50 cm³ of a 0.1 M KNO₃ solution. The sealed bottles were then placed in a thermostat shaker overnight, after which the equilibrium pH value of the mixture was measured. The limiting pH was taken as the value of pH_{pzc} (Memendez *et al.* 1995).

Methods

Adsorption isotherms of metal ions

The equilibrium adsorption isotherms were measured by adding different amounts of the activated carbon to 50 cm³ or 100 cm³ volumes of adsorbate solutions with fixed concentrations at a controlled pH value. Aqueous solutions (0.002 M) of copper sulphate, zinc sulphate and nickel nitrate, and a 0.01 M solution of potassium chromate (520 ppm Cr) were used. The pH values of the initial solutions were adjusted either by the addition of 0.1 N NaOH or 0.1 N HCl solutions, as required. All solutions were then maintained in a thermostatic shaking bath for 3 d at 22°C to reach equilibrium. The initial and equilibrium concentrations of the metal ion solutions were measured by flame atomic absorption spectroscopy using a Shimadzu AA-6500 spectrophotometer. The amount of metal ion adsorbed at equilibrium per unit weight of carbon (q) was calculated from the relationship:

$$q = \frac{(C_i - C_e) \cdot V}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium metal ion concentration, m is the weight of carbon (g) and V the volume of solution (ml) used. The effect of the initial solution pH on the uptake of metal ions was examined for pH values between 3 and 7.

RESULTS AND DISCUSSION

The point of zero charge of the activated carbon (pH_{pzc}) in a 0.1 N KNO_3 solution as determined by the mass titration method, was equal to 4.81.

The adsorption isotherms for Cu(II), Zn(II) and Ni(II) ions at various pH levels are shown in Figures 1, 2 and 3, respectively. Figure 4 shows the uptake of Cr(VI) ions at three different pH values. Within the concentration ranges studied, a maximum adsorption capacity of 56.4 mg for Cu(II) ions, 37.2 mg for Zn(II) ions and 9.2 mg for Ni(II) ions per g carbon was observed at pH values of 6, 7 and 6, respectively. Adsorption of the metal cations onto the carbon was strongly dependent on the pH of the aqueous solution. Thus, adsorption at $\text{pH} \leq 3$ was negligible but increased sharply in the pH range between 4 and 7. The adsorption capacity for Cu(II) ions increased from 0.24 to 1.8 mequiv/g as the pH increased from 4 to 6 at $C_e = 0.5$ mequiv/dm³; for Zn(II) ions at $C_e = 1.8$ mequiv/dm³, q increased from 0.24 to 1 mequiv/g when the pH was varied from 5 to 7; while Ni(II) ions at $C_e = 1.5$ mequiv/dm³, q varied from 0.16 to 0.26 mequiv/g as the pH was varied from 4.5 to 6. All experiments were undertaken over pH and concentration ranges where metal cation removal was only associated with adsorption, and not to a combination of adsorption and metal hydroxide precipitation. As indicated in Figure 1, a pale blue precipitate of copper hydroxide was observed on the carbon surface at a pH of 6 and an equilibrium Cu(II) ion concentration higher than 0.488 mequiv/dm³.

During the adsorption of the anion form of Cr(VI), the amount adsorbed increased from 9.5 to 100.9 mg/g as the pH decreased from 6.5 to 3 for an equilibrium Cr(VI) ion concentration of 200 ppm. Also in this case, the adsorption capacity of the adsorbent was clearly pH-dependent. However, the effect of pH on the adsorption capacity was the opposite of that found for metal cations. This behaviour regarding the effect of solution pH on the adsorption of cations and anions was consistent with previous findings (Babic *et al.* 2002; Hamadi *et al.* 2001).

