

A NOVEL CARBONATED CALCIUM ALUMINOSILICATE MATERIAL FOR THE REMOVAL OF METALS FROM AQUEOUS WASTE STREAMS

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ABSTRACT

Carbonated ordinary Portland cement (COPC) has been investigated as a potential sorbent for heavy metal ion species from concentrated aqueous waste streams. The affinity of nickel, lead, cadmium, copper, cobalt, zinc, molybdenum, strontium and cesium for COPC has been evaluated in this study. Equilibrium and kinetic aspects of metals sorption were also investigated. The following uptake capacities were obtained from sessile batch experiments in which 1 g of COPC was added to 250 cm³ single metal ion solutions at concentrations of 1000 ppm with respect to the metal ion: Cd – 170 mg/g; Pb – 170 mg/g; Zn – 141mg/g; Mo – 102 mg/g; Sr – 108 mg/g; Co – 65 mg/g; Cu - 60 mg/g; Ni – 59 mg/g; Cs – 36 mg/g. The results of this preliminary investigation indicate that this novel synthetic material demonstrates potential as a low-cost and readily available substrate for the removal and concentration of toxic and radioactive metals from industrial effluents.

INTRODUCTION

The anthropogenic impact of heavy metal pollution on the living environment results primarily from industrial and mining activities, transport, and the application of sewage sludge to land. Industrial effluents and leachate from landfill sites containing industrial by-products may contain a variety of toxic metals in high concentrations.

Generally applied methods for metals removal include precipitation, ultra-filtration, electrolytic processes, reverse osmosis, adsorption, solvent extraction and biotechnology. A range of materials including activated carbon, polymers, minerals, biomass, hydrated oxides and waste materials have been shown to be effective in the removal of metal species from metal-bearing solutions. Major problems regarding the application of the above mentioned sorbent materials are high cost, low sorption capacities and limited selectivity for a wide range of metals. Hence, there is an increasing demand for the development of inexpensive sorbents with high sorption capacities.

A range of single and multi-phase inorganic materials having silicon, aluminium, iron and calcium as principal constituents, for example, clays (1-7), zeolites (8-10), silica gel (11-14), aluminium and ferric oxides-hydroxides (12, 14-18), recycled materials and wastes (19-24) and carbonate minerals (21, 25-27) can be distinguished among other known sorbents. They are generally inexpensive, but exhibit limited sorption capacities for metal species. Moreover, the use of ashes and recycled wastes often causes secondary pollution of treated effluents.

The objective of the present study was to investigate a novel cost-effective inorganic sorbent, produced by carbonating ordinary Portland cement clinker, for heavy and radioactive metals removal from concentrated aqueous waste streams. The characterisation and sorption kinetics of COPC as a function of pH are reported in this paper.

SORBENT SYNTHESIS AND CHARACTERISATION

The carbonated ordinary Portland cement, COPC, used in this study, was produced by the reaction of 99.99% carbon dioxide gas at a pressure of 2 bar with ordinary Portland cement in the presence of water (at a water:cement ratio of 0.2). The composition of the ordinary Portland cement used in this investigation is listed in Table 1.

Table 1

% oxide content of ordinary Portland cement						
SiO	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	SO ₃	other
22	7	57	3	7	2	2

As a result of accelerated carbonation an activated reaction product with specific physical and chemical properties was obtained. Crystalline phases were identified using X-ray diffraction analysis (Siemens D5 100). Textural analysis was carried out on a Quantachrome Automated Gas Sorption System AS-6 and scanning electron microscope JEOL JSM-5310LV. COPC was found to be composed of an aluminosilicate framework, calcite and aragonite, (polymorphs of calcium carbonate). COPC does not retain hydraulic properties and remains essentially anhydrous. The specific surface areas of the material prior to and following reaction with carbon dioxide were 10.7 m² and 48.9 m², respectively. Ordinary Portland cement clinker was found to be non-porous whereas COPC exhibited funnel shaped pores of approximately 40 Angstroms in diameter.

