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Removal of metal ions from aqueous solution by adsorption on the natural adsorbent CACMM2

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Abstract

The adsorption of Cd^{+2} , Cr^{+3} , Cu^{+2} , Fe^{+3} , Ni^{+2} , Pb^{+2} and Zn^{+2} from aqueous solution was used to study the sorption properties of the adsorbent CACMM2 extracted from a cactus. Quantitation of the cation concentrations was performed by HPLC with diode array detection using on-column complex formation with 8-hydroxyquinoline. Removal degree from 100 $\text{mg M}^{n+} \text{ l}^{-1}$ solutions followed the series: $\text{Cu} > \text{Cd} > \text{Fe} > \text{Ni} > \text{Cr} > \text{Zn}$. Henry and Freundlich constants were determined since adsorption did not reach saturation plateaux in the studied concentration interval. Sorption of chromium by CACMM2 was stronger than the sorption onto lignin, calcium oxalate and cellulose up to 1000 $\text{mg Cr}^{3+} \text{ l}^{-1}$. Copper and iron were desorbed to a greater extent, while lead adsorption was practically irreversible. CACMM2 was able to remove more than 83% of chromate in a freshly prepared and exhausted chromate commercial solution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Chromate waste; Metal cations

1. Introduction

The pollution of water and soil with metal cations has increased dramatically in the last 50 years as a consequence of the expansion of industrial activities. The well-established toxicity of metals in solution at sufficiently high concentrations affects humans, animals and vegetation [1]. Most of the international drinking water standards are in the range of 0.005–0.01 mg l^{-1} cadmium and 5 mg l^{-1} zinc and are related with the relative toxicity of cadmium and zinc. The total mean concentration of cadmium and

zinc from 13 locations along the Kuwaiti coast [2], for example, was 0.466 and 6.58 mg l^{-1} , respectively, while the respective metal contents in surface water from the Mexican Lake, Pom-Atasta, were 0.029 and 0.009 mg l^{-1} [3], the level of lead, 0.069 mg l^{-1} , was above the Mexican allowed level of 0.025 mg l^{-1} .

Major sources of metals in the environment are wastewaters from industries like batteries manufacture, metal extraction, surface finishing and paints. Different processes can be used for the removal of metallic pollutants from aqueous media. One such method, adsorption onto solids, is an attractive alternative to chemical precipitation and ion-exchange for metals removal. The removal efficiency of new and inexpensive adsorbents can be tested first in model aqueous solutions (deionised water) and

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then in spiked ground or drinking water. Fundamental research examining the solid–solute interactions can also be used to gain understanding of the phenomenon and to assess environmental utility.

Sorbents prepared from natural organic wastes used in the removal of cadmium, chromium, copper, iron, nickel, lead and zinc includes groundnut husks [4], bark [5–7], sunflower stalks [8], bagasse [9], rice husk [10] and sawdust [11,12]. The solids commonly used for this sort of water decontamination are cation-exchangers like resins [13] and zeolites [14]. Bentonite might exhibit different removal efficiency for diverse cations. Its affinity with cadmium for example was high and with zinc ions it was medium [15].

In previous papers we have reported that chemically treated cactaceous powder [16] can be used to adsorb water [17] and organic vapors [18]. In this work we studied the adsorption of metallic ions from aqueous solution by this natural adsorbent denominated as CACMM2.

2. Experimental

2.1. Materials

Samples of CACMM2 were prepared by extracting the pulp of cactus as described in Ref. [16]. The extracted particles were then dried and sieved. The fraction used in this work had a particle diameter of 420 μm , a specific surface area of 11 $\text{m}^2 \text{g}^{-1}$ and mesopores (50 \AA). To remove residual water, the samples thus obtained were dried for 3 h at 100°C under vacuum (10^{-6} mmHg; 1 mmHg = 133.322 Pa). Other organic compounds used in this work were: cellulose triacetate (Aldrich CAS 9012-09-3), lignin hydrolytic (Aldrich CAS 8072-93-3) calcium oxalate monohydrated (Aldrich CAS 5794-28-5) and 8-hydroxyquinoline (Aldrich CAS 148-24-3). The following inorganic salts were used: $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 from J.T. Baker, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Reactivos Monterrey), PbCl_2 (Fisher) and Na_2CrO_4 (Merck). The concentration of the metallic ions is always given as the concentration of elemental cation. All solutions for the batch experiments and for the HPLC analysis were prepared with deionised water Milli-Q.