The Freundlich equation (2) and a previous developed expression (Romero *et al.* 2003), equation (3), were employed for modelling the adsorption isotherms:

$$q = a_F \cdot C_e^{b_F} \quad (2)$$

$$q = \frac{a \cdot C_e}{(1 + b \cdot C_e)(1 - c \cdot C_e)} \quad (3)$$

where q is expressed in mequiv/g and C_e in mequiv/dm³.

The Freundlich equation gave satisfactory results for Ni(II) and Zn(II) cations, and for Cr(VI) anions. However, for Zn(II) ions at pH values of 5 or lower, the adsorption followed equation (3). Similarly, for pH values between 4 and 6, the adsorption of Cu(II) ions followed the isotherm represented by equation (3). The constants calculated from the two models, along with the values of σ^2 (the sum of the squares of the difference between the experimental and estimated adsorption capacities) and the average relative error, are reported in Table 2.

From the adsorption isotherms, the amount of metal cations adsorbed at a given equilibrium concentration increased in the order Ni(II) < Zn(II) < Cu(II). To explain the order of metal cation uptake, the electronegativity was selected as one of the correlating parameters since a higher electronegativity would correspond to a greater attraction between the metal ion and electrons. Dastgheib and Rockstraw (2002) have pointed out that if complexation of the metal cations with surface functional groups were also probable, then the stability constant of the metal cation would also be a relevant parameter. Shawabkeh *et al.* (2002) have suggested that another parameter for consideration might be the charge/volume ratio of the metal ion. A further parameter could be the size of the adsorbing ion (ionic radius).

However, irrespective of the parameter considered, no correlation was found between these parameters and the adsorption level. Nevertheless, when the combined effect of electronegativity and surface complexation of the metal cation was considered this led to a reasonable correlation. Table 3 shows the values of the logarithm of the product of the first stability constant and electronegativity of the metal cation (A) that explain the uptake order of the metal cations. This suggests an adsorption mechanism that includes ion exchange and surface complexation reactions.

According to Stumm and Morgan (1996), adsorption consists of a contribution associated with a specific chemical process and an electrochemical adsorption stage. However, it is difficult to separate the process into its chemical and coulombic contributions. For ionic adsorption, the chemical contribution would oppose the electrostatic contribution. All this suggests that any proposed mechanism must involve electrostatic repulsion acting against the adsorption process. This was clearly visible in the adsorption of Cu(II) and Ni(II) ions at pH values of 4 and 4.5 and of Cr(VI) anions at pH values of 6.5 and 5.

CONCLUSIONS

The adsorption of Cu(II), Zn(II) and Ni(II) ions onto activated carbon produced from peanut shell was studied as a function of the pH of the aqueous solution and the metal ion concentration. The peanut shell activated carbon proved to be an effective adsorbent for removal of these ions from aqueous solutions. It could be useful employed for the economic treatment of wastewater containing the heavy metals studied, as the adsorbent was derived from an agricultural waste by-product and had a high adsorption capacity. The amounts of metal cation adsorbed increased with increasing pH value. However, adsorption was negligible at pH values lower than that corresponding to the point of zero charge. Surface precipitation occurred at pH 6 and Cu(II) ion concentrations greater than 0.48 mequiv/dm³. The uptake of metal cations at a given pH and concentration decreased in the order: Cu(II) > Zn(II) > Ni(II).

At pH > pH_{pzc}, the adsorption isotherms of the metal cations studied showed a good correlation between uptake and a combination of the metal ion electronegativity and the first stability constant for the metal hydroxide. This suggests the operation of a dual adsorption mechanism.

It was also shown the adsorbent produced exhibited a good performance towards the removal of Cr(VI) ions. The effect of solution pH was opposite to that found in the adsorption of cations, with the amount adsorbed increasing as the solution pH decreased. The carbon produced from peanut shell

was effective in removing Cr(VI) anions from aqueous solution at pH values near to or below the pH_{pzc} for the carbon.

Freundlich and BET-type equation models fitted all the adsorption isotherms.

