Hydrophilic hypercrosslinked polymers for remarkably efficient fluoride capture

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Fluoride contamination of groundwater is a significant issue in parts of the developing world. Excessive fluoride consumption can cause dental and skeletal fluorosis. The World Health Organisation (WHO) recommends a fluoride concentration in drinking water of ≤ 1.5 mg L^{-1}. Many forms of fluoride are highly labile and may readily leach from solid waste and contaminate groundwater. For example, spent potlining waste from the aluminium industry contains ~14% fluoride, of which $\leq 30\%$ is soluble in water. Uncontrolled landfill disposal for this waste is still commonplace in some countries. Ironically, fluoride is also becoming a scarce resource. Its parent mineral fluorspar (CaF_2) has < 35 years-worth of global reserves remaining (U.S. Geological Survey, 2015). There is an urgent need both for effective methods for defluoridation of water and processes for the capture of fluoride and its regeneration in a usable form. The established Nalgonda precipitation technique, practised in many rural, developing areas is economical, but ineffective at larger fluoride concentrations and higher pH. An alternative is adsorption of the fluoride on to a solid phase, but most low-cost sorbents suffer from low capacity, limiting their applied feasibility.

Hypercrosslinked polymers (HCPs) are composed entirely of light elements and synthesised in a one-pot process using cheap and readily-available starting materials. They exhibit very high accessible surface areas of >1000 m^2g^{-1}, as measured by N_2 adsorption. HCPs are therefore promising candidates for decontamination of aqueous waste-streams, although the majority of research so far has focussed on their applicability for gaseous adsorption (Lee *et al*., 2006). We have thus synthesised a small family of hydrophilic HCPs, which can be activated for defluoridation purposes by loading with calcium ions in a facile and repeatable single-step process. Two such polymers have been thoroughly characterised and assessed for their potential as sorbents for fluoride capture/storage and are presented in this work.

Experimental

Two hydrophilic hypercrosslinked polymer networks (HHCP1 and HHCP2) were synthesised from monomers 2,2-biphenol and bisphenol A, via Friedel-Crafts alkylation, using dimethoxymethane as a crosslinker. Synthesis followed the "knitting" technique, pioneered by Li *et al.* (2011). The polymers were loaded with calcium ions by contacting 1.0 g with 50 mL solution of $Ca(OH)_2$ in 1:1 deionised water and methanol (1.80 g L^{-1}). Samples were placed on an orbital shaker for 3 hours at 5°C, then washed with deionised water until the pH of the filtrate was neutral. The metal-loaded polymers HHCP1-Ca and HHCP2-Ca were dried in a vacuum oven for 8 hours at 40°C. The two-step synthesis is shown in Figure 1. Polymers, at various processing stages, were analysed by X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM). Surface areas were calculated via N_2 adsorption using the 5-point BET method. Ca-loading was determined by acid-digestion of solid samples, followed by inductively-coupled plasma (ICP) optical emission (ICP-OES) spectroscopy. Ion-exchange capacites of HHCP1 and HHCP2 were determined using the Fisher-Kunin back-titration method.
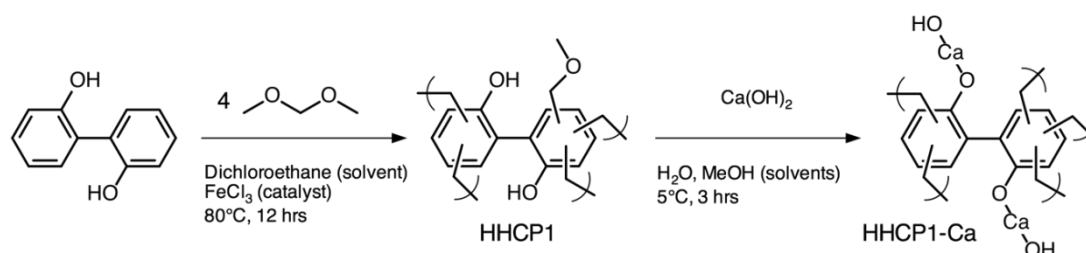

Figure 1. Scheme for the synthesis of HHCP1.

