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Removal of Metal Ions from Aqueous Solution by Cellulose Ion Exchangers

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ABSTRACT

The sorption of metal ions [Cd(II), Cu(II), Co(II), Pb(II), Zn(II), Cr(III), V(IV), V(V)] from aqueous solution by Whatman cellulose ion exchangers was investigated as a function of pH. Whatman P-11 (ammonium cellulose phosphate) exhibited better performance than a fibrous anion exchanger (Whatman Cellect-Ion Exchanger DT-1) with respect to their sorption capacities for Cd(II), Cu(II), Co(II), Pb(II), Zn(II), and Cr(III). The Cellect-Ion anion exchanger (DT-1) had a higher sorption for V(IV) and V(V). The ionic form of cellulose phosphate (P-11) influenced their metal sorption capacities.

INTRODUCTION

Ion-exchanging celluloses and their use as chromatographic adsorbents were first presented by Sober and Peterson during the late 1950s (1). Cellulose ion exchangers present a hydrophilic molecular network which is not tightly fixed and which is crosslinked by hydrogen bonds. Cellulose phosphate was defined as a cation-exchange medium in the bioprocessing industry (2). The

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sorption of metal ions to Whatman cellulose phosphate (P-11) was reported by Levison et al. (3).

Chelating celluloses have been synthesized by the introduction of an electrophilic group into cellulose (4). Iminodiacetic acid with chelating properties for Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, and Zn was attached to cellulose by using an aminomethyl cellulose. Thus-prepared cellulose containing iminodiacetic acid has been used for the sorption of trace elements from soil extracts (4). Cellulose exchangers carrying suitable functional groups were investigated with respect to their sorption properties for UO_2(II), Fe(III), Ni(II), and Pb(II) (5). A cellulose exchanger containing 8-oxa-2,4,12,14-tetraoxopentadecane as the chelating group was prepared by Fischer et al. and used for the selective removal of uranium from seawater (5). In a separate work, Fischer et al. reported the synthesis of cellulose exchangers carrying a chelating anchor group such as carboxyl, amidoxime, hydroxamic acid, and amidrazone hydrazide for the selective separation of uranyl ions (6). Cellulose ion exchangers have been successfully used for the selective separation of some metal ions for analytical purposes. Cellex P, a cellulose ion exchanger with phosphonic groups, was used for the separation of Bi from a large excess of Pb, Cd, Cu, Co, Ni, Fe, Mn, and Zn in the presence of a complexing agent (7). It was also used for the preconcentration of Pb and other trace metals from water (8). The cellulose anion exchanger Cellex T gave a high preconcentration factor for Pd and Ir (9). Preconcentration of Ni was performed by Cellex CM (10). Cellulose adsorbents containing phosphonic acid and carboxymethyl groups were used for the separation and preconcentration of Pb in water (11).

Recently, Levison et al. reported that the treatment of silver-bearing wastewaters was successfully performed with the DEAE (diethylaminoethyl)-substituted fibrous anion-exchange cellulose (Whatman Cellect-Ion exchanger DT-1) (12). However, the sorption behavior of Cellect-Ion-DT-1 for other metal ions has not been reported in the literature. On the other hand, Whatman cellulose phosphate (P-11) was used for the sorption of some divalent and trivalent metal ions [Cd(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II)] to determine the selectivity of binding of these metal ions from an aqueous cocktail of these eight metal ions (3). In addition, the effect of the counterion on selectivity has been reported (3).

In this study the sorption performances of Whatman cellulose phosphate (P-11) and Whatman Cellect-Ion anion exchanger (DT-1) for Cd(II), Cu(II), Co(II), Pb(II), Zn(II), Cr(III), V(IV) and V(V) are compared. The effect of pH on the sorption performances of both P-11 and DT-1 has been studied. In addition, the effect of a counterion on the metal sorption behavior of P-11 has been investigated as a function of pH.

