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Selective Removal of Copper(II) from Natural Waters by Nanoporous Sorbents Functionalized with Chelating Diamines

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Copper has been identified as a pollutant of concern by the U.S. Environmental Protection Agency (EPA) because of its widespread occurrence and toxic impact in the environment. Three nanoporous sorbents containing chelating diamine functionalities were evaluated for Cu^{2+} adsorption from natural waters: ethylenediamine functionalized self-assembled monolayers on mesoporous supports (EDA-SAMMS), ethylenediamine functionalized activated carbon (AC-CH_2-EDA), and 1,10-phenanthroline functionalized mesoporous carbon (Phen-FMC). The pH dependence of Cu^{2+} sorption, Cu^{2+} sorption capacities, rates, and selectivity of the sorbents were determined and compared with those of commercial sorbents (Chelex-100 ion-exchange resin and Darco KB-B activated carbon). All three chelating diamine sorbents showed excellent Cu^{2+} removal (∼95–99%) from river water and seawater over the pH range 6.0–8.0. EDA-SAMMS and AC-CH_2-EDA demonstrated rapid Cu^{2+} sorption kinetics (minutes) and good sorption capacities (26 and 17 mg Cu/g sorbent, respectively) in seawater, whereas Phen-FMC had excellent selectivity for Cu^{2+} over other metal ions (e.g., Ca^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+}) and was able to achieve Cu below the EPA recommended levels for river and sea waters.

Introduction

Copper has been identified as a pollutant of concern by the U.S. Environmental Protection Agency (EPA) because of its widespread occurrence and toxic impact in the environment. Copper is also one of the important trace transition metals found in the human body and many living organisms and is involved in redox processes of a number of biomolecules (*1, 2*). Copper is present in waste effluents generated by various industries (i.e., electroplating, wood, painting, textile, and paper industries), and can accumulate in the environment and food chain, especially in fish. Excess copper in the human body has been reportedly linked to serious health threats such as cellular or organ damage and Wilson's disease (*1, 2*). Recent reports present evidence that copper is one of the transition metals (along with zinc and iron) that play a role in Alzheimer's disease (*3–6*). Copper is believed to be involved in both the aggregation of amyloid-β protein (Aβ) and generation of oxidative stress in the patient's brain, which are key characteristics of Alzheimer's disease (*3–6*). Chelation therapy has been suggested as a promising therapeutic strategy for these diseases (*4, 7, 8*). Although copper is necessary for growth and reproduction of species living in many aquatic environments, levels just slightly above the required level are toxic to various life stages of these organisms. For example, abnormal embryo development has been reported in the blue mussel after exposure to seawater containing 10 ppb of copper (*9*). The dissolved cupric ion (Cu^{2+}) is believed to be more toxic than complexed, precipitated, and adsorbed forms of Cu^{2+} (*10*). Although copper discharge limits have been set at ≤1 ppm to avoid causing environmental problems, accumulation in natural waters is still a problem (*11, 12*). According to the 2000 Toxic Release Inventory (TRI), the release of total copper in the United States was over 690,000 tons/year (*13*), resulting in increased accumulation of Cu^{2+} in natural waters. In some areas, the concentration of Cu^{2+} has been reported to be as high as 50–80 ppb (*9*). To avoid significant toxic effects on aquatic ecosystems, a cost-effective method to remove excess Cu^{2+} from natural waters is needed.

Adsorption technologies have proven to be effective methods for removing various metal ions from aqueous solutions. Various porous sorbents with natural and chemically modified surfaces have been investigated for copper adsorption, including mesoporous silica (*14*), synthetic polymers (*15, 16*), magnetite and biomolecule based materials (*17–19*), and low cost natural materials (*20–22*). Among these sorbents, a number of sorbents have shown very high capacities (∼50–330 mg/g sorbent) for the removal of Cu^{2+} from aqueous solutions. However, these Cu sorption capacities have been measured in deionized water, a simple matrix that fails to account for the effects of metal ion speciation, complexation, competing ions, and fouling of the sorbent materials by biomolecules often encountered in the real waters.

