Түйін

Организмге улағыш заттардың әсерін ескере отырып пектинмен, табиғи жеміс-жидек толтырғыштармен, антиоксиданттық дәрумендермен, сонымен қатар селен және мырышпен байытылған қышқыл сүт негізде мамандандырылған өнімдер өңделген болатын

Summary

In view of the pathogenesis of toxic poisoning of the body of foreign substances have been developed specialized products to dairy-based, enriched with pectin, natural fruit fillings, antioxidant vitamins and selenium and zinc.

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NANOPOROUS SILICA POLYAMINE COMPOSITES FOR METAL ION CAPTURE FROM RICE HULL ASH

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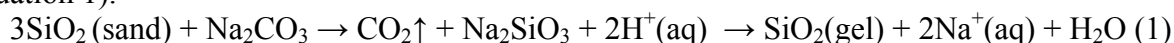
Abstract

Rice Hull Ash (**RHA**) was converted to amorphous silica gel using a modified version of published literature procedures. The gels were characterized by a comparison of their CPMAS ^{29}Si NMR and Scanning Electron Microscopy (SEM) images with commercial silica gels. The resulting gels were silanized with a 7.5:1 mixture of methyltrichlorosilane and chloropropyltrichlorosilane and then reacted with poly(allylamine) (**PAA**) to produce the silica polyamine composite (**SPC**) **BP-1**. The **BP-1** was then further modified with pyridine-2-carboxaldehyde to form the copper selective **SPC**, **CuSELECT.** This procedure follows that used to produce the commercialized version of these composite materials from commercially available amorphous silica gels. The composites were characterized by solid state NMR techniques, elemental analysis, SEM, porosimetry, and metal ion capacity and selectivity. The overall goal of the project was to determine the feasibility of using **RHA** to make **SPC**. The observed strengths and weaknesses of this approach are discussed.

Key words: silica gel**,** poly(amine) composite materials, metal ion capture, solid state NMR, rice hull ash

Introduction

Amorphous silica gels are most often manufactured commercially from sodium silicate solutions by precipitation with mineral acid. Sodium silicate is made in open hearth furnaces operating at temperatures in excess of 1300°C by the fusion of silicon dioxide with soda ash (equation 1).

$$3SiO_2 \text{ (sand)} + Na_2CO_3 \rightarrow CO_2\uparrow + Na_2SiO_3 + 2H^+(aq) \rightarrow SiO_2(gel) + 2Na^+(aq) + H_2O \text{ (1)}$$

Although the basic methods of this process are outlined by Iler[1,] the specifics of the modern commercial process remain the proprietary information of the manufacturers. Depending on the conditions of the precipitation and subsequent processing, silica gels with a range of porosities, surface areas and particle sizes can be produced.

An alternative to this high energy process is offered by the conversion of Rice Hull Ash (**RHA**) to silica gel. The ash is produced from the combustion of rice hulls obtained from rice grain processing for making heat and electricity at rice processing facilities. The ash consists mostly of silicates (~60-90%) and activated carbon. Because of the micro-structure of the silicates in the ash they can be dissolved in 1M NaOH at 100°C and then reprecipitated and dried to form amorphous silica gel.[2-5] Other low temperature processes for the dissolution of silica gel have also been reported but involve the use of organic reagents such as catechol or ethylene glycol.[6-8] Tetraalkyl ammonium hydroxides have also proven very useful for the dissolution of **RHA** and the resulting solutions provide an entry way into silsesquioxane-based nanomaterials.[9] The gels produced by these low temperature routes have proven to be useful for typical applications of silica gel particles such as drying agents and adsorbents.[2-5] Recently, it has been reported that the addition of

tetraethoxysilane (**TEOS**) to the hydrosol formed after dissolution of **RHA**, but before gelation, provides a silica gel with greater mechanical stability and improved porosity by increasing crosslinking between oligomers of silicic acid molecules, thus stabilizing the pores and decreasing the amount of cracking when the gel is dried.[10] These properties are critical to the synthesis of composite materials. In particular, we have been studying silica polyamine composites (**SPC**), inorganic-organic hybrid materials designed for selective ion capture for applications in the mining and environmental remediation industries.[11-22] This is a commercialized technology which would greatly benefit from a cheaper and more environmentally benign method of making silica gel.[23-26]