2.2. Methods

Batch adsorption experiments were conducted in a constant temperature room (23°C) on a three-dimensional shaker (100 rpm) during 1 h and then static during 24 h using 50-ml glass vials. The solid–liquid system consisted of 50 ml containing 5 g of the adsorbent. After contact time the solution was filtered and the filtrate was analyzed by HPLC. The chromatographic system consisted of a Beckman Gold system with diode array detector. The chromatographic separations were performed on a Spherisorb Phenyl (Phase Sep) stainless steel column (15 $\text{cm} \times 4.6$ mm I.D.). Mobile phase composition was acetonitrile–8-hydroxyquinoline ($7 \cdot 10^{-5}$ M) (30:70, v/v) solution. The eluent vessel was covered with a black tissue during analysis to avoid decomposition with light. Flow rate was 0.7 ml min^{-1} and analysis was performed at ambient temperature. Detection wavelength of the metal–hydroxyquinoline complexes formed on-column was 242 nm for Cu^{2+} , Ni^{2+} and Zn^{2+} and 250 nm for Cd^{2+} , Cr^{3+} , Fe^{2+} and Pb^{2+} .

The adsorption isotherm was constructed by varying the initial ion concentrations from 0.1 up to 1.5 mM of the respective cation. For higher chromium concentrations and hexavalent chromium in chromate solutions the analysis of was carried out by UV spectroscopy at 376 nm using methacrylate cuvettes and running the respective blanks of the leached solids. A dilution factor of 1:1000 was used for the construction of calibration curves and for the adsorption experiments of chromate from commercial chromate solutions. These solutions were donated from metal finishing industry in Puebla, Mexico.

For the desorption trials CACMM2 in the batch solutions was filtered after adsorption. It was dried on filtering paper and then at 100°C for 3 h. A weighed amount containing sorbed ions was put in contact with water. After 7 days the supernatant solution was analyzed by HPLC.

3. Results and discussion

3.1. Adsorption of metal cations from aqueous solutions

In adsorption processes particle size and chemical

nature are important physico-chemical aspects affecting sorption capacity. The quantitation of the adsorbed amounts can be carried out by spectrophotometric, electrochemical, atomic absorption and chromatographic methods. The determination of metal ions by both normal- and reversed-phase HPLC with UV–Vis detection is based on the pre-column, on-column or post-column formation of stable metallic chelates. We used 8-hydroxyquinoline as on-column ligand [19] for the RP-HPLC determination of the adsorption equilibrium concentrations and introduced the use of a phenyl column. We looked for the reported dissociation pK_1 values [20] of the metal hydroxyquinolinates to assure complex stability during analysis. They were greater than the corresponding values for other organic ligands. Fig. 1A and B show, respectively, the spectra of the hydroxyquinolinates (HQs) formed on column and the corresponding chromatographic peaks. 8-Hydroxyquinoline has maxima at 202 and 242 nm (Fig. 1A). All of the metal hydroxyquinolinates had absorption

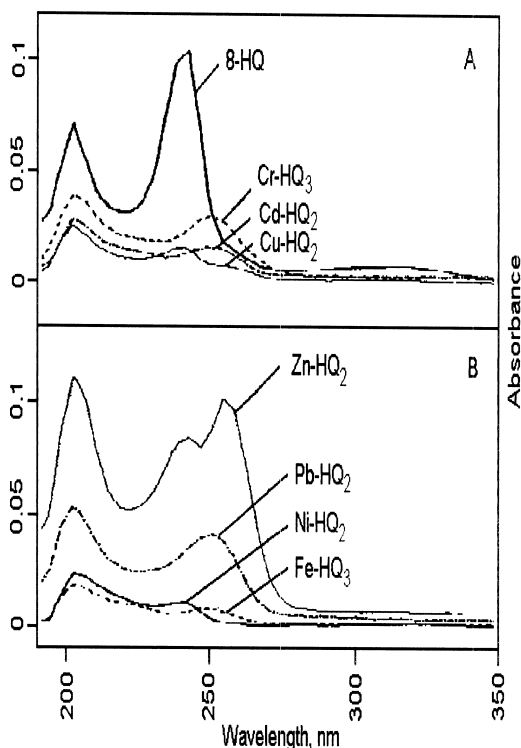


Fig. 1. UV spectra of a 10- μ l injection of 8-hydroxyquinoline (1 mM) and of the hydroxyquinolinates formed on column scanned during a chromatographic run.

bands at 202–206 and 242–250 nm. The complexes Cu–HQ₂ and Zn–HQ₂ showed additionally a third band at 258 and 254 nm, respectively (Fig. 1B). Since we performed quantitation of one-component solutions, in our work chromatographic conditions were established to achieve short retention time for individual peaks (Fig. 2A) instead of separation at multicomponent mixtures. A phenyl column was used as it was reported in Ref. [19] for a C₁₈ stationary phase. Individual calibration plots were prepared for all the metals over the concentration range 0.15–1.5 mM. Excellent linearity was observed over the studied range (see Table 1). Slopes in the series varied 12-fold indicating the different sensitivity for each metal. To show how the method