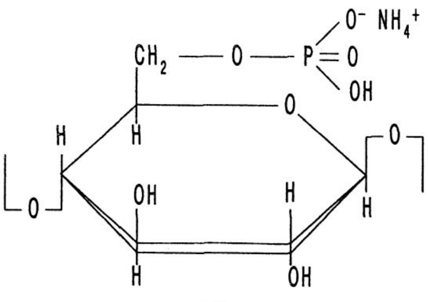
TABLE 1
Properties of Cellect-Ion DT-1

Chemical name and synonyms		Diethylaminoethyl cellulose
Trade name and synonyms		Cellect-ion Exchanger DT-1
Chemical family		Polysaccharide
Formula		Cellulose—O—$(CH_2)_2N(C_2H_5)_2$(HCl form)
Moisture content		70.8%
Regains:	Free base	2.02 g/g of dry weight
	HCl	1.65 g/g of dry weight
Metal ion capacity		1.04 meq/g of dry weight

EXPERIMENTAL

Materials

Cellulose phosphate in the ammonium form (P-11) (**1**) and Cellect-Ion anion exchanger (DT-1) (**2**) were kindly supplied by Whatman International Ltd., UK.


(1)

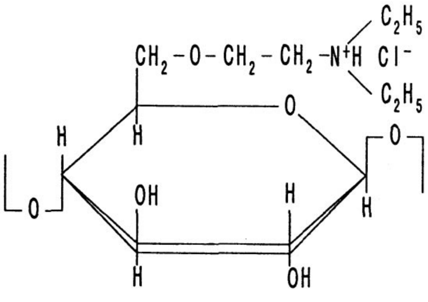

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TABLE 2
Properties of Cellulose Phosphate P-11 (NH_4^+ form)[a]

Chemical name and synonyms		Phosphocellulose
Trade name and synonyms		P-11
Chemical family		Polysaccharide
Formula		Cellulose—O—$PO_3H^- \cdot NH_4^+$
Functional group		Ester-linked orthophosphoric acid
Moisture content		4.2%
Insoluble phosphate		28.2% of dry weight
Soluble phosphate		1.9% of dry weight
Metal ion capacity:	a	3.2 meq/g of dry weight
	b	5.3 meq/g of dry weight
Mean fiber length		50–250 μm

[a] Where ''a'' = strong group and ''b'' = total of strong and weak groups.

The properties of cellulose ion exchangers are given in Tables 1 and 2. In order to prepare various cellulose phosphate salts containing K^+, Na^+, and Ca^{2+} as counterions, ammonium cellulose phosphate (P-11) was equilibrated with 0.5 M KCl, 0.5 M NaCl, and 0.5 M $CaCl_2$, respectively. The thus-treated cellulose phosphates were filtered, washed with deionized water in order to remove the excess amount of the electrolyte, air-dried, and then dried under vacuo at 40°C.

Batch Sorption Tests

The solutions of Cd(II), Cu(II), Zn(II), Co(II), Pb(II), Cr(III), V(IV), and V(V) were prepared at various pHs, and a 50 cm^3 of each metal ion solution (50 mg M^{n+}/dm^3) was contacted with 50 mg of cellulose sample with continous shaking at 30°C for 2 hours.

Metal Ion Analyses

Metal ions in the solutions were determined with a Varian (10 Plus Model) Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

Effect of pH on the Sorption of Metal Ions

The effect of pH on the metal sorption performance of both Cellect-Ion anion exchanger (DT-1) and ammonium cellulose phosphate (P-11) is compared in Figs. 1–4. Whatman cellulose phosphate (P-11) exhibited better performance