We report here our efforts to reproduce the **SPC** technology starting from **RHA** including a structural comparison of the materials made from **RHA** with the previously reported **SPC** materials, and testing of the final products for metal ion capture and selectivity. Although papers have been authored by researchers concerning the production of silica gel from **RHA** there has been little work done on the further conversion of these silica gels to composite materials.[2-5, 10] We have employed the method of Teng and Li for the conversion of **RHA** to silica because of the methods available in the literature their method seemed to provide a gel most adaptable to the **SPC** technology.[10]

The overall process for converting amorphous silica gel to an SPC is illustrated in Figure 1. First, the surface is silanized, using a mixture of methyltrichlorosilane and chloropropyltrichlorosilane in a 7.5:1 ratio which has been shown to give **SPCs** with the highest metal-loading capacity. The silanized surface is then reacted with poly(allylamine) (**PAA**) to form the **SPC** referred to herein as **BP-**1 and finally a metal selective ligand is grafted to the polymer via a C-N or amide bond (Figure 2). For the purposes of this study we converted **BP-1** to the copper selective composite **CuSelect** and compare its properties with the previously reported versions of this material.[25,26]

Experimental Materials

Rice hull ash was obtained from Riceland Inc, Stuttgart, Arkansas. Raw silica gel (25.4 nm average pore diameter, 150-250 and 350 -650 μm particle size, 450 m^2/g surface area) was obtained from INEOS, UK or from Qing Dao Mei Gow, Qing Dao, China. Sulfuric acid and NaOH were obtained from EMD. Reagent grade methanol was obtained in bulk from Fisher Scientific.. Poly(allylamine) (15000 MW) was obtained from Summit Chemicals Inc., Summit, NJ. Chloropropyltrichlorosilane and methyltrichlorosilane were obtained from Aldrich Chemicals and used as received. Tetramethoxysilane was obtained from Gelest Inc. and used as received. Copper (II) solutions (50 mmol/L) were prepared by dissolving 25 g of reagent grade $CuSO_4 \cdot 5H_2O$ in 2L of water, pH adjusted to pH 2 with 0.2 mol/dm^3 H_2SO_4. Deionized water was used throughout.

Methods

Solid state ^{13}C and ^{29}Si CPMAS NMR data were obtained on a Varian NMR systems NMR spectrometer at 125 MHz and 99.5 MHz respectively using ramped cross-polarization and SPINAL64 and TPPM decoupling techniques with sample spinning speeds of 10-15 kHz.

Scanning electron microscopy data was obtained through the University of Montana Electron Microscope Facility with a Hitachi S-4700 cold field emission SEM. Atomic Absorption Spectroscopy (AAS) experiments were done using a S2 FAA spectrometer manufactured by SOLAAR, UK. The samples were diluted using 2% HNO_3. An air/acetylene flame was used to analyze iron and copper. Inductively coupled plasma/atomic emission spectroscopy experiments (ICP-AES) were done using a Perkin-Elmer instrument using standards from Fisher Scientific Co.The dilutions were done in triplicate and standards were analyzed every ten samples for both methods. Elemental analyses were performed by Galbraith Laboratories, Knoxville TN. A calibrated ThermOrion model 250 portable pH meter was used for all pH measurements. Mercury porosimetry was performed using a Micromeritics Autopore 9500 available at Montana Tech University, Butte, MT.

Synthesis of Silica gel from Rice Hull ash

Rice Hull Ash (33.3 g) was added to 1 L NaOH (1M) and held at reflux for 90 minutes with overhead stirring. The solution was filtered through Whatman #41 ashless filter paper and allowed

to cool to room temperature. The carbon portion was discarded. The mineral content of the sodium silicate solution was determined to be 24.15 g/L sodium and 11.12 g/L silicon by ICP-AES. A 100 mL aliquot of the sodium silicate solution was titrated to pH 7 using 1 M H_2SO_4. The requisite amount of acid to titrate the remainder of the sodium silicate solution was determined and introduced using high speed magnetic stirring. A volume of tetraethoxysilane (**TEOS**) equivalent to 1/30 the volume of the solution (sodium silicate and acid solutions combined) was added concurrently. Stirring was continued until the solution took on a bluish hue, indicating that gelation was about to occur. After gelation occurred the gel was aged *in situ* for 24 hours. Two liters of reagent grade methanol were then added to the beaker, and exchanged after 12, 24, and 48 hours. After 72 hours the methanol was removed via aspiration and the gel broken, placed in a pyrex dish, and placed in an oven at 80°C until dry (24-36 h).