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FIGURE CAPTIONS

Figure 1. Isotherms for Cu(II) adsorption at different pH values. Data points: ■, pH = 4.0; π, pH = 5.0; □, pH = 6.0; ∙, surface precipitation.

Figure 2. Isotherms for Zn(II) adsorption at different pH values. Data points: ■, pH = 5.0; □, pH = 6.0; π, pH = 7.0.

Figure 3. Isotherms for Ni(II) adsorption at different pH values. Data points: ■, pH = 4.5; π, pH = 6.0.

Figure 4. Isotherms for Cr(VI) adsorption at different pH values. Data points: ■, pH = 3.0; ★, pH = 5.0; □, pH = 6.5.

TABLE 1. Surface Properties of Activated Carbon

$S_g(\text{BET})$ (m^2/g)	$S_g(\text{iodine})$ (m^2/g)	$V_T(P/P^0 = 0.95)$ (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Mean pore width (nm)	Maxima of bimodal PSD peaks (nm)
1735	1693	1.12	0.91	0.21	1.3	0.8–1.6

TABLE 2. Constants Derived from the Freundlich Equation (2) or from Equation (3) for the Adsorption of Cu(II), Zn(II), Ni(II) and Cr(VI) Ions

(a) Constants derived from Freundlich equation (2)

Metal ion	pH	a_F	b_F	σ^2	Er%
Zn(II)	7	0.7874	0.41153	8.5e-3	3.5
	6	0.4644	0.46426	1.34e-3	3.1
Ni(II)	6	0.2386	0.26719	1.76e-4	2.0
	4.5	0.1305	0.30359	4.75e-5	2.1
Cr(VI) ^a	3.0	18.1362	0.32401	31.6879	3.3
	5.0	4.2915	0.40512	11.329	4.7
	6.5	1.57635	0.33861	1.23368	6.6

^aConstant values for q in mg/g and C_e in mg/dm³.

(b) Constants derived from equation (3)

Metal ion	pH	a	b	c	σ^2	Er%
Cu(II)	4	49.097	210.098	0.2926	0.01753	6.1
	5	7.7157	7.7405	0.4127	0.005936	2.2
	6	61.5563	72.899	1.13713	0.030247	6.6
Zn(II)	5	0.34804	1.7626	0.2270	0.002048	4.0

TABLE 3. Electronegativities of Metal Cations and Stability Constants of Metal Hydroxides

Metal ion	Electronegativity	$\log K_1^a$	A
Cu(II)	2.0	6.5	6.80
Zn(II)	1.6	5.0	5.20
Ni(II)	1.8	4.1	4.35

^a $K_1 = [(MOH)/(M)(OH)]$ (Dastgheib and Rockstraw 2002).**RUNNING HEADS**Left running head: *L.C. Romero et al./Adsorption Science & Technology Vol. 22 No. 3 2004*Right running head: *Adsorption Capacities of Peanut Shell Activated Carbon*