This manuscript is a systematic comparison of three new classes of nanoporous sorbents materials, designed around chelating diamine functionality, and tailored for Cu sorption in complex real waters. The materials were built upon a scaffold of mesoporous silica, mesoporous carbon, or activated carbon. They are ethylenediamine functionalized activated carbon (AC-CH_2-EDA), ethylenediamine terminated self-assembled monolayers on mesoporous supports (EDA-SAMMS, SAMMS is a registered trademark of Battelle Memorial Institute), and 1,10-phenanthroline functionalized mesoporous carbon (Phen-FMC) for Cu^{2+} adsorption from river water and seawater. These materials are believed to be the best Cu binding materials among their classes. For a comparison purpose, a representative ion-exchange resin (Chelex-100) and unmodified activated carbon (Darco KB-B) were also studied. Our goal is to make the recommendation on the best Cu sorbent materials for removal Cu from natural waters or other similar matrices.

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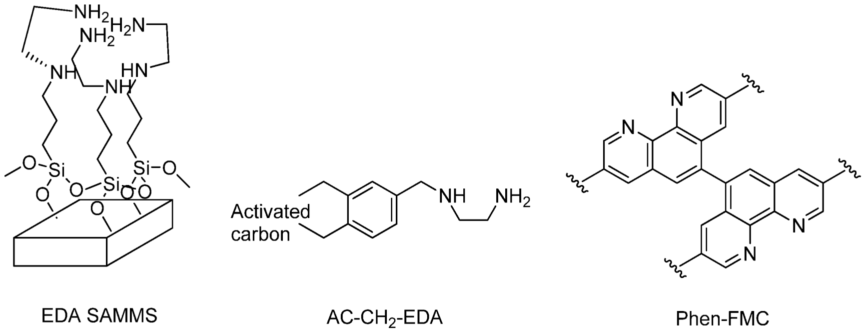

FIGURE 1. Solid phase sorbents built around chelating diamine ligands, designed for Cu capture: EDA-SAMMS, AC-CH_2-EDA, and Phen-FMC.

Experimental Procedures

Sorbent Synthesis. *Ethylenediamine Self-Assembled Monolayers on Mesoporous Silica (EDA- SAMMS).* The EDA-SAMMS was prepared as described previously (*23*). BET surface area analysis revealed a specific surface area of 105 m^2/g, and an average pore size of about 38 Å. Thermogravimetric analysis (TGA) revealed a functional density of ~2.6 mmol of EDA per gram of sorbent.

Ethylenediamine Modified Activated Carbon (AC-CH_2-EDA). The chloromethylated activated carbon (AC-CH_2-Cl) was made as described previously (*24*). BET surface area analysis revealed a specific surface area of 1200 m^2/g. Elemental analysis (Galbraith Laboratories) revealed 4.33 wt % N (which correlates to approximately 1.5 mmol EDA per gram of sorbent; indicating essentially quantitative displacement of the benzylic chloride by the EDA nucleophile).

1,10-Phenanthroline Functionalized Mesoporous Carbon (Phen-FMC). Phen-FMC was made as previously described (*25*). It had a specific surface area of 870 m^2/g, an average pore size of 35 Å, and 8.2 wt % N (which correlates to approximately 2.9 mmol Phen per gram of sorbent).

The chemical structures of the three sorbents are presented in Figure 1.

Batch Sorption Experiments. Batch metal sorption experiments were performed with river water (Columbia River, Richland, WA) and seawater (Sequim Bay, WA). Seawater normally contains (approximately) Ca^{2+} (400 ppm) and Mg^{2+} (1300 ppm) as major divalent cations; Na^+ (10 000 ppm) and K^+ (400 ppm) as major monovalent cations; and Cl^- (20 000 ppm), SO_4^{2-} (3000 ppm), and HCO_3^- (150 ppm) as major anions. River water contains (approximately) Ca^{2+} (20 ppm) and Mg^{2+} (5 ppm) as major divalent cations; Na^+ (10 ppm) and K^+ (1 ppm) as major monovalent cations; and HCO_3^- (70 ppm), SO_4^{2-} (20 ppm), Cl^- (10 ppm), and NO_3^- (1 ppm) as major anions. Both waters had a starting pH of 7.7−8.0. The waters were used after filtering through a 0.45-μm cellulose membrane (MF-Millipore). The metal ion solutions were prepared from ICP standard solutions, purchased from Aldrich. After adding the metal ion stock to natural waters, the solutions were incubated for 30 min. Then the sorbent was added to achieve desired liquid per solid ratio (L/S in mL/g). The sample was then shaken for 2 h (to ensure complete equilibration based on the kinetics data) at 200 rpm on an orbital shaker. After 2 h, the suspension was filtered with 0.45-μm Nylon-membrane syringe filters. The filtrate was kept in 2 vol. % HNO_3 prior to metal analysis using inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA). The metal concentrations in the control (no sorbent) with and without filtration were tested in order to check for precipitation of metal ions; reduced Cu concentrations in the filtrates from those in the nonfiltered solutions would indicate that Cu forms insoluble species that are collected on the filters. No precipitation of Cu was observed within the reported data. For studying the pH effect, the waters were adjusted with HNO_3 and/or NH_4OH to the desired pH (in our previous work added NH_3 was found to increase the solubility of transition metals in natural waters (*26*)). The solution pH was measured once prior to adding sorbents and again after the batch sorption was completed; the latter values were reported along with the sorption data. No significant pH change occurred, owing to the buffer properties of the natural waters and the very low solid per solution ratio (e.g., 0.2 g/L). More details of each batch study can be found in the Supporting Information. All batch experiments were performed in triplicate and the average values are reported.

