



Transition metal ion capture using functional mesoporous carbon made with 1,10-phenanthroline[☆]

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ABSTRACT

Functional mesoporous carbon has been built using 1,10-phenanthroline as the fundamental building block, resulting in a nanoporous, high surface area sorbent capable of selectively binding transition metal ions. This material had a specific surface area of 870 m²/g, an average pore size of about 30 Å, and contained as much as 8.2 wt% N. Under acidic conditions, where the 1,10-phenanthroline ligand is protonated, this material was found to be an effective anion exchange material for transition metal anions like PdCl₄²⁻ and H₂VO₄⁻. 1,10-Phenanthroline functionalized mesoporous carbon ("Phen-FMC") was found to have a high affinity for Cu(II), even down to a pH of 1. At pHs above 5, Phen-FMC was found to bind a variety of transition metal cations (e.g. Co(II), Ni(II), Zn(II), etc.) from filtered ground water, river water and seawater. Phen-FMC displayed rapid sorption kinetics with Co(II) in filtered river water, reaching equilibrium in less than an hour, and easily lowering the [Co(II)] to sub-ppb levels. Phen-FMC was found to be more effective for transition metal ion capture than ion-exchange resin or activated carbon.

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There has been a great deal of interest over the last decade in the design and synthesis of functional nanoporous materials for selective metal ion capture. Most of this work however has focused on the selective removal of "soft" transition metal ions, like Hg, Pb, Cd, Pt and Pd [1–9], from the lower right portion of the second and third row of the transition series. While this is understandable due to the toxicity of these heavy metals, today's environmental concerns are by no means limited to this select group of metal ions. There are hazards associated with the first row transition metals as well – for example, Cu and Ni are RCRA metals that are often associated with leachate from mining operations, ⁶⁰Co is a potential hazard from terrorist activities (i.e. a "dirty bomb"), Mn containing effluents have been associated with the pulp and paper industry, and V is known to contaminate fossil fuels and their products. The ability to selectively and efficiently remove these potentially problematic species from water supplies is something that can clearly have a beneficial impact on human health and quality of life.

The synthesis of templated mesoporous carbons has been an area of active research for the last decade [10–18]. Typically, these syntheses involve the use of a nanostructured template (commonly some form of mesoporous silica), which is then coated with an

organic precursor (e.g. sugar, monomer, polymer, etc.). This pre-assembly complex is then subjected to reaction conditions (e.g. acid catalysis) to polymerize the organic component and provide a stable silica-polymer composite, which is then subsequently subjected to carbonization at elevated temperatures (typically 800–900 °C). After carbonization, the silica template is generally removed by NaOH or HF digestion. Because of the high temperatures associated with the carbonization step, many types of organic functionality that are useful for binding metal ions (e.g. alcohols, amines, thiols, carboxylic acids, etc.) cannot survive the processing, and are therefore not readily integrated into these materials. Many of these templated mesoporous carbon syntheses have utilized precursors such as sugars [10], and phenolic resins [12], and since these feedstocks lack strong ligands, weak binding and poor specificity are anticipated in the metal binding chemistry of these materials.

Recently, we reported the synthesis of a templated mesoporous carbon built around the 1,10-phenanthroline unit (see Fig. 1) [18]. 1,10-Phenanthroline has been long established as an excellent ligand for typical transition metal cations [19]. 1,10-Phenanthroline functionalized mesoporous carbon (abbreviated hereafter as "Phen-FMC") was found to have a surface area of 870 m²/g, an average pore size of about 28–35 Å, and contain about 4.9–8.2 wt% N (depending on carbonization conditions) [19]. These materials were demonstrated to be capable of binding Ni(II), but under saturation conditions it was found that not all of the N functionality was available to bind transition metal ions [19].

[☆] Affectionately dedicated to the memory of my friend and mentor B. Patrick Sullivan, a learned practitioner of phen and bipy chemistry.