Figure 1

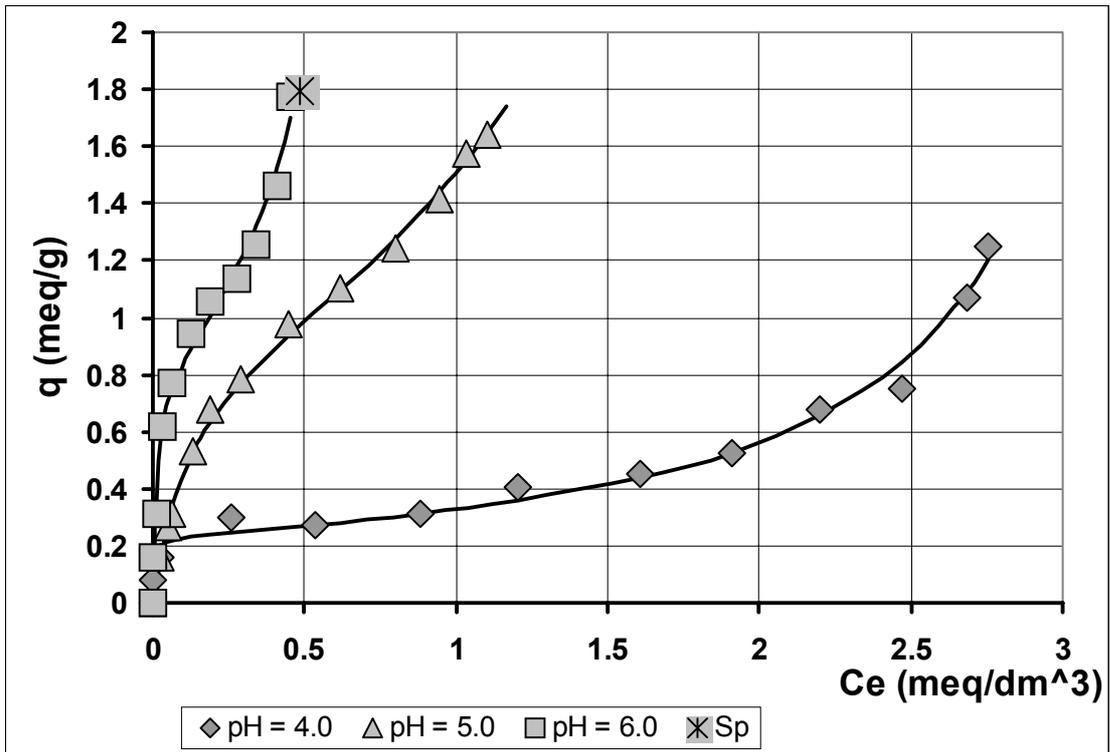


Figure 2

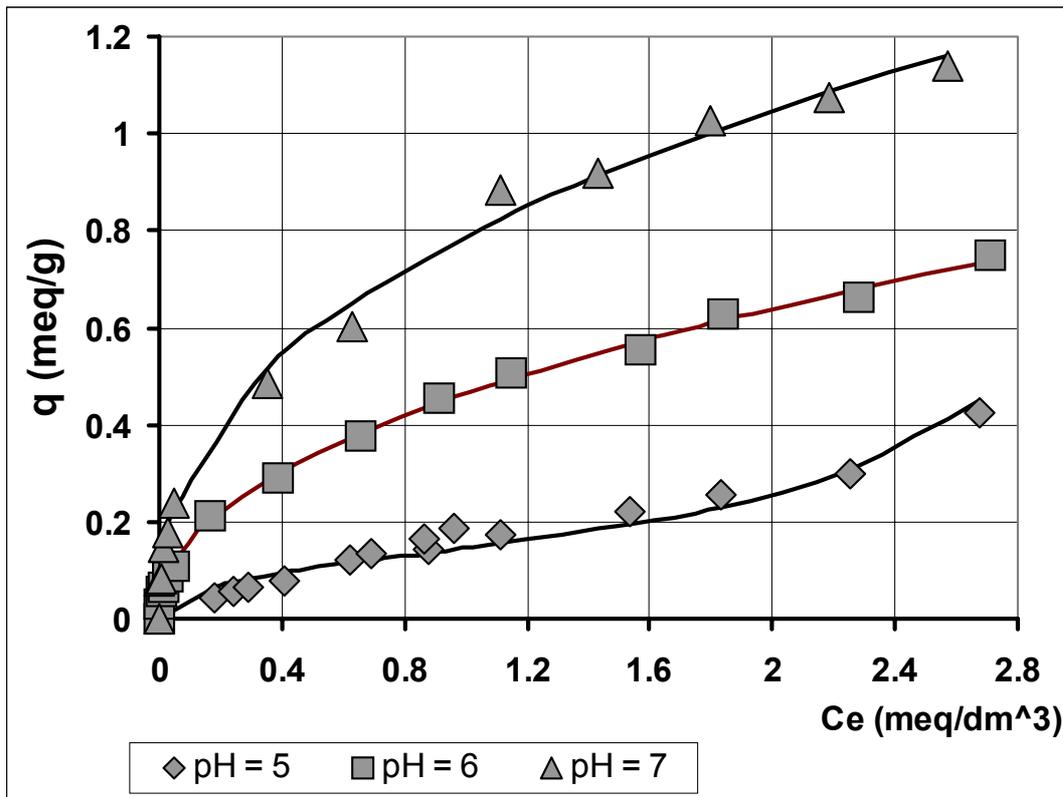


