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SORPTION OF Ni^{2+} BY DIFFERENT SYNTHETIC HYDROXYAPATITE

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Abstract

Two hydroxyapatite (HAP) samples of different crystallinity were studied as a nickel immobilization matrix. Sorption isotherms were obtained by batch equilibration method, in the concentration range $1 \cdot 10^{-4} - 8 \cdot 10^{-3} \text{ mol/dm}^3$. Low crystalline sample has sorption capacity of 0.212 mmol/g, and due to its higher specific surface area and lower Ca/P ratio it was found to be better sorbent for Ni^{2+} than crystalline HAP (0.092 mmol/g).

Introduction

Nickel is a member of group VIII of the periodic table, similar to iron in its physical properties. The earth's crust contains 0.008% nickel [1]. Due to natural geochemical activity and weathering, nickel occurs naturally in all soils, sediments and waters. Nickel has large industrial importance, and its salts in small amounts are essential to many life forms, including humans. In large amounts, however, they can be extremely toxic. The physico-chemical properties of the receiving environment (pH, redox potential, hardness, complexing and precipitating agents, ionic strength, other cations, temperature, solid organic and inorganic matter, cation exchange capacity) control the fate and bioavailability of nickel [2]. HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a naturally occurring mineral, also known as a good matrix for heavy metal and radionuclide immobilization by means of ion exchange, sorption and precipitation processes [3].

Experimental

Ni^{2+} immobilization by highly crystalline synthetic HAPc, obtained by neutralization method [4] and by commercial product from Bio-Rad Laboratories was investigated. Sorption isotherms were obtained by batch method. HAP samples were equilibrated with $\text{Ni}(\text{NO}_3)_2$ solutions (solid to liquid ratio 1:200) for 24 h, at room temperature ($20 \pm 1^\circ\text{C}$). Initial concentrations of Ni^{2+} were in the range $1 \cdot 10^{-4} - 8 \cdot 10^{-3} \text{ mol/dm}^3$, and ionic strength for all solutions was added to 0.1 mol/dm^3 , by KNO_3 addition. After filtration, final pH values were measured and remainder concentrations of Ni^{2+} in solutions were determined by AAS.

Results and Discussion

Sorbate samples were characterized by standard physico-chemical analyses. HAPc and Bio-Rad commercial product have crystal structure of HAP, but different fraction of crystalline phase (0.90 and 0.28), Ca/P ratio (1.70 ± 0.02 and 1.53 ± 0.02) and specific surface area (24 and 63 m^2/g). Point of zero charge (pH_{PZC}) obtained by batch

method, using $0.1 \text{ mol/dm}^3 \text{ KNO}_3$ as an inert electrolyte, was 6.6, for both HAP samples. Batch test results for Ni^{2+} sorption on two HAP samples are presented in Figure 1.

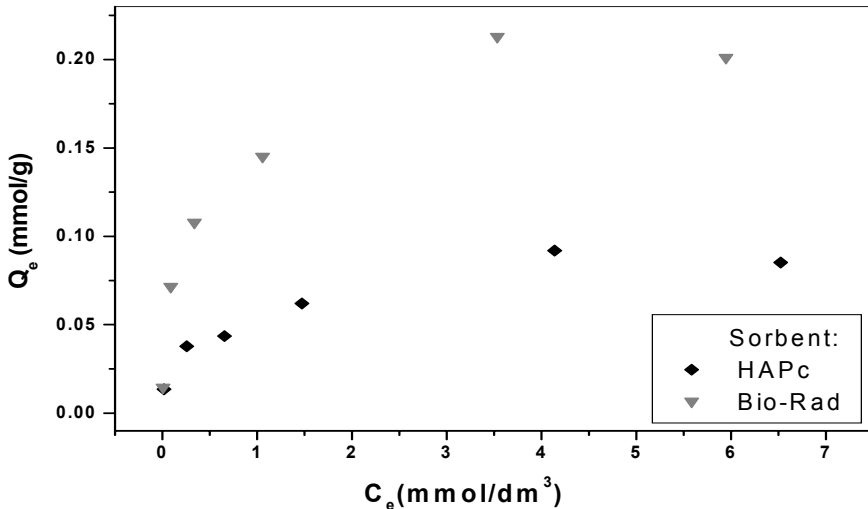


Figure 1. Sorption isotherms for Ni^{2+} on HAPc and Bio-Rad samples.

The increase in the initial metal concentration resulted in an increase in the Ni^{2+} sorption, until equilibrium was reached. Experimental results were found to be well represented by linear form of Langmuir adsorption isotherm:

$$C_e/Q_e = 1/X_m K + 1/X_m \cdot C_e$$

where Q_e (mmol/g) and C_e (mmol/dm³) presents the equilibrium concentration of sorbate in solid and liquid phase, K (dm³/mmol) is the Langmuir constant related to the energy of adsorption and X_m (mmol/g) is the maximum sorption capacity. Results of linear fit are summarized in Table 1.

Table 1. Linear form of Langmuir isotherms for Ni sorption on HAP samples.

Sorbent	Linear form of Langmuir Isotherm	X_m (mmol/g)	K (dm ³ /mmol)	R
HAPc	$C_s/Q_s = 4.55 + 10.80C_e$	0.092	2.371	0.993
Bio-Rad	$C_s/Q_s = 1.11 + 4.71C_e$	0.212	4.245	0.997

Bio-Rad sample is approximately two times better sorbent for Ni^{2+} , than crystalline HAPc (0.212 versus 0.092 mmol/g). It can be correlated to its lower crystallinity, higher specific surface area, and lower Ca/P ratio. Sorption is followed by pH changes (Table 2.)

Table 2. Initial pH and pH values after equilibration with HAPc and Bio-Rad sample.

Initial Ni ²⁺ conc. (mol/dm ³)	pH _{initial}	pH _{final} HAPc	pH _{final} Bio-Rad
1.10-4	6.17	6.65	6.63
5.10-4	6.00	6.36	6.38
1.10-3	5.92	6.38	6.21
2.10-3	5.88	6.30	6.12
5.10-3	5.87	6.26	5.91
8.10-3	5.86	6.00	5.85

Final pH increases comparing to initial pH, as a result of HAP amphoteric surface and buffer capacity. On the other hand, as the initial concentration of Ni increases, as well as the amount of sorbed Ni, the final pH decreases. This effect is more pronounced for Bio-Rad sample. The decrease of final pH comparing to pH_{PZC} (6.6) suggests specific cation sorption.

Sorption capacity of HAP towards Ni²⁺ is generally lower in respect to other heavy metals, such as Pb, Cd, Zn and Cu [5]. Maximum sorption capacity obtained for Bio-Rad HAP is similar to capacity of spent animal bones [6].

Conclusion

Bioavailability of nickel is correlated with toxicological effects of hydrated Ni²⁺ ion. HAP addition decreases concentration of chemically labile and bioavailable Ni²⁺ ion from aqueous solutions, by sorption processes. Low crystalline synthetic HAP, which is more similar to natural occurring apatites, have significantly higher sorption capacity than highly crystalline and pure sample.

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