The fluoride uptake behaviour of HHCP1-Ca and HHCP2-Ca was studied by producing loading isotherms over a fluoride concentration range of 100 – 2000 mg L^{-1}, using 25 mg polymer in 2.5 mL NaF solution. Static kinetic experiments were performed over a 90-minute timeframe, using 1.0 g polymer in 100 mL NaF solution.

Results and discussion

An overview of the properties of HHCP1 and HHCP2 is found in Table 1. Both polymers took the form of brown powders and SEM images showed a morphology of rough, fused spheres, consistent with similar materials previous reported (Dawson *et al.*, 2012).

Table 1. Comparison of characteristics and fluoride uptake of HHCP1 and HHCP2.

Parameter	HHCP1	HHCP2
Yield (%)*	115	117
BET surface area (m^2 g^{-1})	440	455
Proton capacity (mmol g^{-1})	6.34	4.57
Ca loading (mg g^{-1})	89.9	57.4
Langmuir theoretical maximum fluoride capacity (mg g^{-1})[#]	109	74.6
Pseudo 2nd-order rate constant for fluoride uptake (g mg^{-1} min^{-1})[#]	7.15×10^{-3}	28.1×10^{-3}
Pseudo 2nd-order adsorption half-time (min)[#]	1.24	0.581

*Based on full crosslinking occurring at every available aromatic carbon.
[#]Measurements taken for the Ca-loaded versions of the polymers.

The acquired XPS data suggested that Ca-loading occurred via two mechanisms. The first was an ion-exchange process with the acidic phenolic protons and the second appeared to be precipitation of crystalline $CaCO_3$ within the micropores. We attribute this behaviour to the ability of HCPs to capture atmospheric CO_2 gas under ambient conditions (Wang *et al.*, 2015). This would then have formed HCO_3^- under the alkaline Ca-loading conditions and consequently the stable $CaCO_3$ salt, with the hydrophilic pores acting as nucleation sites. To the best of our knowledge, this behaviour in microporous polymers has not previously been recorded. Fluoride-capture was hence achieved by both hydroxyl/fluoride exchange by the organically-bound Ca centres and the formation of CaF_2 from the precipitated $CaCO_3$.

Both polymers displayed high capacities for fluoride ions and fast kinetics (Table 1), with HHCP2-Ca reaching equilibrium within 20 min. The shape of fluoride-loading isotherms varied between the two materials. HHCP1-Ca adsorption could be well-described by Temkin isotherm, indicating that the energy of binding changed as a function of surface coverage. HHCP2-Ca adsorption more closely followed the classical Langmuir model, suggesting monolayer adsorption only. The difference could be attributed to variations in the pore size distribution between the polymers, with HHCP1-Ca demonstrating a greater fraction of pores in the 1 nm range, which may be more conducive to CaF_2 formation. The greater fluoride capacity of HHCP1-Ca can be attributed to its superior Ca-loading capacity, which can be correlated to the acidity of the polymer functional group, as well as the pore characteristics. HHCP2-Ca has greater fluoride affinity at lower solution concentrations and may be better-suited to remediation of drinking water, whereas HHCP1-Ca would be more appropriate for fluoride capture and recycling from more concentrated industrial wastewater and leachate.

Both polymers could be successfully regenerated for further fluoride uptake by treatment with 1 M HNO_3, followed by repeating the Ca-loading procedure previously described. Regenerated polymers retained ~100% of the fluoride-loading capacity of the original materials.

Conclusions

Two hydrophilic, microporous polymers have been successfully synthesised and shown to have potential as novel and economical sorbents for fluoride. Although their functional groups were chemically identical, large variations in uptake behaviour were observed simply from the variation in the linkage between phenol rings in the original monomers. The extent of Ca-loading was increased by an unexpected $CaCO_3$ precipitation phenomenon and this in turn, improved the fluoride uptake potential of the materials to a level above nearly all other previously reported sorbents. Overall, we propose that metal-loaded hydrophilic HCPs have considerable potential in the fields of fluoride removal and recycling. These and similar materials clearly warrant further investigation from a chemical engineering perspective.

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