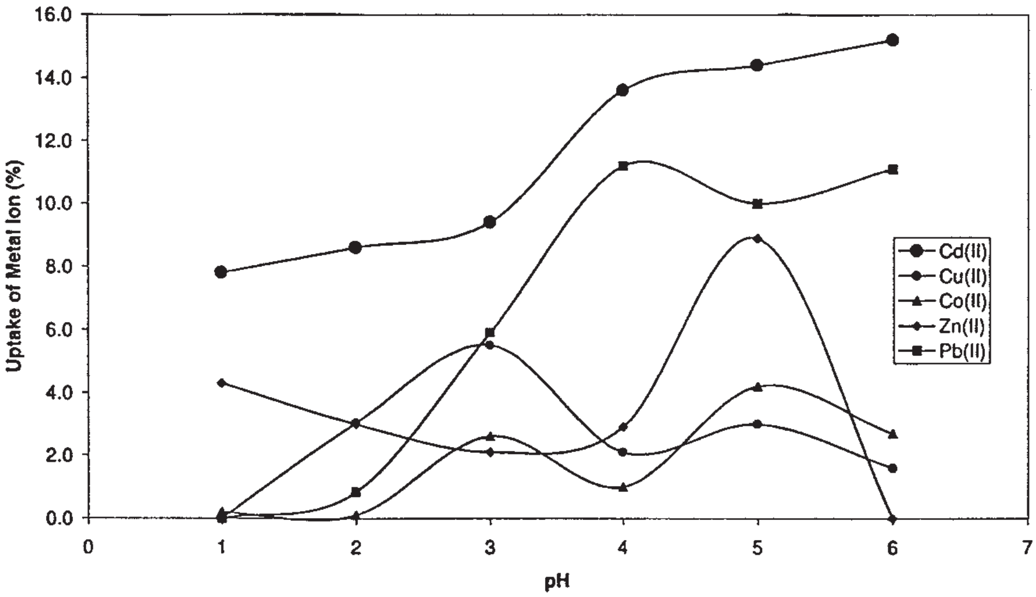

FIG. 1 Effect of pH on the uptake of metal ions by Cellect Ion (DT-1).

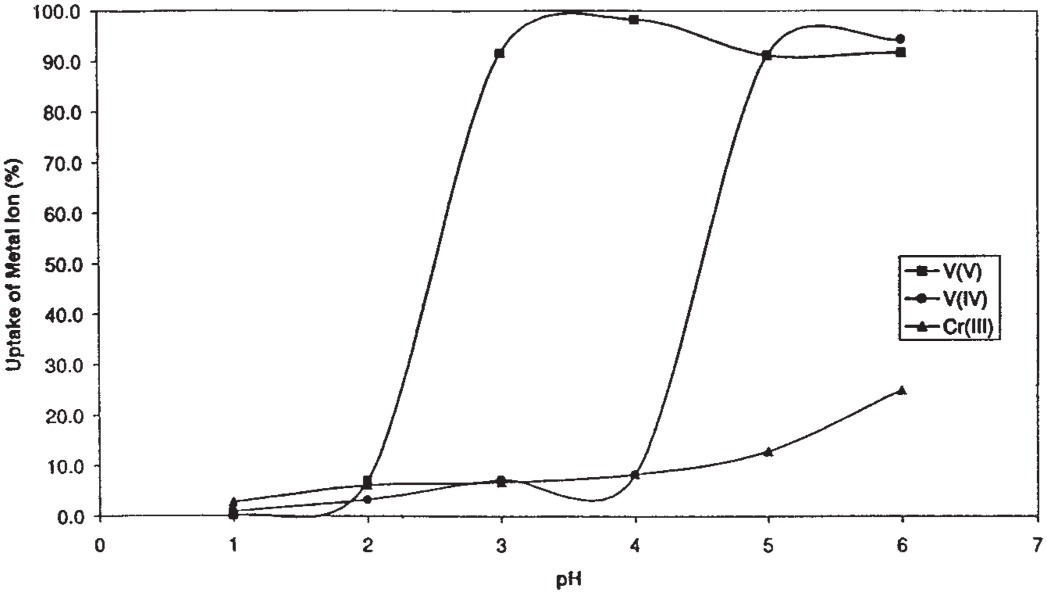

FIG. 2 Effect of pH on the uptake of metal ions by Cellect Ion (DT-1).