The dried gel was ground using a mortar and pestle and sieved to a particle size between 250 and 495 μm. The resulting powder was washed to remove residual salts using 1 M HCl and then dried again. The final yield of silica gel was 14.1 g.

Conversion of silica gel made from RHA to CuSelect

The silica gel made by the above procedure was converted to **BP-1** using previously published procedures.[12,13,16] The synthesis of **CuSelect** reported as described herein has not been previously published. **BP-1**, 5g in 20 mL chilled methanol was combined with 3.0 g (2.8 mmole) pyridine-2-carboxaldehyde and 3.9g (1.9 mmole) sodium triacetoxyborohydride was added. The mixture was allowed to stir for one hour in an ice bath, then an additional 3.9g (1.9mmole) of sodium triacetoxyborohydride was added. The ice bath was allowed to come to room temperature and stirred overnight. The material was washed with water, 5% H_2SO_4, water and finally with methanol. After drying at 50°C 3.2g of **CuSelect** was obtained. Elemental analyses for the composite materials at each stage of the synthesis are given in Table 1.

Measurement of the Copper batch Capacity for BP-1

Copper batch capacity for **BP-1** was determined using air/acetylene Atomic Absorption Spectroscopy (AAS). A 100 mg sample of **BP-1** was placed in a sample vial and 10 mL of 1.5 g/L $CuSO_4$ (intrinsic pH ~3.5) was introduced. The system was allowed to come to equilibrium overnight on a shaker and the concentration of Cu^{2+} remaining in solution was measured. From this, the amount of copper adsorbed by the composite was determined to be 102.9 mg/gram of composite.

Selectivity of Copper over Iron for the CuSelect made from RHA

The selectivity of the **CuSelect** made from **RHA** for copper over iron was tested by generating a breakthrough curve using a 5 mL column packed with 3.00 g of **CuSelect**. This was done by passing 300 mL of a solution containing 1000 ppm Cu(II) as $CuSO_4$ and 2600 ppm in Fe(III) as $Fe_2(SO_4)_3$ at a pH =1.5. The solution was passed through the column at a rate of 0.5 column volumes per minute. Aliquots were collected every 10 mL and subjected to AAS after 1000:1 dilution. The results are shown in Figure 6 and are discussed below. Based on prior breakthroughs of this type errors are estimated to be ±10% per graphed point.[12, 26]

Attrition testing of the silica made from RHA and comparison with commercial silica gel

The mechanical stability of the **RHA** silica (250-495 micron particle size) was tested by placing 10 g in a 25 mL Nalgene bottle and adding 10 mL of deionized water. The mixture was then rotated on a mechanically driven rotor bed for 24 h and then sieved to determine the mass of composite that had degraded below the starting particle size distribution. A sample of the commercial silica gel was then tested in an identical manner. The results are shown in Table 2 and are discussed below.

Results and discussion

Digestion of the **RHA** in 1M NaOH gave a solution that contained 24.15 g/L and 11.12 g/L of sodium and silicon respectively, as determined by ICP-AES. This corresponds to a mole ratio of Na: Si of 1.0:0.4, in reasonable agreement with principal species in solution being Na_2SiO_3 containing an excess of NaOH.

The method of Li and Wong[10] used for the conversion of the silicate solution to silica gel, reported surface areas and pore size distributions most similar to the gels used in the commercially produced SPC. Other methods were tried and gave gels with much lower surface areas, wider pore size distributions or poor mechanical strength.[2-4, 27-30] In most of these references these properties are not reported. The method of Li and Tang does involve the addition of a small amount of tetraethoxysilane (**TEOS**) to the sol prior to gelation. This apparently helps to develop polymerization of the silicate and gives a more porous yet mechanically more robust gel. The final yield of 14.1g after grinding to the desired particle size, washing and drying represents a 59 mole % recovery of the silicon in the starting silicate solution and 42 weight % recovery from the starting **RHA**. This does not take into account the losses during grinding and sieving. Also, based on the silicon concentration in the starting **RHA** solution, the RHA was approximately 73 % SiO_2. The elemental analysis of the gel showed a relatively low carbon content of 0.53% indicating that the initial separation of the silicon dioxide from the carbon in the **RHA** was fairly efficient (Table 1).