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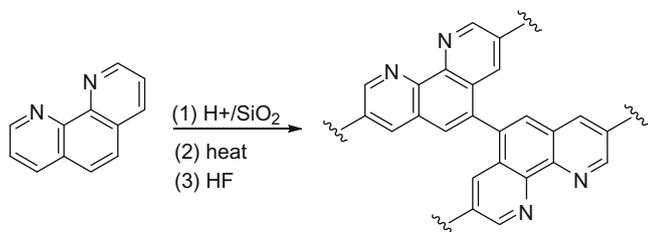


Fig. 1. Synthesis of the functional mesoporous carbon derived from 1,10-phenanthroline.

Being “born of fire” (i.e. the high temperatures necessary for carbonization), functional mesoporous carbons (FMCs) inherently have excellent thermal stability. FMCs have also been shown to have outstanding chemical stability. For example, sulfur-containing FMCs (S-FMC) built around the thiophene subunit have been shown to survive boiling for 24 h in a variety of pH buffers from pH 1 to pH 13 [16]. S-FMC was also shown to be a highly effective sorbent for “soft” heavy metal ions (e.g. Hg(II)) over this entire pH range [16]. We wanted to see if Phen-FMC was as effective for binding transition metal cations, for potential application in water treatment/purification, catalyst and precious metal recovery, medical diagnostic screening, dialysis and chelation therapy of radioactive Co from dirty bomb explosion, as well as processing of nuclear waste. In addition, recently there has been significant interest in integrating functional nanomaterials into electrochemical sensors to enhance the sensor’s sensitivity and selectivity [20–30]. Since the Phen-FMC backbone is potentially conductive, these materials could be very well-suited to electrochemical sensor applications. Phen-FMC is anticipated to be an effective sorbent for these transition metal separations and sensors, but first it is important to evaluate its affinity for transition metal ions in order to understand where it works and where it does not. The composition of the matrix can have a significant impact on the performance of a sorbent material due to the presence of competing ions, complexing anions, dissolved organic matter and suspended colloids. Therefore, it is important to evaluate potential sorbent materials in matrices that accurately represent those conditions under which it will likely be employed. For environmental remediation and environmental sampling, the importance of surface water to agriculture, industry and human health make river water, ground water and sea water logical choices for such testing. This communication summarizes our results in this area, with a special focus on transition metal ion capture in natural waters.

Experimental. *K_d measurements.* Batch metal sorption experiments were performed with natural waters, simulated acid wastes, and dialysate (PrismaSate[®], BGK4/2.5, Gambo Inc., Lakewood, CO). The natural waters include river water (Columbia River, Richland, WA), seawater (Sequim Bay, WA), and groundwater (Hanford, WA) which were used after filtering through a 0.45 μm cellulose membrane (MF-Millipore[™]). The transition metal ions tested were V⁵⁺, Mn²⁺, Co²⁺, Ni²⁺, Ru³⁺, Cu²⁺, Rh³⁺, and Pd²⁺ (from ICP standard solutions, Aldrich Co). Some of these metals form insoluble species in these natural waters, hence the waters were modified to contain 0.01 M NH₄Cl prior to adding the multi-component metals at 50 μg/L each. After 30 min of incubation, it was aliquoted into 4.9 mL volumes in a 20 mL polypropylene vial. The solution was then spiked with 0.1 mL of a suspension of solid sorbent and deionized distilled (DI) water at liquid per solid ratio (L/S in the unit of mL/g throughout) of 100. This resulted in a final L/S of 5000. The control was performed in the same fashion but without solid sorbent. The sample was then shaken for 2 h at 200 rpm on an orbital shaker. After 2 h, the solution was removed by filtering thru 0.20-μm syringe Nylon-membrane filters and the filtrate was kept in

2 vol.% HNO₃ prior to metal analysis. The concentrations in the control (no sorbent) and the test solutions (after being contacted with a sorbent material) were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA). For measuring the effect of solution pH on *K_d*, the filtered river water containing 0.01 M NH₄Cl was further adjusted with HCl and/or NH₄OH to the desired pH values prior to adding the metal ions. All batch experiments were performed in triplicates and the averaged values were reported.