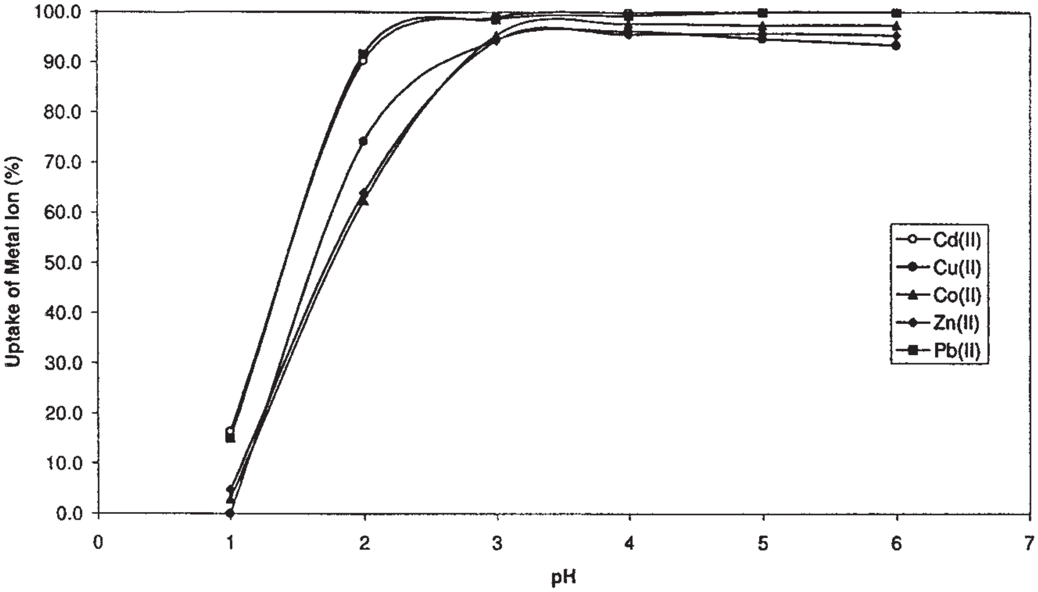

FIG. 3 Effect of pH on the uptake of metal ions by ammonium cellulose phosphate (P-11).

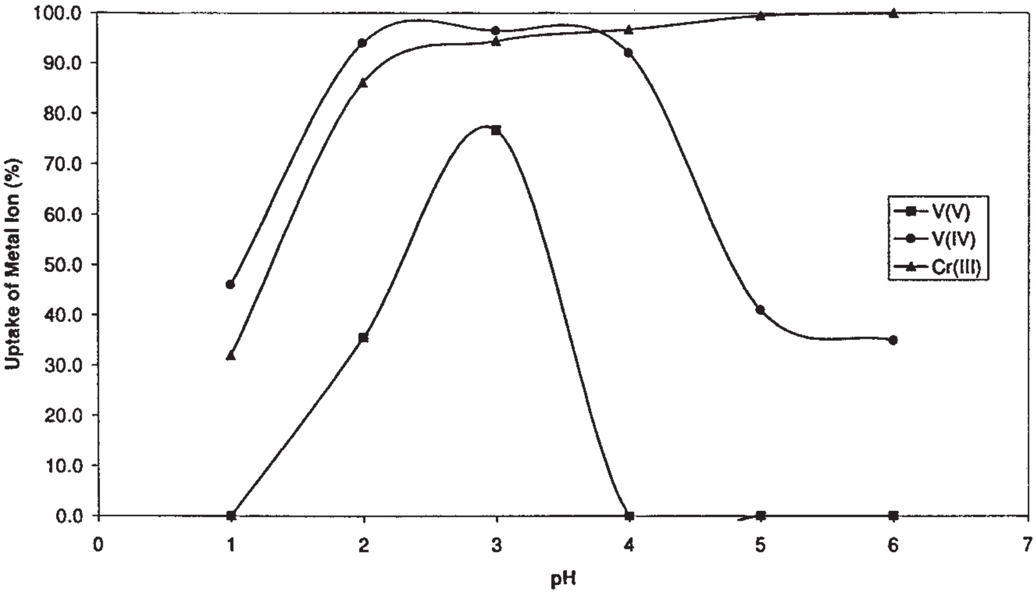

FIG. 4 Effect of pH on the uptake of metal ions by ammonium cellulose phosphate (P-11).

than Cellect-Ion anion exchanger (DT-1) for the sorption of Cd(II), Co(II), Cu(II), Zn(II), Pb(II), and Cr(III). These metal ions were wholly sorbed by P-11 at pH > 2. On the other hand, Cellect-Ion anion exchanger (DT-1) exhibited a higher sorption for V(V) at pH ≥ 3 and for V(IV) at pH ≥ 5 than did P-11. Whatman cellulose phosphate (P-11) gave a sorption peak for V(V) at pH 3 and then a dramatic decrease with a further increase in pH. A similar trend was also observed during the sorption of V(IV) at pH > 4. This was most probably due to the formation of anionic species for V(V) at pH > 3 and for V(IV) at pH > 4. It is believed that these anionic forms are sorbed easily by Cellect-Ion anion exchanger (DT-1) but not by cellulose phosphate cation exchanger (P-11).