Experimental

An investigation to assess the rate and efficacy of the sorption of heavy metal ion species by COPC was carried out as outlined below:

Cobalt, copper, molybdenum, lead, cadmium, zinc, nickel, cesium and strontium ion stock solutions (10 000 ppm) were prepared from analytical reagent grade nitrate salts. 1g of COPC was placed into 250 cm⁻³ polypropylene container to which was added 200 cm⁻³ single metal ion solution having an initial concentration of 1000 ppm. Control solutions containing metals without sorbent were also set up to account for ageing and sorption onto the surface of the containers. Sessile batch experiments were carried out in triplicate for each metal listed above. The supernatant liquor from centrifuged solutions were collected after 6, 24, 48, 72 and 120 hours contact time and analysed for Ca, Al, Si, Na, Mg, K and the relevant heavy metal. Metal analysis was conducted by inductively coupled plasma - optical adsorption analysis using an Iris simultaneous ICP-OES with the exception cesium which was determined by atomic adsorption spectrophotometry (Philips PYE UNICAM SP9-AAS).

To study the influence of pH on metal uptake by COPC a similar experiment was conducted for Mo, Cs, Ni, Co, Sr solutions having initial pH values that differed from those of the original metal nitrate solutions. Sodium hydroxide and hydrochloric acid were used for pH adjustment.

The addition of 200 cm⁻³ water to 1 g COPC causes partial dissolution of calcium carbonate, which elevates the pH to approximately 8.5. Hence, to estimate the contribution of metal hydroxide precipitation to the total concentration of metal ion species removed from solution at this pH a supplementary experiment was carried out in which the extent of metal hydroxide precipitation at pH 8.5 was measured in the absence of COPC.

RESULTS AND DISCUSSION

Kinetics of metal sorption by COPC

Analysis of control specimens indicated that 1-7% of metal species were sorbed by the internal surface of the polypropylene containers in which the batch experiments were conducted. These values were subtracted from the total uptake of metals.

The rates of uptake of metal species by COPC as functions of time are presented in Fig.1 and Fig. 2. Equilibrium uptake was not achieved for the specimens containing Mo(VI), Zn(II), Co(II), Ni(I) Sr(II), Cs(I) and Cu(II) following a contact time of 120 hours. Conversely, equilibrium was achieved for the systems containing Cd(II) and Pb(II) after 24 - 48 hours. In the latter cases the equilibrium times were comparable with those reported by Langella et al. for metal-clinoptilolite sessile batch systems in which equilibrium was achieved in three days (10). More commonly, researchers have selected batch sorption experiments in which the specimens are subjected to agitation or stirring. Equilibrium times reported for agitated systems tend to be in the order of a few hours (5 - 9, 11 -21). In addition, equilibrium times for the sorption onto porous substrates such as COPC can be extended due to the diffusion of metal species through the pore network.

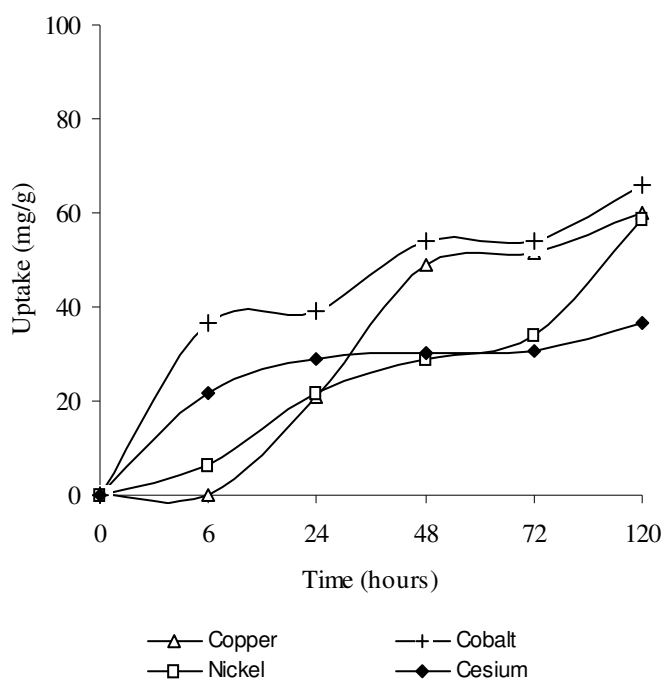


Fig.1 Equilibration sorption curves for Cu, Ni, Co,Cs by COPC (initial metal concentration 1000ppm)