Results and Discussion

EDA-SAMMS, AC-CH_2-EDA, and Phen-FMC were selected for Cu capture because they all contained chelating diamine, known to form a strong complex with Cu^{2+} (*27*). Although the synthesis and initial evaluation of these sorbents have recently been reported by our research group (e.g., *23, 24, 26*), none of the work has truly focused on copper capture. This is also the first time that the three sorbents are systemically compared in the same matrices with the goal of recommending the best sorbent materials for various Cu capture needs. The Cu^{2+} complexes formed with both EDA and Phen consist of 5-membered rings and are particularly stable. Both complexes involve σ-donation of the N lone pairs to the Cu^{2+}, and in the case of Phen, additional bond strength is obtained through π back-bonding from the populated d orbitals on Cu^{2+} to the π^* orbitals of the Phen aromatic ring system.

Effect of Solution pH and Matrices. The pH and ionic strength of a solution are known to play important roles in the binding of metal ions to the surface functional groups of sorbents. The solution pH affects the surface charges of functionalized sorbents and the speciation of metal ions, and hence the interactions between metal ions and sorbent surfaces. At pH below 6, cupric ion (Cu^{2+}) is a dominant and soluble form. In natural waters, Cu^{2+} may form complexes with common anions, including SO_4^{2-}, OH^-, PO_4^{3-}, HCO_3^-, NO_3^-, and CO_3^{2-}. In general, the precipitate formation depends on the Cu^{2+} concentration, other cation concentrations, types and concentrations of anions, temperature, and time to reach equilibrium. The most frequent Cu precipitates in natural waters are $Cu(OH)_2$ (K_{sp} of $10^{-19.3}$) and $Cu_2(OH)_2(CO_3)$; the latter forms at high bicarbonate content and high pH (e.g., in groundwater).

The effect of solution pH on Cu^{2+} binding affinity of a sorbent is presented by the distribution coefficient, K_d (mL/g), which is simply mass-weighted partition between Cu on the sorbent phase and Cu in bulk solution (see Supporting Information). The K_d values of Cu on the three sorbents measured in pH-adjusted river water and seawater (the latter inherently has much higher ionic strength) are shown in Figure 2A and B, respectively. The initial pH of the test solutions was varied from 1 to 8, and the solutions were monitored to ensure no

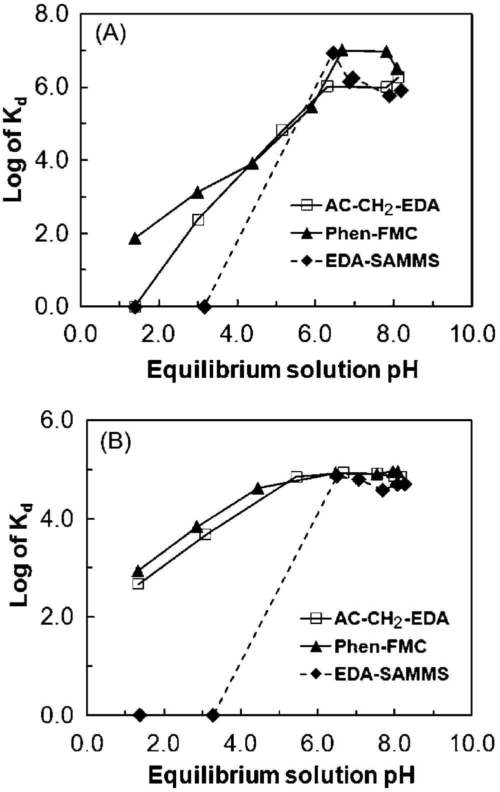

FIGURE 2. Effects of solution pH on Cu^{2+} adsorption by EDA-SAMMS, AC-CH$_2$-EDA, and Phen-FMC; initial Cu^{2+} concentration of ~100 ppb, L/S of 5000 mL/g in (A) pH-adjusted filtered river water, and (B) pH-adjusted filtered seawater.