Effect of Ionic Form of Cellulose Phosphate on Metal Ion Sorption

In order to see the effects of counterions, cellulose phosphate (P-11) in the NH_4^+, Na^+, K^+, and Ca^{2+} forms was used for sorption of various metal ions. The results are summarized in Figs. 5–11. The data indicate that cellulose phosphate shows an almost similar behavior for the sorption of Cu(II), Zn(II), Cd(II), and Co(II) when it contains a monovalent counterion (i.e., NH_4^+, Na^+, and K^+) but a reduced sorption performance when it contains a divalent counterion (i.e., Ca^{2+}). This is probably due to the higher binding strength between Ca^{2+} and the phosphate group on cellulose

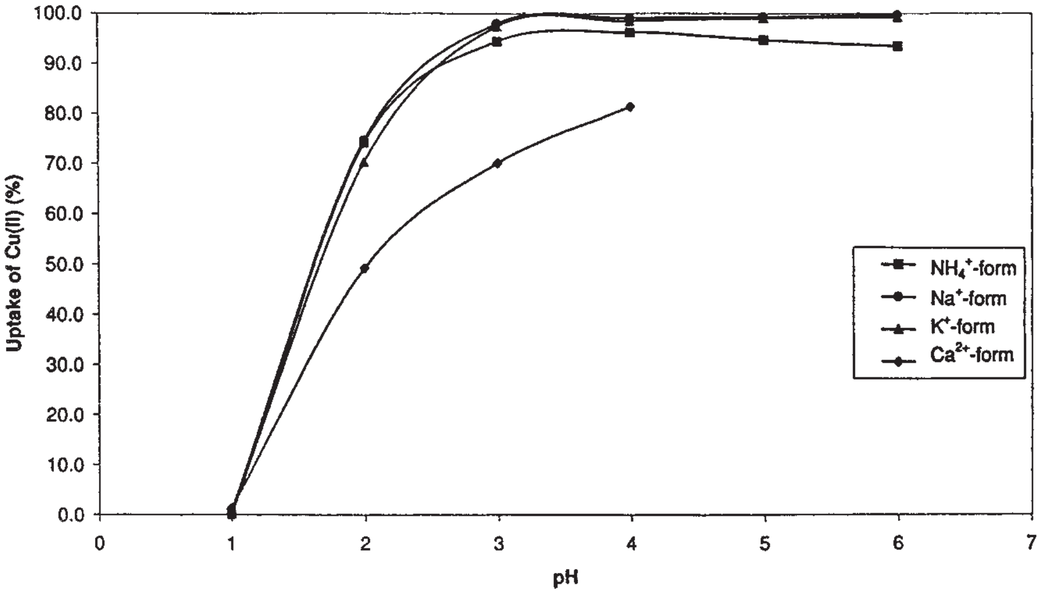

FIG. 5 Effect of ionic form of cellulose phosphate (P-11) on Cu(II) uptake.