The scanning electron micrographs of the **RHA** derived silica and the commercial silica reveals a smoother morphology for the **RHA** silica surface (Figure 3). The RHA derived silica however, is covered with nanometer sized particulates even though the material was thoroughly washed, indicating that these particles may be chemically bound to the surface.

In order estimate the mechanical stability of the **RHA** derived silica relative to the commercial silica gel we used a recommended test which involved rotating 10 g samples of the silica gel suspended in 50 mL of water in a plastic container for 24 h on a rotating bearing bed.[31] The samples were then sieved to determine how much of the silica particle fragmented to below the low end of the starting particle size distribution of 250 -495μm. The results are summarized in Table 2. It can be seen that that the RHA derived silica had 8 times as much particle degradation as the commercial silica. Even with the use of TEOS the resulting gel, in our hands, is still not as mechanically strong as the commercially available silica made by the mineral route.

The silica gel was then converted to the **SPC**, **BP-1** by reaction with a 7.5:1 mixture of methyltrichlorosilane (**MTCS**): chloropropyltrichlorosilane (**CPTCS**) and then **PAA** according to published literature procedures.[12, 13, 16] Elemental analyses for the intermediate silanized gel, M-**CP** are given in Table 1. The 0.71% chlorine (2.0 mmol/g) observed is slightly lower than that observed for the corresponding M-**CP**-gel made from commercial silica gel of 0.98% (2.8 mmol/g) under the same conditions.[12] This suggests that the **MTCS** competes more effectively with the **CPTCS** on the **RHA** derived silica relative to the commercial gel.[12] This resulted in a lower polymer loading as evidenced by the smaller increases in %C and %N relative to the commercial silica (9.8% C and 2.56% N versus 13.8%C and 3.90%N). However, this does not result in a significant decrease in copper batch capacity for the composite which is 102.9 mg/g.

versus 90-105 mg/g for the **BP-1** made from commercial silica gel.[12] This is consistent with our.

previous observations that reducing the number of anchor points (less **CPTCS**) provides more free amines capable of metal coordination.[12, 32] In the case of the **RHA** derived silica the optimum ratio for copper coordination has an even higher ratio of **MTCS:CPTCS**. However, this conclusion must be considered tentative in light of the absence of accurate data for surface coverage which is based on the accepted standard number of surface hydroxyl groups being 8-9 ± 1 μmol/m^2.[33,34] It is possible that this number may be different for silica made from **RHA**. The residual % Cl of 0.13% indicates that 80% of the chlorine atoms on the propyl groups originally present on the surface reacted with the **PAA**, after adjustment for the 12% average weight gain for this reaction.[12]

Mercury porosimetry measurements on the **RHA** derived **BP-1** determined that the average pore diameter is 22.7 nm with a corresponding calculated surface area of 234.6 m^2/g (Figure 4). The average pore diameter of the commercially available gel was determined to be 25.4 nm and the surface area was 268.6 m^2/g m measured under the same conditions. The pore size distribution is almost identical to that of **BP-1** made from commercial silica gel (Figure 4). It should be pointed out that the higher surface area reported in the experimental is based on mercury intrusion measurements done at pressures up to 60,000 psi while those reported here only went up to 30,000

psi and exclude pore diameters of < 1 nm. The pore size distribution is illustrated in Figure 4 and is similar to that observed for **BP-1** made from commercial silica gel measured under identical conditions excluding pore diameters of <5 nm.[32]