significant precipitation of Cu^{2+} at high pH. Groundwater was not tested in this study, but had been tested in our other work and shown to be a matrix more similar to the river water than the seawater in terms of the matrix effect on the metal binding affinity of sorbent materials (*26, 28*).

Solution pH had a significant impact on the binding of Cu^{2+} to these chelating diamine sorbents in both river water and seawater. In river water, the K_d values of the three sorbent materials displayed similar trends, with sharply increased Cu^{2+} binding as the pH increased from pH 1.4 to 6.5 for AC-CH$_2$-EDA and Phen-FMC and from pH 3.0 to 6.5 for EDA-SAMMS. No Cu^{2+} adsorption was found for AC-CH$_2$-EDA at pH < 1.4 and for EDA-SAMMS at pH < 3.2, while moderate adsorption ($K_d \approx 100$) was found for Phen-FMC at pH of 1.4. About 100% of Cu removal was found for the three materials from pH 6.5 to 8.2 (which nicely encompasses natural waters and many wastes). At this pH range, the K_d values of the three materials in river water were as high as 10^6 (and 10^7 for Phen-FMC).

A similar K_d trend for Cu^{2+} adsorption was also found in seawater. In seawater, the AC-CH$_2$-EDA behaved very similar to the Phen-FMC; K_d of $\sim 10^3$ was found at pH as low as 1.4, increased as the pH increased to 6.0, and peaked between pH 6.0 and 8.2. Again, there was no Cu adsorption on EDA-SAMMS at pH < 3.2. The maximum K_d values in seawater (10^5) for the three sorbent materials were about 1 order of magnitude lower than those in river water (10^6-10^7). Seawater contains a variety of metals ions that may be competing for the binding sites on the sorbent interface, making it more difficult for Cu^{2+} to undergo chelation at the binding sites. Seawater also contains high concentrations of many counterions, which likely changes the speciation of the Cu ions, potentially hindering the chelation process. However, all three sorbents still offered excellent K_d values in the range of 10^5. Interestingly, in seawater, the maximum Cu^{2+} adsorptions by all three sorbents remained relatively constant over a wider pH range (pH 6.5−8.3 for EDA-SAMMS, and pH 4.5−8.2 for AC-CH$_2$-EDA and Phen-FMC), compared to those in river water.

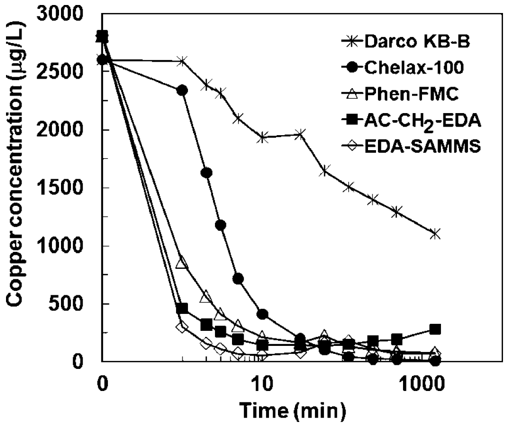

FIGURE 3. Adsorption kinetics of Cu^{2+} on EDA-SAMMS, AC-CH$_2$-EDA, Phen-FMC, Chelex-100, and Darco KB-B in seawater (pH ~7), L/S of 1000 mL/g.

Neutral amine groups (particularly chelating diamines) are more readily able to coordinate/chelate the Cu^{2+} than the ammonium salts (*29*). As a result, amine-based sorbents such as EDA-SAMMS and AC-CH$_2$-EDA tend to display lower Cu^{2+} sorption under acidic conditions than they do at higher pH (similar to a sorbent functionalized by diethylenetriamine (DETA) (*16*)). The precipitation of Cu^{2+} at high pH (>6.5 to 8.2) reported by others (*17, 22, 30*) was not observed in this work. This was presumably due to the much lower Cu^{2+} concentrations (~0.1 ppm) used in this work than those in the previous studies (~25−500 ppm), the higher chloride ions in seawater, and NH_3 used to increase the solution pH.