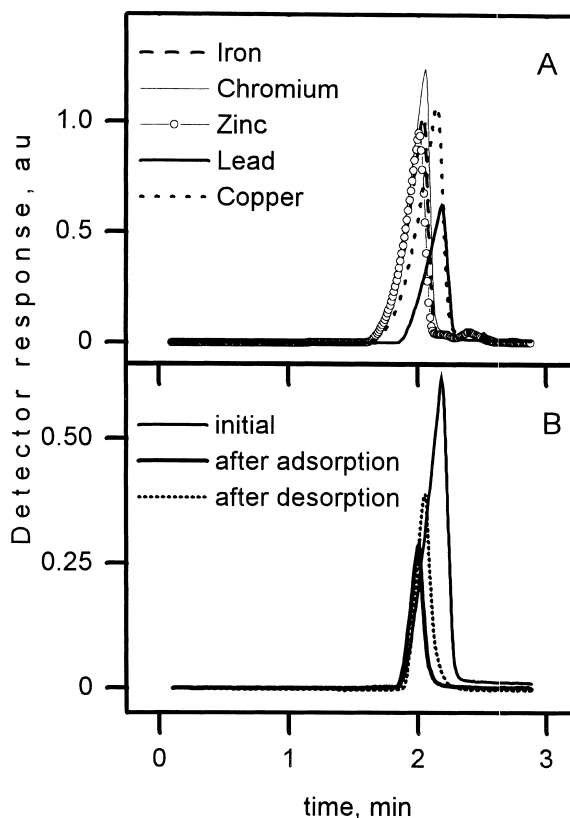


Fig. 2. HPLC chromatograms of 1 mM equiv solutions of metallic ions (A) and of 3 mM equiv solutions of lead before and after adsorption and desorption on CACMM2 (B). Column Spherisorb Phenyl (Phase Sep; 4.6 \times 150 mm). Mobile phase 30% acetonitrile in 2 mM hydroxyquinoline water solution. Flow rate 0.7 ml min⁻¹, detection wavelength 242 nm for Cu²⁺, Zn²⁺ and 250 nm for Cr³⁺, Fe³⁺ and Pb²⁺.

Table 1
Values obtained in the chromatographic and adsorption work

Ion	$A = mC$		pK_1	k_H (cm ³ m ⁻²)	$1/n$
	m	R^2			
Zn ²⁺	32.2	0.992	8.50	0.50±0.01	1.3
Fe ³⁺	54.8	0.998	8.0	0.47±0.01	1.1
Cu ²⁺	66.6	0.996	12.2	0.50±0.02	1.3
Pb ²⁺	73.3	0.988	9.02	0.42±0.01	1.1
Cr ³⁺	114.5	0.998		0.45±0.01	1.0
Ni ²⁺	190.9	0.990	9.9	0.48±0.04	1.0
Cd ²⁺	399.4	0.970	7.2	0.51±0.02	1.4

Slope m and correlation factor R^2 in the linearised equation of calibration curves for the HPLC determination of cations as 8-hydroxyquinolates and dissociation pK_1 values of hydroxyquinolate complexes [20]. Henry k_H and Freundlich $1/n$ adsorption constants at low concentration range and 23°C onto CACMM2.

was applied, Fig. 2B shows the chromatographic peak of a lead solution before and after contact with the adsorbent CACMM2, as well as after desorption. Integration of the chromatographic peaks and application of the calibration plots were performed to calculate adsorption–desorption equilibrium concentrations and to construct the adsorption isotherms depicted in Fig. 3A. According to the initial portion of the curves, the isotherms covered the linear Henry region. Except for lead, the adsorption isotherms of all metals practically overlapped, indicating no metal specificity. Comparable adsorption magnitudes were reported in the literature for example for zinc [15]

onto bentonite, copper [21] onto peat and cadmium [22] onto activated carbon from a solution concentration of 20, 6, and 75 mg l⁻¹, respectively. The studied by us concentration range was larger than the range one can find in the literature, where adsorption isotherms normally reach saturation. In Ref. [23] saturation plateau magnitude onto sunflower stalks decreased in the order Cd>Zn>Cu>Cr in a concentration range similar to that studied in this work. In order to examine the adsorption equilibrium of the CACMM2 sample in relation to the different ions, the Henry k_H and Freundlich $1/n$ adsorption constants were calculated. Langmuir isotherm equation was not utilized to evaluate the results, since any of the obtained adsorption isotherms did present the typical Langmuirian form. Table 1 shows practically no differences among constant values for all ions and that the $1/n$ values were close to unity. Henry constants decreased as follows Cd>Zn≈Cu>Ni>Cr>Fe>Pb. This series partially agrees with the results obtained with bentonite [15] and sunflower material [23].