Based on the prior investigations of silica and modified silica surfaces it is possible to make accurate assignments for the various siloxane species present in these types of materials (Figure 5).[32, 35-39] Although the different siloxane species present experience different degrees of cross polarization enhancement it is possible to make semi-quantitative conclusions across an analogous series of samples for related ^{29}Si resonances. Thus it can be seen that the starting **RHA** derived silica has the same ^{29}Si resonance profile as the commercial gel dominated by the mono-hydroxyl, surface Q_3 resonance. On silanization however very different ^{29}Si NMR spectra are observed. The **RHA** derived **M-CP** shows a much higher relative amount of T_3 sites relative to T_2 sites compared with the commercial gel. This means that more surface hydroxyls react per silane and suggest a higher density of surface hydroxyls. The higher ratio of T:Q sites in the RHA-M-CP relative to the commercial **M-CP** is more difficult to understand. It could be due to separation of bulk siloxane from the surface as a result of the lower mechanical stability of the **RHA-M-CP** or to a narrower wall thickness on average between pores in this sample. In any case this difference is not apparent after reaction of silanized material with **PAA** to give **BP-1**. Here we see a dramatic increase in T_3 sites for the commercial gel that we have previously observed and followed by ^{13}C NMR.[32] The basic **PAA** promotes further reaction of the silane hydroxyl with the surface hydroxyls. This is not observed with the **RHA BP-1** where an increase in $T_2:T_3$ ratio is seen. Although difficult to rationalize these differences clearly point to significant differences between to the two surfaces. This requires further investigation of the **RHA** derived materials with an emphasis on demonstrating reproducibility as has been done with the commercialized SPC.[40] The ultimate test of the feasibility of using the **RHA** derived silica for the proven applications of the **SPC** technology is the modification of the polyamine with a metal selective ligand. We chose conversion to the composite, **CuSelect** that has shown selectivity for copper over ferric ion at low pH.[40,41] This composite was previously reported as **CuWRAM** and was made by the reaction of **BP-1** with 2-picolyl chloride (Figure 2).[40,41] We have since developed a more convenient synthesis using a hydroamination procedure with 2-pyridine carboxaldehyde followed by reduction with sodium tris(acetoxy)borohydride (Figure 1). The **SPC** made by this route is now referred to as **CuSelect**. The reaction with the **RHA-BP-1** was conducted under the same conditions as the commercially produced **CuSelect**. Elemental analysis show a significant increase in %C and %N and the % increase in N can be used to estimate the degree of ligand modification of the **BP-1** after correction for the average 12% increase in mass observed for this reaction (Table 1).[40,41] This analysis gives a ligand loading of 0.56 mmol/g and a polymer nitrogen loading of 1.59 mmol/g. Thus about 35% of the available polymer amines are modified to give the desired picolyl ligand.[40-41] Proof of the loading of the pyridine ring comes from the solid state CPMAS ^{13}C NMR which shows the expected aromatic pyridine resonances at ~163 ppm as well the expected resonances due to the silane methyl, silane propyl and the methylene protons associated with PAA (Figure 6).[12, 32] These shifts agree well with our previous SS NMR data for the **CuWRAM** made by the previous method, but the lower polymer loading realized with the RHA **BP-1** leads to lower signal to noise for the aromatic and polymer resonances relative to the silane resonances.[41]

The selectivity of the **RHA-CuSelect** is clearly demonstrated by the breakthrough test illustrated in Figure 7. The more concentrated ferric ion reaches the feed concentration after 20 mL have been fed through the column. The feed concentration of the cupric ion is not attained until 130 mL have been passed through the column. From the data on this graph we can estimate that the selectivity for cupric over ferric ion is approximately 11:1. This selectivity is not as high as that previously reported (>50:1) but the particle size used here was 250-495 μm (commercial **CuSelect** now uses this particle size range in the manufacture of **CuSelect**) as opposed to the prior work which used 150-250 μm at same feed rate of 0.5 column volumes/min.[40-41] The observed selectivity under the reported conditions is sufficient for this proof of concept study.

Conclusions

Starting from the available waste product **RHA** we have been able to demonstrate that the resulting silica gel can be used to produce a commercially utilized composite material, **CuSelect**. However, mechanical stability is not nearly that of the commercial product and the spectroscopic studies reported here suggest that there are significant differences in the surface features and behavior of the **RHA** derived materials. Nonetheless this work represents a good start and has defined the problems associated with using RHA as a starting point for composite materials in general. What lies ahead are detailed studies for improving mechanical strength by modifying the procedure for converting the RHA to silica used.[10] One possibility is the use tetramethoxysilane (**TMOS**) instead of **TEOS** as we have found that this crosslinking agent is more reactive.[32] It is anticipated that improving mechanical stability will narrow the gap in performance between the **RHA** derived and commercially produced **SPC** and perhaps elucidate some the unusual surface features reported here as measured by solid state CPMAS ^{29}Si NMR.