Sorption capacity. The sorption capacity of sorbents for metal ions was measured in the same fashion as with the *K_d*, but only a single element (e.g. Co) was used and its concentration was varied in the solution until maximum sorption capacity was obtained. This was accomplished by using a large excess of metal ions to the number of binding sites on the sorbent materials (e.g. 0.1–2.5 mg/L of Co at L/S of 10,000 mL/g).

Sorption kinetics. The kinetics of metal sorption was performed in the same fashion as with the equilibrium studies except that 1 mL of well-mixed aliquot was removed and filtered at 0, 1, 2, 3, 5, 10, 30, 60 min, 2, 4, 8, and 24 h and the initial sample volume was increased to 50 mL to minimize the change in L/S.

Results and discussion. The distribution coefficient (*K_d*) is useful measure of a sorbent’s affinity for a specific analyte, under that particular set of conditions. *K_d* is a mass-weighted partition coefficient, as defined in Eq. (1) (with units of mL/g):

$$K_d = [(C_i - C_f)/C_f] \times (V/M) \quad (1)$$

where *C_i* and *C_f* are the initial and final concentrations of the analyte respectively (at equilibrium), *V* is the volume of solution in the experiment and *M* is the mass of sorbent used. The higher the *K_d* value, the more effective the sorbent is for capturing that metal ion. Generally speaking, a *K_d* value of 5000 and above is considered good, and a *K_d* value greater than 50,000 is considered excellent. The *K_d* values for Phen-FMC with a variety of transition metal ions in pH-adjusted river water are summarized in Table 1. Several trends are apparent from these data. First, it is clear that Phen-FMC has little affinity for most transition metal ions under acidic conditions, suggesting that once the metal ions are bound to the Phen-FMC, it should be possible to wash them off the sorbent with a simple acid wash. The p*K_a* for protonated 1,10-phenanthroline has been reported to be 4.35 [31], 4.96 [32] and 5.2 [19], and clearly the protonated ligand is not going to be able to chelate a metal cation as effectively as the neutral diamine. Indeed, even the Fe(phen)₃ complex is known to be unstable below a pH of 3 [32]. From the data in Table 1, there are two notable exceptions to this trend, Cu and Pd, both of which are captured effectively by Phen-FMC over a wide range of pHs, even acidic solutions. It has been recognized for over a century that Cu(II) has a high affinity for chelating diamines like ethylenediamine [33], forming very stable complexes. Likewise, 1,10-Phen also forms very stable complexes with Cu(II) [34]. This complex has been shown to be stable towards acidic conditions (it precipitates out of acidic solution, but the metal-ligand adduct remains intact [34]). The stability of this adduct appears to be preserved in the nanoporous architecture of the Phen-FMC, leading to this remarkable acid-side stability.

Another trend apparent in the data in Table 1 is that Pd(II) is bound very effectively, across a wide range of pHs, but especially so under acidic conditions. These experiments were carried out in the presence of excess chloride ion, and Pd(II) is known to form strong complexes with chloride ion [35], suggesting that the Pd(II) was most likely present as the PdCl₄²⁻ anion. Under acidic conditions, the Phen-FMC will be protonated, making an effective anion exchange material, and it appears that the protonated Phen-FMC is undergoing an anion exchange process with the PdCl₄²⁻ anion. What role (if any) hydrogen bonding might play in this complexation is not clear at this point. Such anion exchange with the PdCl₄²⁻

Table 1
Effect of solution pH on the distribution coefficient (K_d) of transition metals on Phen-FMC.

pH	Distribution coefficient, K_d (mL/g sorbent) ^a								
	Vanadate	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ru(III)	Rh(III)	Pd(II)
0.1	180	100	60	30	3600	0	450	420	1,800,000
1.0	0	0	0	0	17,000	770	160	130	930,000
2.0	390	1	40	150	150,000	700	550	340	1,100,000
3.7	63,000	21	980	2000	940,000	1300	1900	330	1,100,000
5.6	14,000	760	24,000	61,000	490,000	31,000	60,000	270	310,000
7.6	1100	14,000	1,700,000	420,000	390,000	570,000	NA ^b	14	25,000
8.1	1600	29,000	3,200,000	590,000	370,000	500,000	NA ^b	230	78,000

^a All measured in triplicates in pH-adjusted Columbia River water (filtered with 0.45 μ m cellulose ester membrane) and averaged; the water contained 0.01 M NH_4Cl and its pH was adjusted by either HCl or NH_4OH prior to adding metals; initial metal concentration of 50 $\mu\text{g/L}$ (each); L/S of 5000 mL/g.