3.2. Adsorption of chromium and chromate

To explore the individual behavior of some of the CACMM2 prototype components, chromium adsorption was measured spectrophotometrically onto CACMM2, lignin, calcium oxalate and cellulose in a larger concentration range. Little differences can be

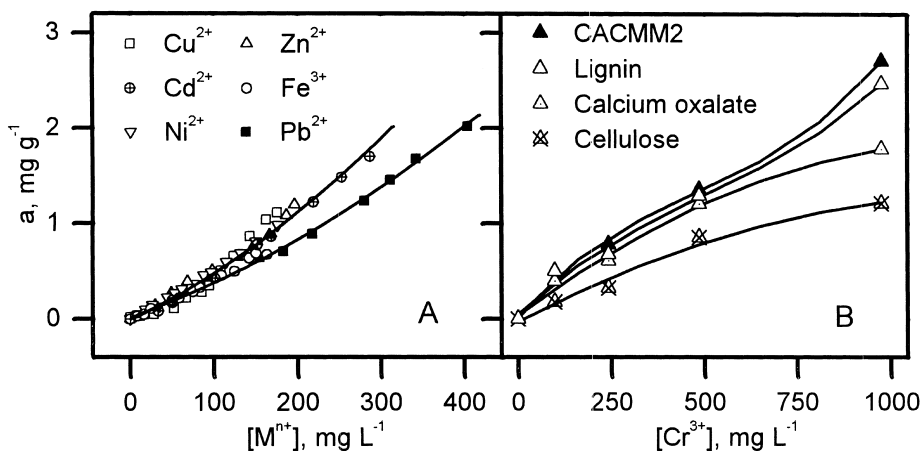


Fig. 3. Adsorption isotherms in the Henry region for the studied metallic ions on CACMM2 (A, B) and adsorption isotherms of Cr³⁺ aqueous solutions onto different solids related with the cactaceous powder CACMM2. Temperature: 23°C.

observed in Fig. 3B between the adsorption isotherms using CACMM2 and lignin. However, the curves corresponding to calcium oxalate and cellulose lie below and showed a different character. This set of curves depicted the relative ability of three materials to retain chromium and their possible contribution in the adsorption capacity of CACMM2.

It is known that in most of the natural soils hexavalent chromium is only adsorbed under acidic conditions, which were provided in the leaching solution of CACMM2 (pH 5.5). On the other hand metal finishing industrial wastes contain normally both Cr^{3+} and Cr^{6+} forms. Removal of hexavalent chromium in aqueous chromate solutions and in metal-finishing waste solutions (pH 4) was also investigated by using CACMM2 as adsorbent. Table 2 shows the removal efficiency of CACMM2 for Cr^{3+} and Cr^{6+} in comparison with other metallic ions in 100 mg l^{-1} solutions. Although chromium and zinc were removed to a lesser extent than copper, cadmium, iron and nickel; 20% removal of chromium was achieved. Besides that, we found that both trivalent and hexavalent chromium were removed when we tested the adsorption of chromate. This anion was removed 16% from a 100 mg CrO_4^{2-} l^{-1} solution prepared in deionized water. When chromate concentration was lower as was the case in the studied real metal finishing mixture, removal reached 83–89%. This means that the chromium concentration can be lowered in the used solution from 11 to 1.8 mg l^{-1} (84%), which is still above the recommended maximum level of 0.05 mg l^{-1} for chromium. However, it was found that the presence of many other components (wetting, emul-

sifying agents, organic and inorganic stabilisatory resins), in the metal finishing solution did not affect the removal efficiency of CACMM2.

3.3. Desorption study

The desorption degree of the studied ions (see Table 2) was very low and decreased as follows: copper (18%)>iron>chromium≈nickel≈zinc≈cadmium (0.2%). We did not attempt to increase desorption degree by varying pH or polarity of the desorption solvent, as the sensibility and stability of CACMM2 to these factors have not been determined. However, marked coloration of the CACMM2 powder was observed in some cases after adsorption and it remained after desorption.

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Table 2

Adsorption and desorption efficiency of CACMM2 for ions (100 mg l^{-1}) in deionised water solutions and of metal finishing chromate solution fresh (18 mg l^{-1}) and exhausted (11 mg l^{-1})

Adsorbate	% Adsorbed	% Desorbed
Cu^{2+}	96	18
Cd^{2+}	93	0.2
Fe^{3+}	79	3.2
Ni^{2+}	58	0.7
Cr^{+3}	20	1.5
Zn^{2+}	13	1.0
Chromate in deionised water solution	16	1.1
Chromate in fresh metal finishing solution	89	—
Chromate in used metal finishing solution	83	—

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