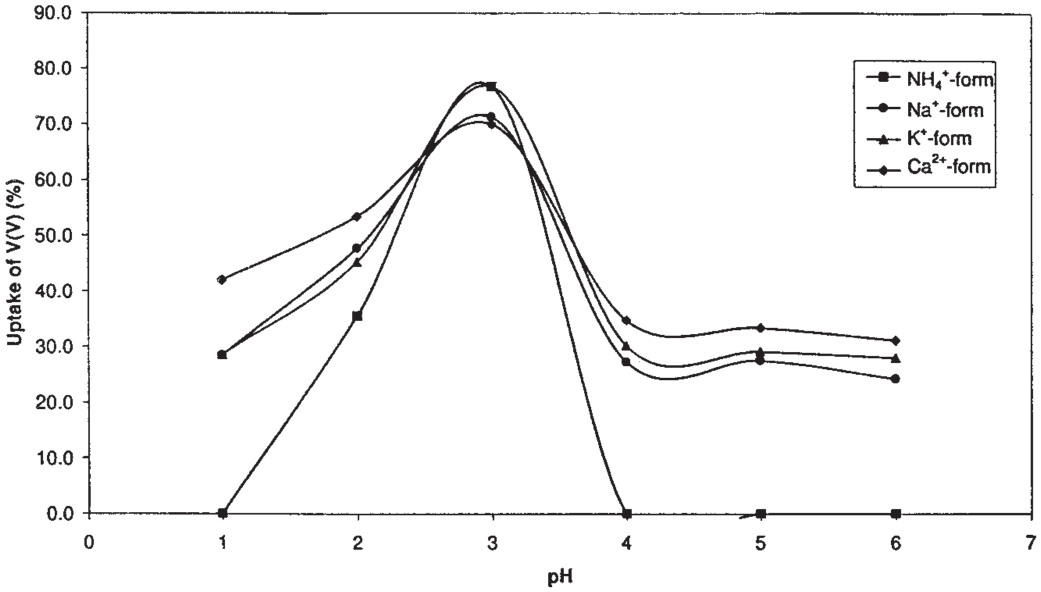

FIG. 6 Effect of ionic form of cellulose phosphate (P-11) on V(V) uptake.

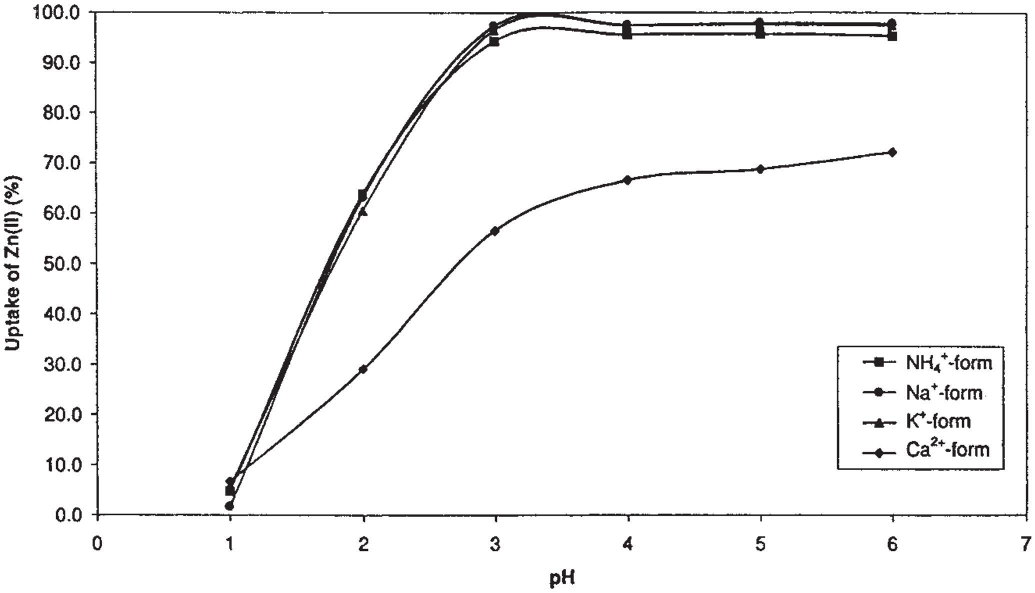

FIG. 7 Effect of ionic form of cellulose phosphate (P-11) on Zn(II) uptake.