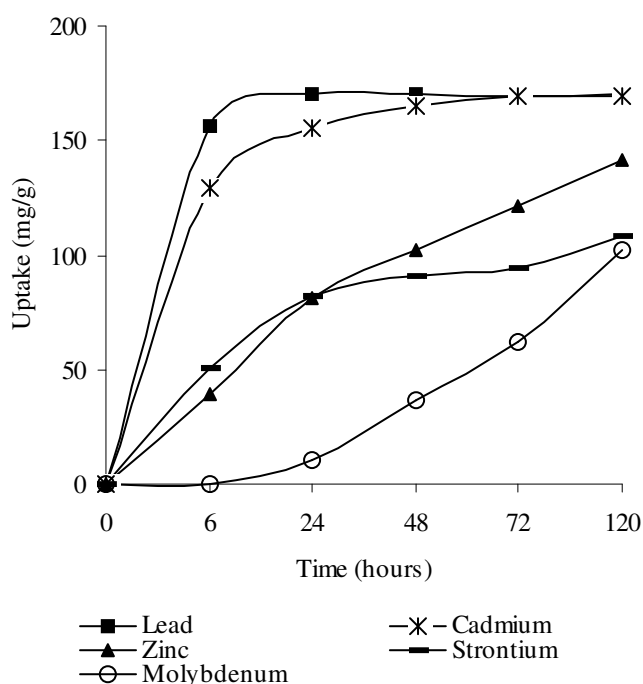


Fig.2 Equilibration sorption curves for Pb, Cd, Mo, Sr, Zn (initial metal concentration 1000ppm)

It should be noted that the equilibrium sorption time may be reduced by increasing the proportion of sorbent material relative to that of the solution volume and metal ion concentration. In this investigation, however, a relatively low solid/liquid ratio (1:200) was employed to observe the sorbent performance in unsaturated conditions.

Co, Ni, Cu, Sr and Cs sorption curves have sigmoidal form which indicates the development of new active sites for sorption during contact time. The development of new active sites during sorption processes may be attributed to a number of mechanisms including the dissolution of sorbent phases and solute multi-layer formation.

Mechanisms of metal sorption

The possible mechanisms for metal sorption by COPC are as follows:

1) In the pH range where the solubility of metals decreases, metals tend to form hydroxide and hydroxo-metal complexes (29). On the basis of free energy considerations, Reed and Cline (28) proposed that the formation of such complexes on the surface of oxide-type sorbents is favoured over the discrete precipitation of these species from solution. Other studies have shown that the formation of hydroxide and hydroxo-metal complexes on the surface of sorbents is irreversible at low pH values where discrete precipitates undergo re-dissolution (19-21).

The supplementary experiment carried out with metal solutions in the absence of COPC at pH 8.5 showed that only copper and lead were significantly precipitated (Fig. 3) indicating that, under the sessile experimental conditions, a proportion of discrete precipitate would be expected in addition to that sorbed to the surface of COPC. Conversely, significant proportions of discrete precipitate in the systems containing nickel, cobalt and zinc are less likely.