Sorption Kinetics. It is important that a sorbent material offer rapid sorption to minimize the time required to remove metal ions, particularly in natural waters where the Cu content is low, which means that a sorbent must overcome higher diffusion limitation for the transport of Cu^{2+} from the bulk solution to the sorbent interface, compared to wastes with high Cu content. Adsorption kinetics of the three nanoporous sorbents and two commercial sorbents were measured in seawater (pH ~7.0) with initial Cu conc ~2.8 ppm and L/S of 1000 mL/g. Figure 3 shows the residual Cu^{2+} concentration in seawater as a function of time that it was in contact with each sorbent (e.g., from 0 to 24 h, with several time points within the first 10 min in which equilibrium normally is reached). The adsorption kinetics of divalent metal ions on sorbent materials assuming chemisorption has often been described as pseudo-second-order (*31*). Herein, such a model could describe the Cu kinetics very well ($R^2 > 0.999$). Table 1 shows the pseudo-second-order kinetic rate constants of the sorbents, which are in the decreasing order of EDA-SAMMS > AC-CH$_2$-EDA > Phen-FMC > Chelex-100 > Darco KB-B.

The sorption rates of Cu^{2+} on all three sorbents were very rapid, and reached equilibrium within ~5 min. This rapid adsorption rate is directly owed to the rigid, open-pore structure of these sorbents and the ready accessibility of the chelating diamines inside the pore walls, making it easy for the Cu^{2+} to undergo chelation. On the other hand, the adsorption rates of Cu^{2+} on commercial sorbents were much slower, with Chelex-100 reaching equilibrium after 30 min, and Darco KB-B not reaching equilibrium even after 24 h. To achieve 95% of Cu^{2+} removal, it took EDA-SAMMS 3 min, AC-CH$_2$-EDA 10 min, and Phen-FMC 30 min, whereas it took Chelex-100 about 1 h. Darco KB-B was not able to achieve 95% Cu^{2+} removal even after 24 h. In addition to the suitable

TABLE 1. Pseudo-Second-Order Kinetics and Langmuir Adsorption Parameters of Cu(II) Measured in Seawater

	kinetics[a]		Langmuir isotherm[b]	
sorbent	k (g/mg/min)	q_e(mg Cu/g)	Q_{max}(mg/g)	K_L(L/mg)
EDA-SAMMS	11.52	2.74	26.9	26.6
AC-CH_2-EDA	2.92	2.68	17.1	7.7
Phen-FMC	1.03	2.67	10.3	22.7
Chelex-100	0.10	2.65	NA	NA
Darco KB-B	0.02	1.53	NA	NA

[a] By fitting data in Figure 3 to the linearized pseudo-second-order kinetics model, given by $t/q_t = 1/kq_e^2 + 1/q_e\ t$, where q_t is the adsorption capacity at a given time, t is the contact time (min), q_e is the estimated steady state adsorption capacity (mg/g), and k is the kinetic constant (mg/g/min). [b] By fitting data in Figure 4 to the linearized Langmuir model given by $C_e/Q_e = 1/K_L Q_{max} + 1/Q_{max}\ C_e$, where Q_e (mg/g) and C_e (mg/L) is the equilibrium concentration of Cu^{2+} on the sorbent and in solution, respectively, Q_{max} is the estimated maximum adsorption capacity (mg/g), and K_L (L/mg) is the Langmuir constant.

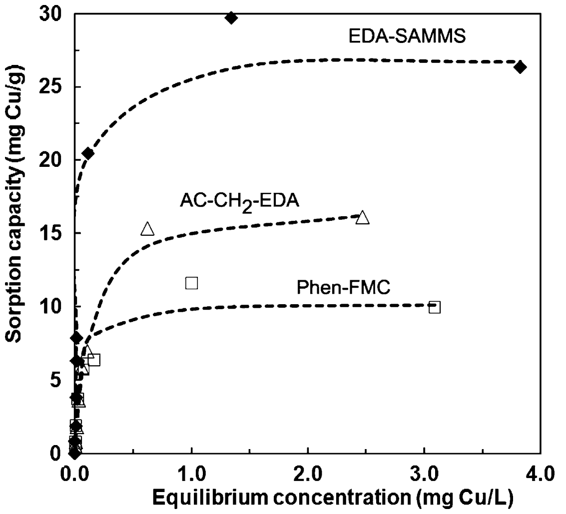

FIGURE 4. Adsorption isotherm of Cu^{2+} on EDA-SAMMS, AC-CH_2-EDA, and Phen-FMC in seawater (pH ~7.5–8.0), L/S of 10 000 mL/g, symbols represent data, and dashed lines represent Langmuir isotherm fitting.