^b Precipitation was observed.

anion has been observed before with other protonated nanoporous sorbents [36]. Under more alkaline conditions, where somewhat weaker Pd binding is observed, it appears that the neutral Phen ligand is displacing the Cl ligands to chelate the Pd(II) ion in the traditional manner.

The binding of vanadate anion is worthy of comment. Under strongly acidic conditions, vanadate exists as the hydrated $\text{VO}_2(\text{H}_2\text{O})_4^{2+}$ cation [37], and not surprisingly, the protonated Phen-FMC did not bind this species at all. In a narrow pH “window” between about 2.5 and 3.0, vanadate is present as the neutral H_3VO_4 [37]. Above a pH of ~ 3 , the aqueous chemistry of vanadium gets to be rather complex, but the predominant species are all anionic (e.g. H_2VO_4^- and various polynuclear oxometallate anions). At pHs between about 3 and 5, the protonated Phen-FMC was able to bind these anions very effectively via anion exchange. Under more alkaline conditions, where the Phen-FMC is neutral, this binding mechanism is no longer available, and the binding affinity for vanadate was observed to fall off significantly.

Other transition metal cations (e.g. Mn, Co, Zn, Ru) demonstrated increasing K_d with increasing pH, particularly above a pH of 5, consistent with the Phen ligand being deprotonated and being made available for metal cation chelation. Under near-neutral conditions, Phen-FMC appears to have good affinity for binding a variety of transition metal cations (e.g. Co, Ni, Cu and Zn). The reason for the poor capture of Rh is not entirely clear at this point, although we have observed similar behavior with iminodiacetic acid chelating sorbents [36]. A pair of control experiments was performed with Rh(III) in filtered river water which the 2 h contact time was extended to 20 h and the K_d was observed to increase 4.5-fold (from 200 to 900), indicating that for Rh(III) the system has not reached equilibrium in only 2 h, and that the apparent low K_d values for Rh(III) in Table 1 are due to slow binding kinetics.

Good efficacy at near neutral pH suggested that Phen-FMC should be a useful for binding transition metal ions in natural waters, so a series of experiments were performed to evaluate this hypothesis. The results of these experiments are summarized in Table 2. The general trend is that Phen-FMC seems to be very good at binding transition metal cations from groundwater and river water matrices at their native pH (around 7.5–8), with the excep-

tions of vanadate anion and Rh(III). Another trend apparent from the data in Table 2 is that K_d s in seawater are somewhat lower for the transition metal ions than those in groundwater or river water, however Phen-FMC is still effective at capturing these metal ions from seawater. Presumably this attenuation is due to the higher ionic content of the seawater, impacting the binding equilibrium. For example, with Pd(II) the much higher Cl concentration in seawater clearly has an impact on Pd(II) binding by inhibiting the displacement of Cl by the Phen. It should be noted that the dissolved organic matter inherent to these matrices did not seem to interfere significantly with the metal ion binding chemistry of the Phen-FMC.

A series of experiments were performed in which the performance of Phen-FMC was compared to that of ion-exchange resin (Chelex 100) and a typical activated carbon (Darco KB-B). The results of these experiments are summarized in Table 3. None of these sorbents are particularly effective under acidic conditions (except, as previously noted, for anions like PdCl_4^{2-}). Above pH 7, Phen-FMC shows much higher affinity for transition metal cations like Co, Ni and Pd than do the other sorbents. It is worth noting that Rh(III) is not bound by any of these sorbents, supporting the conclusion that slow Rh(III) ligand exchange is responsible for this poor binding efficiency. $\text{Rh}(\text{H}_2\text{O})_3\text{Cl}_3$ is reported to be very stable [38], and since these batch contacts were only carried out for only 2 h, there was not sufficient time for to achieve equilibrium for Rh(III) if ligand exchange was slow for any reason (e.g. as has been observed with thiol/Pt binding [8]). A control experiment (vide supra) confirmed that the binding kinetics for Rh(III) were much slower than observed with other metal ions (e.g. Co(II)), and that equilibrium had not been achieved in only 2 h for Rh(III).