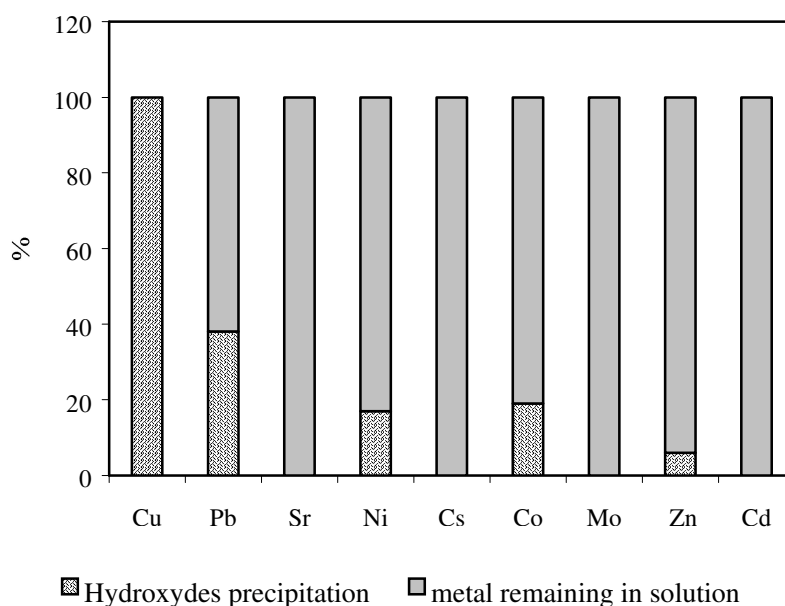


Fig.3 The extent of precipitation of metal species from 1000 ppm solutions at pH 8.5 in the absence of sorbent material

The above mentioned mechanism of pH-controlled precipitation is not applicable to cesium, strontium, molybdenum and cadmium in this instance.

2) Exchange and/or sorption of metals to carbonate minerals (calcite, aragonite, dolomite, magnesite, siderite etc.) cause an initial rapid uptake of metals from solution followed by the slower formation of complex precipitates on the surface of the minerals (30,31). The latter step is favoured when the adsorbed metal concentrations approach lattice limits which drives the diffusion of metals through a hydrated surface layer and promotes the formation of $(Me)_m(CO_3)_n$ bonds by a nucleation and precipitation mechanism.

Partition coefficients λ_{Me} ($\sim 10^{-3}$) applied to the fixation of metals by calcium carbonates indicate that the incorporation of metals investigated in this study (with the exception of cesium and strontium) into carbonate forms is significant (32).

$$\lambda_{Me} = \frac{X_{Me}[Ca]}{X_{Ca}[Me]}$$

Where, X_{Me} , and X_{Ca} are the mole fractions of the co-precipitated metal and calcium at the $CaCO_3$ surface, relatively, and $[Me]$ and $[Ca]$ are the solution concentrations of metal and calcium at equilibrium.

Curti (26) presents a detailed discussion on quantitative modelling of radionuclides, which are coprecipitated with calcite. On the basis of systematic correlations the partition coefficients for Cs and Sr were predicted. The partition coefficient of cesium is less than 10^{-2} and its ionic radius greatly exceeds that of calcium indicating that bonding of cesium to carbonate complexes is negligible. A similar argument applies to strontium ($\lambda_{Me} \sim 0.4$) for which isomorphous substitution for calcium is limited.

It is important to mention that two polymorphs of (aragonite and calcite) were detected by XRD in the COPC structure. The polymorphism exhibited by $CaCO_3$ is likely to influence sorbent efficiency, since some scientists have discovered different sorption affinity of metals for aragonite and calcite (33).

Adsorption of metals to COPC surface-carbonate complexes is a reversible process, however, these complexes are assumed to be more stable in acidic environments in comparison with the pH values afforded by pure carbonates.

3) Ion exchange is a commonly exploited mechanism of metals removal. It was observed that all metals investigated in this study were sorbed by COPC while Mg^{2+} , Na^+ , K^+ , Ca^{2+} were simultaneously released from the COPC matrix, as would be expected for an ion exchange reaction. The magnitude of exchanged alkali ions (Table 2) implies that ion exchange plays an important role in metals removal by COPC. High concentrations of released calcium are relevant to the process of metal-carbonate complex formation.

Table 2

Released ions, mg/g-sorbent			
Mg^{2+}	Na^+	Ca^{2+}	K^+
0-2	0-2	10-100	0-3

4) The aluminosilicate framework of COPC is potentially responsible for the sorption of metal species to active sites. Citations in the literature of sorption of heavy metal species to silica and aluminosilicate matrices are abundant (11-18).