structure of the three nanoporous sorbents, their faster kinetics may also be due to the more basic ligands of EDA and Phen over the carboxylate anions of the Chelex-100 and Darco KB-B. Among the ligands of the three nanoporous materials, EDA is more basic than Phen ligand, hence the EDA-SAMMS and AC-CH_2-EDA yielded more rapid Cu^{2+} removal rate than the Phen-FMC. Even though the kinetics were measured in seawater (i.e., a rather challenging matrix due to the high ionic strength), the adsorption rates of all three chelating diamine sorbents were still faster than those reported for other natural and chemically modified sorbents studied in DI water or buffer solutions (*18–22*). A noteworthy recent report addresses removal of Cu using polyethyleneimine nanoclusters immobilized on macroporous cation exchange resin (*32*), which indicates 2 h for the sorbent to reach equilibrium Cu sorption even at the starting Cu^{2+} of 100 mg/L. Hence it is remarkable that the three nanoporous sorbents reached equilibrium within minutes even in seawater and at much lower starting concentration of Cu^{2+} (~ 2.8 mg/L).

The data in Figure 3 also suggest the stability of the materials; one might conclude that during the 24 h contact with seawater containing Cu, only AC-CH_2-EDA, and not EDA-SAMMS nor Phen-FMC, appeared to somewhat lose its material stability resulting in slightly decrease of Cu uptake starting after 8 h of contact time (which may be due to fouling of the binding sites by seawater constituents). Nevertheless, the excellent stability of the three sorbents is derived from the strong covalent bonding between the organic functional groups and the substrates of the sorbents.

Sorption Isotherms. Adsorption isotherms of Cu on three nanoporous sorbents were measured in seawater at the initial Cu concn. of 0.05–4 mg/L and L/S of 10 000 mL/g. Two-hour period was selected for the contact time to ensure that equilibrium was reached (based on the kinetics study). As shown in Figure 4 (data in low concn. range can be seen in Figure S1 of Supporting Information), the isotherm data of all sorbents were best described by the Langmuir model (all with $R^2 > 0.995$) compared to the Freundlich model (*33*) (which does not predict saturation adsorption) and the Redlich–Peterson model (*34*) (having the exponent of ~1, reducing it to Langmuir model (*35*)). The Langmuir constants are summarized in Table 1. Langmuirian adsorption is indicative of a single monolayer adsorption of Cu that was uniformly distributed across the sorbent surface, not nucleating or precipitating out of solution (*35, 36*). The estimated maximum Cu^{2+} sorption capacities (Q_{max}) of EDA-SAMMS, AC-CH_2-EDA, and Phen-FMC were 26.9, 17.1, and 10.3 mg Cu/g sorbent, respectively (i.e., 0.16–0.42 mmol Cu/g sorbent), while their ligand loading capacities were determined to be 2.6 mmol of EDA/g, 1.5 mmol EDA/g, and 2.9 mmol Phen/g, respectively. This indicates that not all of the binding sites are utilized. Since these chelating diamines are all neutral ligands, the binding of metal cations results in charge accumulation at the sorbent interface. Since metal ion binding is an equilibrium process, this charge accumulation is likely to be playing a role in limiting the Cu^{2+} capacity of these sorbents. Once again, the more basic EDA ligand is seen to out-perform the less basic Phen ligand. What's more, the ordered array of EDA ligands in the EDA-SAMMS (which can allow for multiple metal–ligand interactions) is seen to provide a higher Cu^{2+} capacity than the AC-CH_2-EDA (where the EDA ligands are more disordered, making single metal–ligand interaction more likely). Considering that seawater was used for evaluating the capacities of these three sorbents, it is not surprising that the maximum capacities these sorbents were lower than those measured in buffer solutions (*16, 18, 19, 22, 35*). The Cu sorption capacities of the sorbents in less complex matrices like buffer solutions, river water, and groundwater are projected to be higher than these values reported for seawater.