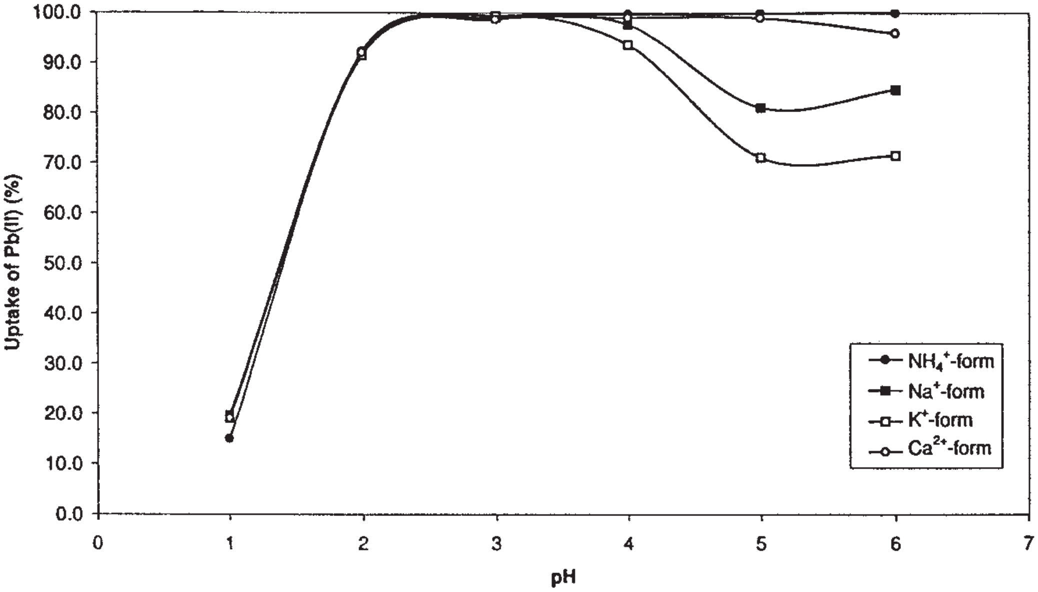

FIG. 8 Effect of ionic form of cellulose phosphate (P-11) on Pb(II) uptake.

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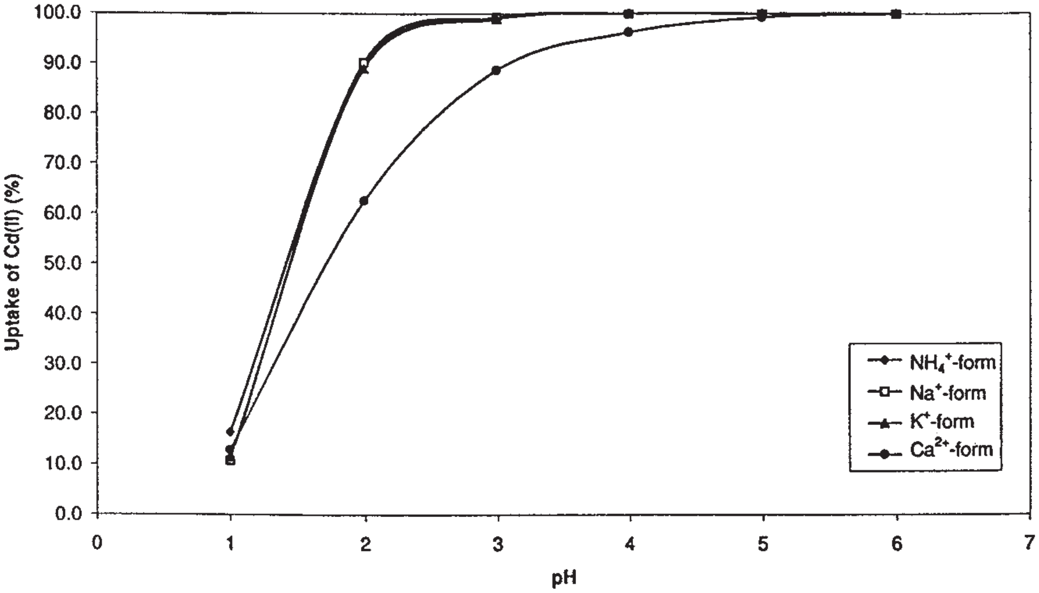

FIG. 9 Effect of ionic form of cellulose phosphate (P-11) on Cd(II) uptake.