Effect of initial pH

The Sr, Mo and Co removal capacity exhibited by COPC is dependent on the initial pH of the metal solutions (Fig. 4-7). Molybdenum was not removed at pH 8.5, whereas for strontium

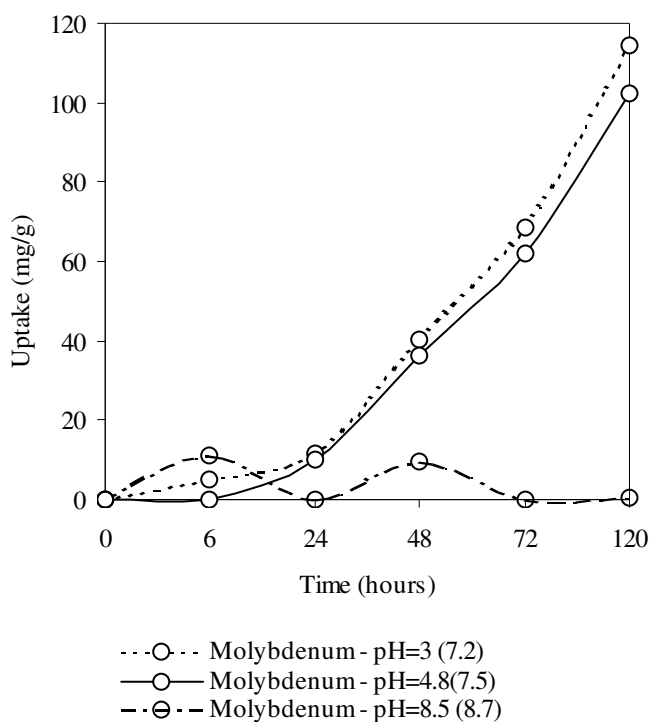


Fig.4 Equilibration sorption curves for Mo at different pH of initial metal solution. pH of final sorbent-metal systems are given in brackets

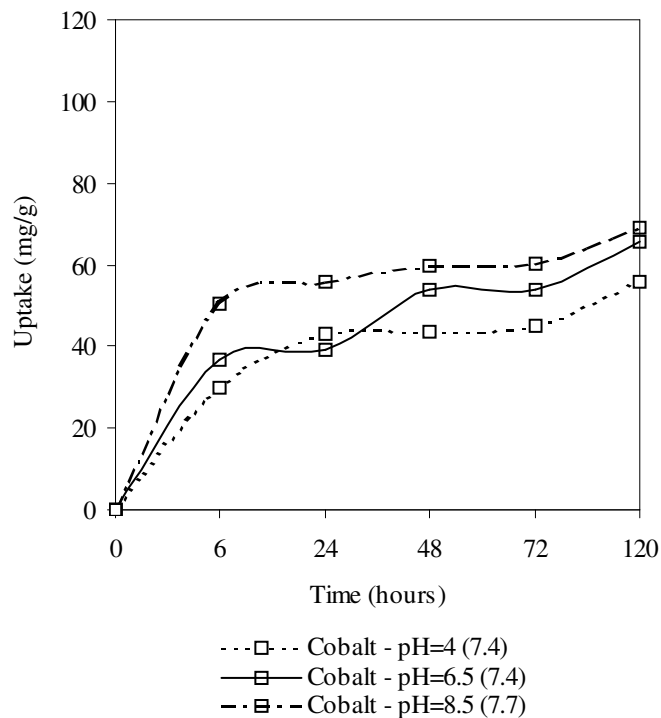
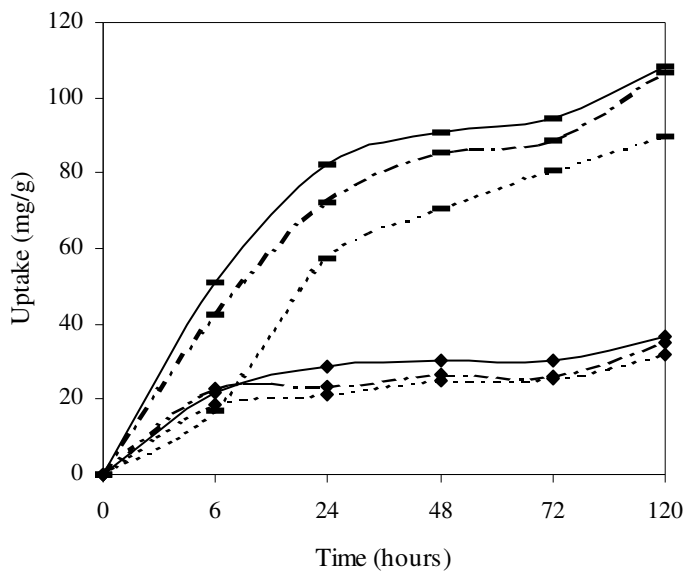