Figure 3

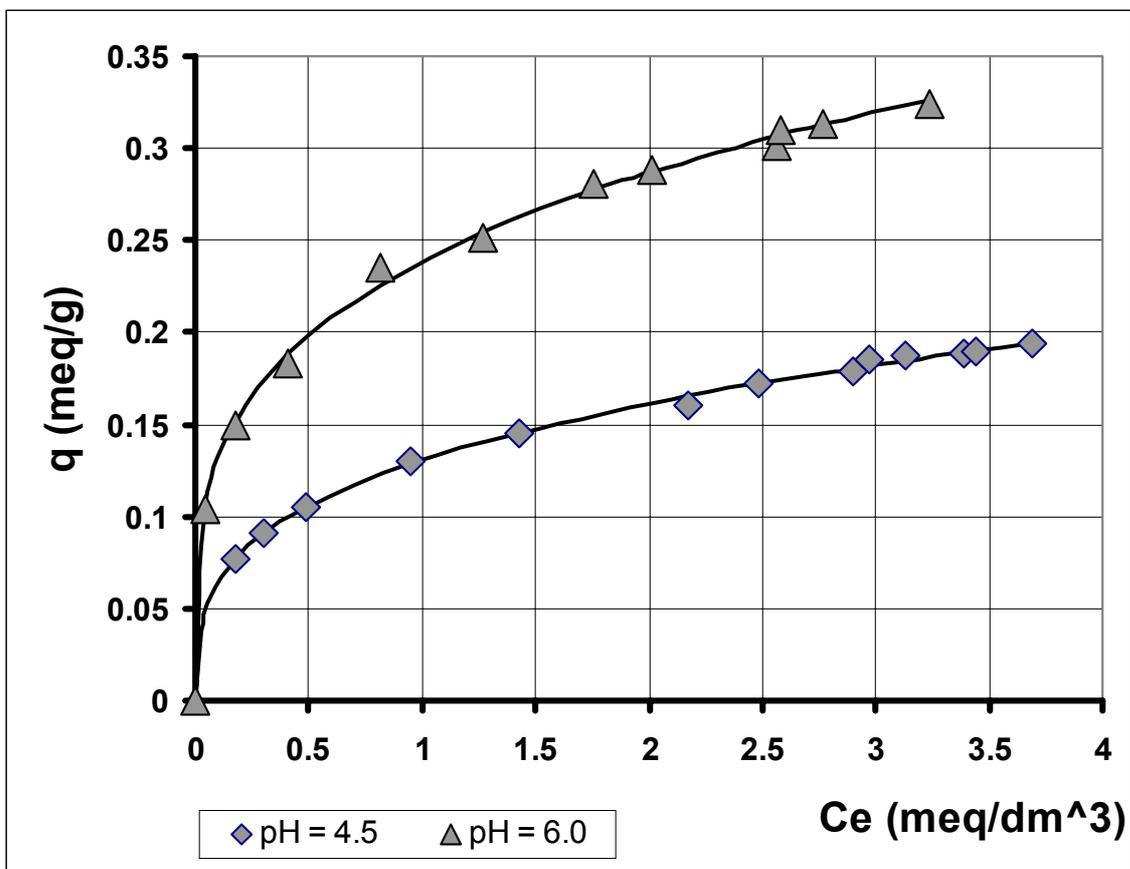


Figure 4