The performance of Phen-FMC in dialysate is noteworthy. Phen-FMC is significantly better at capturing Co, Ni and Pd from dialysate than are either ion-exchange resins (Chelex 100) or activated carbon (Darco KB-B). This suggests that Phen-FMC might be useful for dialysis therapy for patients exposed to toxic doses of such metal ions (e.g. ^{60}Co from a “dirty bomb” explosion). It is also noteworthy that the organic constituents of dialysate do not seem to interfere with transition metal ion chelation in Phen-FMC. Similar nanoporous sorbents have shown exciting new possibilities as an

Table 2
The affinity (K_d) of transition metals on Phen-FMC in natural waters.

Matrix	pH	Distribution coefficient (K_d) (mL/g sorbent) ^a							
		Vanadate	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Rh(III)	Pd(II)
Columbia River water	7.6	1100	14,000	1,700,000	420,000	390,000	570,000	0	25,000
Hanford ground water	8.1	790	15,000	270,000	590,000	750,000	690,000	180	13,000
Sequim Bay seawater	7.7	120	1600	15,000	43,000	140,000	450,000	0	3900

^a All measured in triplicates in waters (filtered with 0.45 micron cellulose acetate membrane) and averaged; the water contained 0.01 M NH_4Cl ; initial metal concentration of 50 $\mu\text{g/L}$ (each); L/S of 5000 mL/g.

Table 3
Transition metal binding affinity (K_d) of Phen-FMC compared to ion-exchange resin and activated carbon, in a variety of matrices.

Sorbent	Matrix	pH	K_d (mL/g) ^a				
			Co(II)	Ni(II)	Ru(III)	Rh(III)	Pd(II)
Phen-FMC	0.01 M HCl	2.5	60	0	6100	6800	4,000,000
	0.01 M HNO ₃	2.5	90	130	3600	3700	4,300,000
	Dialysate	8.6	1,000,000	170,000	720	0	170,000
	Filtered river water	8.1	1,300,000	160,000	NA ^b	110	170,000
Chelex-100 (100–200 mesh)	0.01 M HCl	2.5	0	0	4600	140	140,000
	0.01 M HNO ₃	2.5	0	0	2500	350	52,000
	Dialysate	8.6	17,000	15,000	750	0	4900
	Filtered river water	8.3	18,000	13,000	NA ^b	0	2500
Darco KB-B (100 mesh)	0.01 M HCl	2.5	0	0	0	0	52,000
	0.01 M HNO ₃	2.5	0	0	320	0	41,000
	Dialysate	8.6	870	1400	840	0	13,000
	Filtered river water	8.0	2400	4000	NA ^b	0	42,000

^a Initial metal concentration of 50 µg/L (each); L/S of 5000 mL/g.

^b Precipitation observed.

orally delivered chelation therapy for the decorporation of radionuclides (e.g. Cs) [39]. Being chemically stable in both acidic and alkaline conditions, Phen-FMC may potentially be a viable candidate as an oral chelation therapy to capture toxic transition metals in the gastrointestinal tract (and may even be able to capture some metals like Pd and Cu in acidic environments such as found in the stomach).

The kinetics of Co(II) sorption from filtered river water are shown for Phen-FMC and activated carbon in Fig. 2. Phen-FMC was found to be both fast and efficient, reaching equilibrium in less than an hour, ultimately removing >99.8% of the Co(II) from the river water, quickly and easily getting down to sub-ppb levels. After only 2 min, Phen-FMC had removed more than 90% of Co(II) from filtered river water, and in 30 min >99%. In contrast, activated carbon still had not reached equilibrium after a day, at which point it had removed only ~82% of the Co(II). Clearly, the Phen-FMC is a much faster and more effective sorbent than is activated carbon for capturing Co(II) from filtered river water. No leaching of Co(II) back off of Phen-FMC was observed, even after extended exposure times.