Fig.5 Equilibration sorption curves for Co at different pH of initial metal solution. pH of final sorbent-metal systems are given in brackets

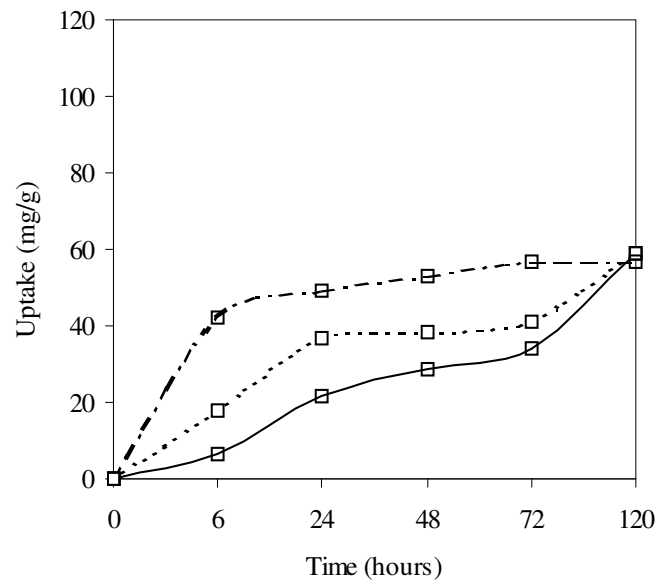
and cobalt uptake was lower at low pH. Such behaviour can be explained by formation of hydrolysed metal complexes in alkaline solution, for which favourable or unfavourable energetic conditions of immobilisation into the sorbent lattice may exist. In acidic environments hydrogen ions also compete with metals for exchange sites.

The Cs and Ni final uptake did not depend upon the initial pH of metal solutions. However, the sorption curve for nickel at pH 8.5 demonstrates that equilibrium is rapidly established and uptake is greater in comparison with that at pH 4 and 6.5 (the natural pH of 1000 ppm nickel nitrate solution). In this case we can assume that Ni (at pH 8.5) was primarily precipitated, whereas Ni at pH 4 and 6.5 could be removed by different sorption mechanisms.



--- Sr - pH=3 (7.8) — Sr - pH=5.3 (8.7)
 - - - Sr - pH=8.5 (8.7) - - - Cs - pH=8.5 (9.3)
 - - - Cs - pH=3 (8.5) — Cs - pH=5.3 (9.3)

Fig.6 Equilibration sorption curves for Cs and Sr at different pH of initial metal solution. pH of final sorbent-metal systems are given in brackets



- - - □ - - - Nickel - pH=4 (7.5)
 — □ — Nickel - pH=6.5 (7.6)
 - - □ - - Nickel - pH=8.5 (7.6)

Fig.7 Equilibration sorption curves for Ni at different pH of initial metal solution. pH of final sorbent-metal systems is given in brackets

CONCLUSIONS

The results of this preliminary investigation indicate that carbonated ordinary Portland cement possesses specific physical and chemical properties, which enable the removal of metal species from aqueous streams by a number of sorption mechanisms. COPC exhibited high sorption capacities for Pb, Cd > Zn > Sr > Mo and moderate capacities for Co > Cu > Ni > Cs. Relatively low concentrations of COPC - 1 g in 250 cm⁻³ 1000 ppm metal solutions - provided up to 90% removal efficiency.

The role of CaCO_3 and the presence of active sites on aluminosilicate surfaces to immobilise metals are considered to be important. Possible mechanisms of metal immobilisation by COPC have been discussed although more substantive evidence by further spectroscopic studies is required.

The prospects of used sorbent disposal/reuse are to be investigated. Results of leaching tests would indicate whether used COPC is a non-toxic sorbent suitable for disposal in open environment. Otherwise, it could be easily solidified to cementous pastes because of its appropriate structural and chemical properties. However, the low cost of the sorbent (£ 0.08 per kg) does not justify recycling options, unless the energy balance is favourable.

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