Competing Divalent Cations. Natural waters and wastewaters may contain a number of other metals that may compete with Cu^{2+} for the binding sites of sorbent materials. To evaluate the impact of other metals on Cu^{2+} removal, competition experiments were carried out in seawater with ~100 ppb (each) of Cu^{2+} and other common transition metals (Fe^{2+}, Zn^{2+}, and Ni^{2+}, all of which may have good affinity for chelating diamine) and ~3 ppm of Ca^{2+} (the latter is inherent

TABLE 2. Selectivity of Sorbents toward the Cu^{2+} in Seawater (pH ~7.5); Initial Metal Concentration of 100 ppb Each and L/S Ratio of 5 g/L

	% removal				
metal ion	EDA-SAMMS	AC-CH_2-EDA	Phen-FMC	Chelex-100	Darco KB-B
Ca^{2+}	1	0	0	7	0
Fe^{2+}/Fe^{3+}	5	0	2	0	0
Ni^{2+}	91	41	14	91	0
Zn^{2+}	97	37	28	96	7
Cu^{2+}	97	97	99	97	80

TABLE 3. Cu^{2+} Removal from Natural Waters; Initial Cu^{2+} Concentration of ∼0.8 ppm and L/S Ratio of 1 g/L

	river water (pH ∼ 7.9)			seawater (pH ∼ 7.9)		
sorbent	initial Cu (ppm)	final Cu (ppb)	% removal	initial Cu (ppm)	final Cu (ppb)	% removal
EDA-SAMMS	0.75	6.3	99	0.79	15.3	98
AC-CH_2-EDA	0.75	10.7	99	0.79	25.1	97
Phen-FMC	0.75	0.1	100	0.79	4.6	99

in the seawater). The % removal of each metal is summarized in Table 2. Under these conditions, all sorbents could remove >97% of Cu^{2+} (with the exception of Darco KB-B, which removed only 80%). However, Phen-FMC had the greatest selectivity toward Cu^{2+}; it removed 99% of Cu^{2+}, with small competition from Ca^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+} (only 0, 2, 14, and 28% removal, respectively). In contrast, EDA-SAMMS and Chelex-100 both showed significant competition from $Ni^{2+}$and Zn^{2+} (at 91−97% removal). On AC-CH_2-EDA, the competition from Ni^{2+} and Zn^{2+} was moderate (∼ 40% removal) and that from Fe and Cu was negligible.

In river and sea waters containing ∼1 ppm of Cu^{2+} (an allowable discharge limit of Cu in waste effluents), at 1 g per liter, all three chelating diamine sorbents were able to remove 97−100% of Cu^{2+} (see Table 3). The most notable one is Phen-FMC, which could reduce Cu content down to 0.1 ppb in river water and 4.6 ppb in seawater, meeting the EPA's recommendation for preventing chronic and acute toxic effects of Cu on aquatic species in both fresh water (9 ppb for chronic, 13 ppb for acute) and salt water (3.1 ppb for chronic and 4.8 ppb for acute) (*11, 12*). Due to the fact that the materials are built based on a strong covalent bonding of organic functional groups and biologically benign silica or carbon substrates, they can potentially be used for purifying river and ground waters into drinking water.

Nanoporous sorbents built around a chelating diamine (e.g., EDA-SAMMS, AC-CH_2-EDA, and Phen-FMC) are highly efficient for Cu^{2+} removal from natural waters. The metal capture ability of a sorbent depends on both functionality (chemistry and loading of the organic groups) and substrates. Overall, their Cu^{2+} binding affinity was found to be Phen-FMC ≈ EDA-SAMMS > AC-CH_2-EDA > Chelex 100 ≫ Darco KB-B, while the selectivity toward Cu^{2+} was found to be Phen-FMC > AC-CH_2-EDA > EDA-SAMMS ≈ Chelex-100. Therefore, the three nanoporous sorbents can be chosen to best suit Cu capture needs; e.g., EDA-SAMMS is best if large capacity and rapid removal are needed; Phen-FMC is best if selective capture of Cu among other transition cations or if reducing low ppm levels of Cu to meet EPA recommended levels is needed; Phen-FMC and AC-CH_2-EDA are best if large working pH window is needed (from pH 1.4 and above).

Acknowledgments

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Supporting Information Available

Detailed experimental approaches for material synthesis and batch contact studies (e.g., adsorption kinetics, isotherms, and competition); equations for distribution coefficient and percent metal removal; and adsorption isotherm data for low Cu concentration range of Figure 4.This material is available free of charge via the Internet at http://pubs.acs.org.

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