Absorption isotherm data is presented in Fig. 3, comparing Phen-FMC and activated carbon (Darco KB-B). The Phen-FMC displayed Langmuirian behavior in the Co(II) adsorption isotherm, indicating interfacial monolayer adsorption of Co(II). The observed binding capacity (12.9 mg Co per g of sorbent) was substantially

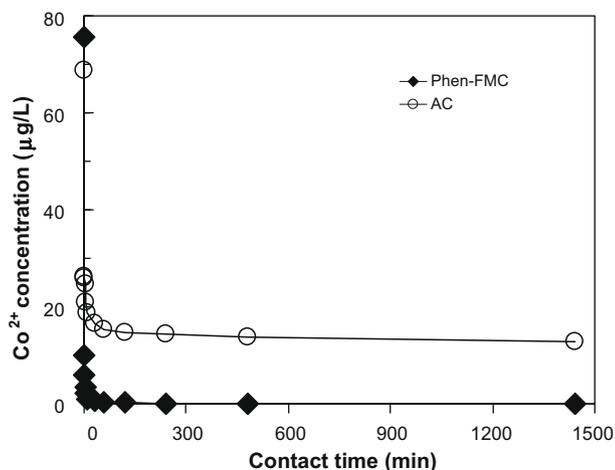


Fig. 2. Kinetics of Co adsorption on Phen-FMC and AC, measured in filtered river water (pH 8.0), L/S of 1000 mL/g.

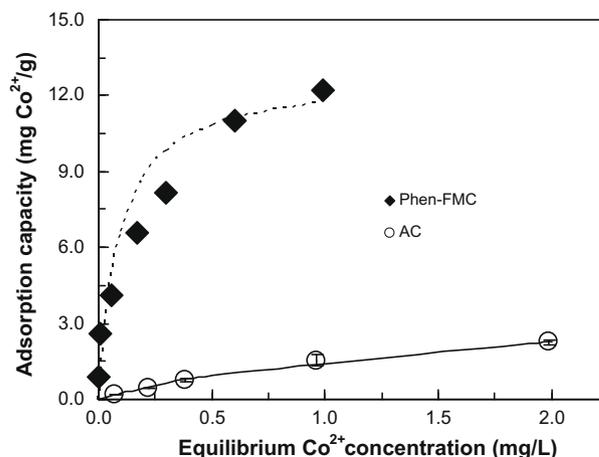


Fig. 3. Isotherms of Co(II) on Phen-FMC and unmodified activated carbon (AC), measured in filtered river water (pH 8.0); L/S of 10,000 mL/g; symbols represent data and lines represent Langmuir isotherm models.

higher than that observed for activated carbon (Darco KB-B, 4.0 mg/g).

Conclusions. Functional mesoporous carbons made using 1,10-phenanthroline (Phen-FMC) is an effective sorbent material for the selective capture of transition metal ions. The Phen ligand appears to be protonated below pHs of ~5, leading to a cationic center that can serve as an anion exchange site for transition metal anions, such as PdCl_4^{2-} and $\text{H}_2\text{VO}_4^{1-}$. Clearly, the primary driver behind this anion exchange is Coulombic, but there may be a contribution from hydrogen bonding as well. In spite of the competing protonation, Phen-FMC still binds Cu(II) ion effectively down to a pH of ~1. This appears to be due to the remarkable stability of the complex formed between the Cu(II) ion and the chelating diamine. Other transition metal cations studied appear to be bound by Phen-FMC at pHs above ~5, making this sorbent very well-suited for application to metal ion capture from natural waters. Phen-FMC was demonstrated to be effective for binding several common transition metal ions from filtered groundwater, filtered river water and filtered sea water, as well as dialysate, suggesting that it might be used to enhance dialysis therapy. Comparisons with other sorbents revealed that Phen-FMC has higher metal ion binding affinities than Chelex 100 and activated carbon, and is significantly faster and more effective at sorbing Co(II) than is activated carbon. Phen-FMC appears to have significant promise for transition metal ion capture and separations in aqueous media.

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