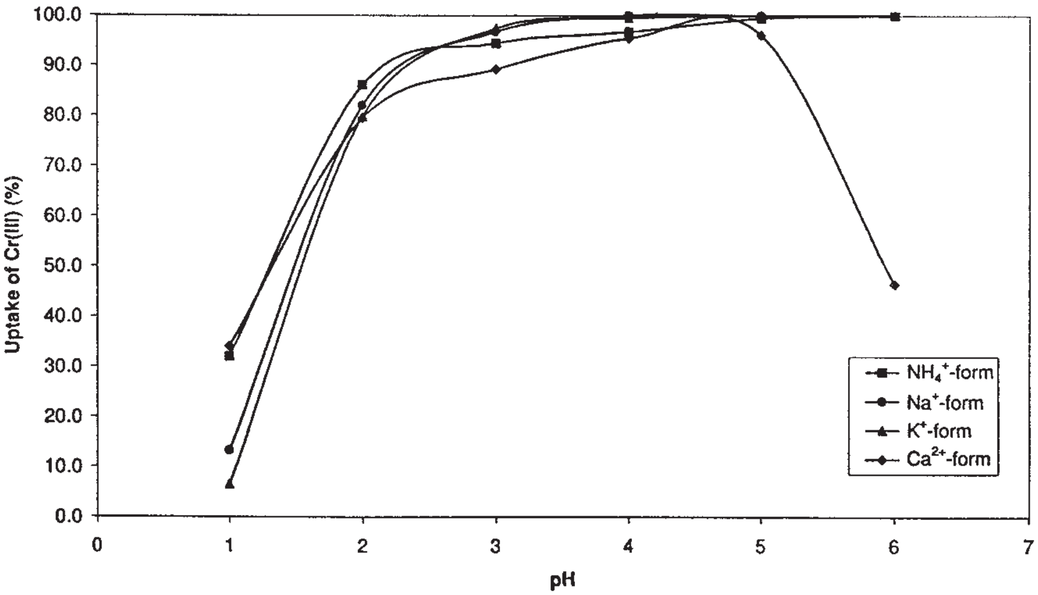

FIG. 10 Effect of ionic form of cellulose phosphate (P-11) on Cr(III) uptake.

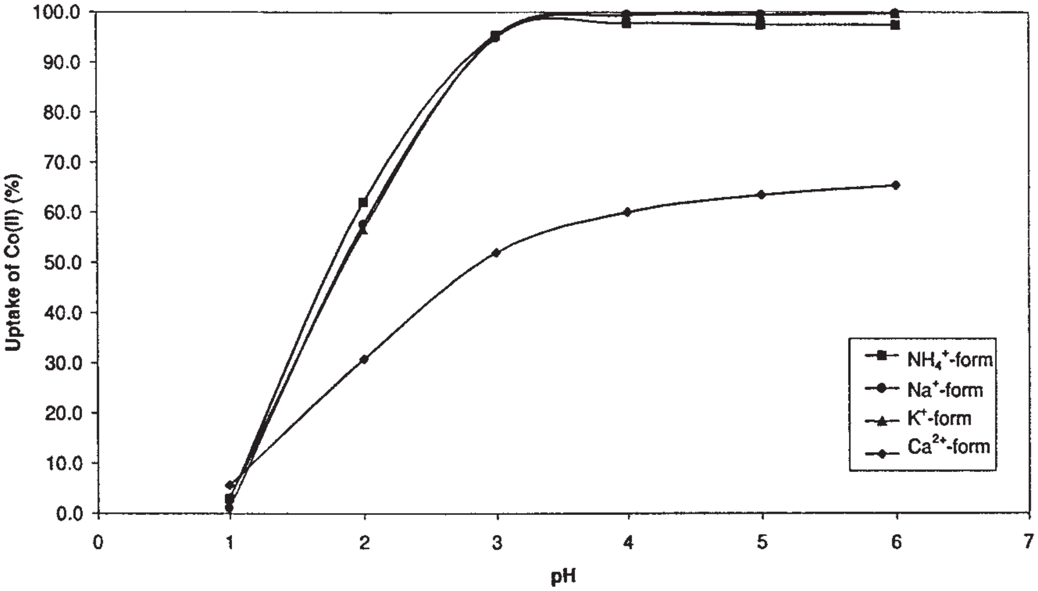

FIG. 11 Effect of ionic form of cellulose phosphate (P-11) on Co(II) uptake.

compared with that exhibited for a monovalent cation. The sorption capacity of ammonium cellulose phosphate for V(V) has small values at pH ≤ 2 and pH ≥ 4 than those in the K^+, Ca^{2+}, and Na^+ forms (Fig. 6). This is believed to be due to the size differences of various ionic forms of V(V) at different pHs. It has been reported that Pb(II) is the metal ion bound preferentially on cellulose phosphate irrespective of the counterion (3). We observed a similar trend up to pH 4 (Fig. 8). As shown in Fig. 8, cellulose phosphate in the Na^+ and K^+ forms exhibited some decrease in Pb(II) uptake at pH ≥ 5. However, there is no change in the sorption performance of cellulose phosphate in either the NH_4^+ or Ca^{2+} form at pH ≥ 2. This was again believed to be due to the effect of pH on the ionic species of Pb(II) in the solution. The effect of the ionic form of cellulose phosphate on Cr(III) uptake was barely apparent at pH > 1 although a sharp decrease was observed in Cr(III) uptake by cellulose phosphate in the Ca^{2+} form when pH > 5 (Fig. 10).

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