Practical Materials for Heavy Metal Ion Chelation: Polyethylenimines
tailed onto The Surface of Porous Silica

*Sibel PÜRÇÜKLÜ, Burçin YILDIZ and Alpay TARALP
Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul – Turkey 34956 *presenting author

SUMMARY

Silica gel was incubated in a dilute solution of polyethylenimine reagent and dried at elevated temperature. Following incubation, an apparently irreversible, non-cova lent adsorption of the compound was verified. The hydrolysis products of trimethoxysilylpropyldiethylenetriamine reagent were also applied for comparison and afforded silica gel covalently attached onto the surface. Surface characterisation using Bruneau-Emet-Teller analyses indicated that accessible areas were reduced following modification. Colorimetric analyses using ninhydrin also showed that surfaces were overlaid with amino groups. Carbon-13 CP-MAS NMR analyses identified repeating units of ethylenediamine upon the silica surface and silicon-29 CP-MAS analyses identified the surface atom originally from trimethoxysilylpropyldiethylenetriamine. NMR attempted on polyethylenimine-overlaid silica revealed that silicon-29 spectra differed significantly from the native silica in terms of line shapes and peak intensities. Functionalized silica was used successfully to chelate metal ions such as chromium, copper, cobalt and nickel in aqueous media. Native surfaces in contrast displayed no ability to retain metal ions. While diethylenetriamine-based metal-ion scavengers have been reported, the polyethylenimine-based synthesis appears unprecedented. Both syntheses proved versatile, as active carbon surfaces were similarly tailored. Following glutaraldehyde activation, catalase enzyme was coupled thereon, affording to our knowledge the first covalently immobilized enzyme upon surface-tailored active carbon.

INTRODUCTION

As a result of heavy metal ion release from industrial wastewater, water pollution has become a serious problem. Waste streams contain solutions of metal ions, such as copper, nickel, cobalt and lead. Many reviews have discussed the removal of metal ions from aqueous solutions using approaches based upon adsorption, precipitation, solvent extraction and polymeric membranes. Recently, researchers have reported the application of trimethoxysilylpropyldiethylenetriamine-functionalized mesoporous silica gels for the removal of copper ion from jet fuel. In contrast to the other methods, the process relied on coordination bonding to the metals. Thus the approach featured advantages over those used in other methods because of its good selectivity for metal ions and sludge-free operation. It followed that a similar polyamine approach could be applied to metal ion-containing aqueous solutions using silica gel coated with polyethylenimines. The principle enabling polyethylenimine to readily transform large-pore silica in passing along its surface is that the bond formed, albeit non-covalent, is practically permanent due to the size of polyethylenimine and its numerous possible surface interactions. This approach therefore described a cost-effective alternative in comparison to the use of an organosilane precursor and was tested in the scavenging of aqueous heavy metal ions. For comparative purposes, a standard silica gel scavenger material was synthesized using trimethoxysilylpropyldiethylenetriamine out of aqueous alcohol solution. Again for comparison, polyethylenimine was coated onto active carbon, however, its performance could not be readily assessed visually. Thus the synthesis was extended to the glutaraldehyde stage and used to immobilize catalase. Colorimetric ninhydrin analysis, FTIR, BET, CP-MAS NMR methods were used to characterize the prepared adsorbents. The feasibility of these materials for application to heavy metal-ion removal from aqueous solutions will be assessed.

EXPERIMENTAL

Surface Modifications of Silica Gel

The control silica gel was incubated in solution consisting of 1%trimethoxysilylpropyldiethylenetriamine (TMSPDT), 94%isopropanol and 5% water, the liquid was suction filtered away, and the ncte was cured. Silica gels were also incubated in methanolic solution of the composition 6% polyethylenimine (PEI), of which three types were selected: (a) linear-low molecular weight (LLMW), (b) high-molecular weight, 50% aqueous (HMWA), and (c) high-molecular weight water-free (HMWF). The vessel was degassed in a dessicator (15min), forcing out air trapped in pockets and allowing chemicals to effectively permeate the matrix. The solutions were removed by suction filtration and the samples were cured overnight at 70°C.

Carbon-13 CP-MAS and Silicon-29 CP-MAS NMR analyses were performed to identify the surface-bound ethylenediamine and silicon atom originating from trimethoxysilylpropyldiethylenetriamine. Solutions of metal ions (0.5M CuSO4, CoCl2, FeSO4 and NiSO4) were passed through the modified silica gels in encouraging a coordination between ligand and metal ion.

Dried samples were tested using ninhydrin and BET as described previously.

Unlike the C-13 CP-MAS results of derivatized silica gel, the carbon signal background was so intense that any signal resulting from derivatization was masked (above, signals from native active carbon).
EXPERIMENTAL

A 5% aqueous solution of glutaraldehyde was added to the aminated active carbon and allowed to incubate 8h. Samples tested using molybdenum reagent no color into solution, indicating that the glutaraldehyde had blocked all accessible amino groups.

RESULTS AND DISCUSSION

Silicon-29 CP-MAS NMR spectra

The spectrum of native silica appears clean as anticipated, with exception to a peak carbon contamination of the probe, that ironically originated from the active carbon. PEI-incubated silica gel showed significant carbon resonances even after extensive washing had been performed. The data was consistent with that of a branched high-molecular weight structure.

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FT-IR Analysis of Active Carbon

Similar spectra were observed for native active carbon and some variants that were heated at 80°C (C). As noted in the spectra, FT-IR analyses were inherently poor. This limitation was due to the extraordinary mechanical processes included hydrogel bonding and multiple sodium bridging.

CONCLUSIONS

• The results herein indicate that chemical surface modifications of silica gel and active carbon were achieved by these methods.
• Chemically modified silica was very effective in adsorbing heavy metal ions such as Cu, Fe, Ni, and Co ions. Thus the polyethyleneimine-silica afforded describes a cost-effective support material that can be used to detoxify aqueous and organic solutions.
• Catalase describes the first reported enzyme that has been covalently immobilized to modified active carbon.