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Table 1 - Elemental analyses for the silica gel from RHA and the SPC

Material	C	H	N	Halogens
Gel	0.53%	1.14%	<0.50%	0.02%
CP-gel	2.73%	1.00%	<0.50%	0.71%
BP-1	9.82%	2.50%	2.56%	0.13%
Cu-Select	16.84%	3.03%	3.73%	0.10%

Table 2 - Results of Particle Attrition Testing[a]

Material	>250μm	<250μm	%Loss
RHA	8.81g	0.80g%	8.35%
Commercial Gel	9.53g	0.11g	1.2%

Captions to Figures
1. Schematic diagram of the synthesis of the silica polyamine composites BP-1 and CuSelect.
2. Ligand modifiers covalently bound to the silica polyamine composites
3. SEM images of a)RHA derived silica, b) commercial silica (Qing Dao Mai Gow)
4. Mercury intrusion versus pore diameter for RHA derived BP-1 (R) overlayed with BP-1 made from commercial silica gel (Q) (both scales are logarithmic).
5. CPMAS ^{29}Si NMR comparing the RHA derived silica, silanized silica (CP), and PAA composite BP-1 with analogous materials made from commercial silica gel (M-CP refers to the fact that these materials were made with a 7.5:1 mixture of MTCS and CPTCS).
6. Solid state CPMAS ^{13}C NMR of RHA-CuSelect (SiPr stands for the propyl group attached to the silane.
7. Breakthrough curve for CuSelect using a solution containing 2600 ppm ferric ion and 1000 ppm Cupric ion at pH =1.5
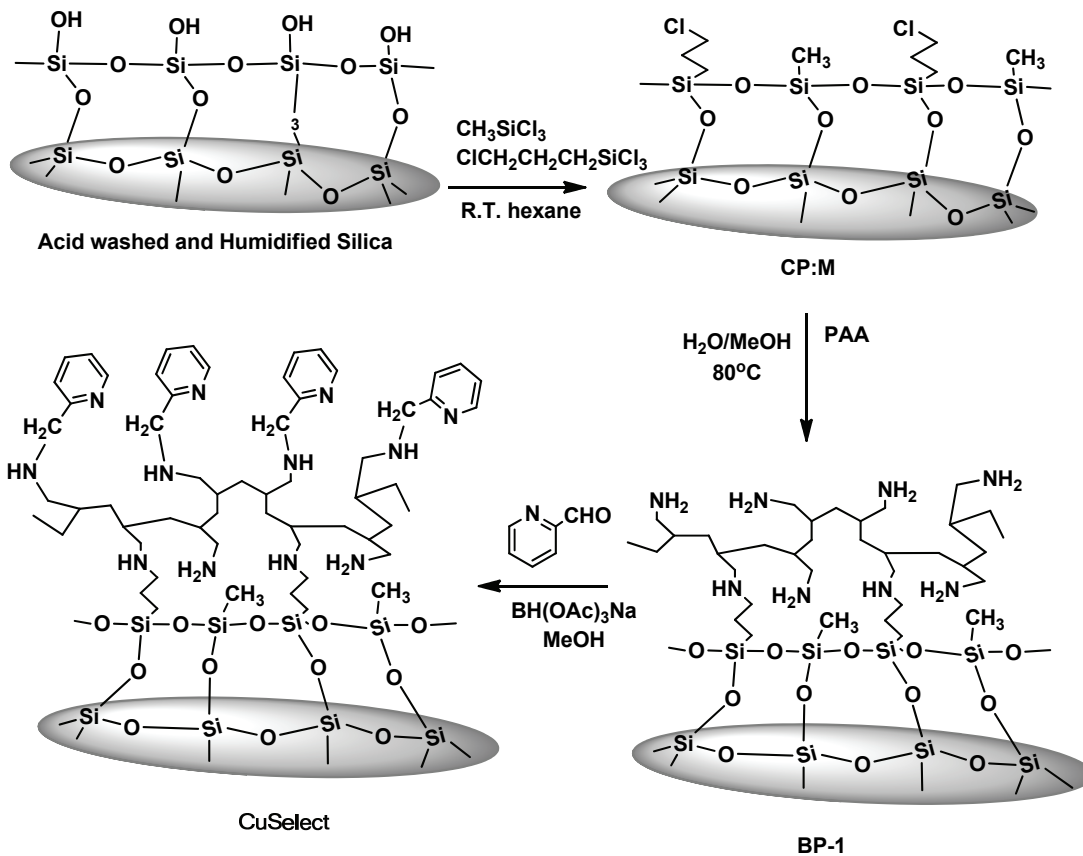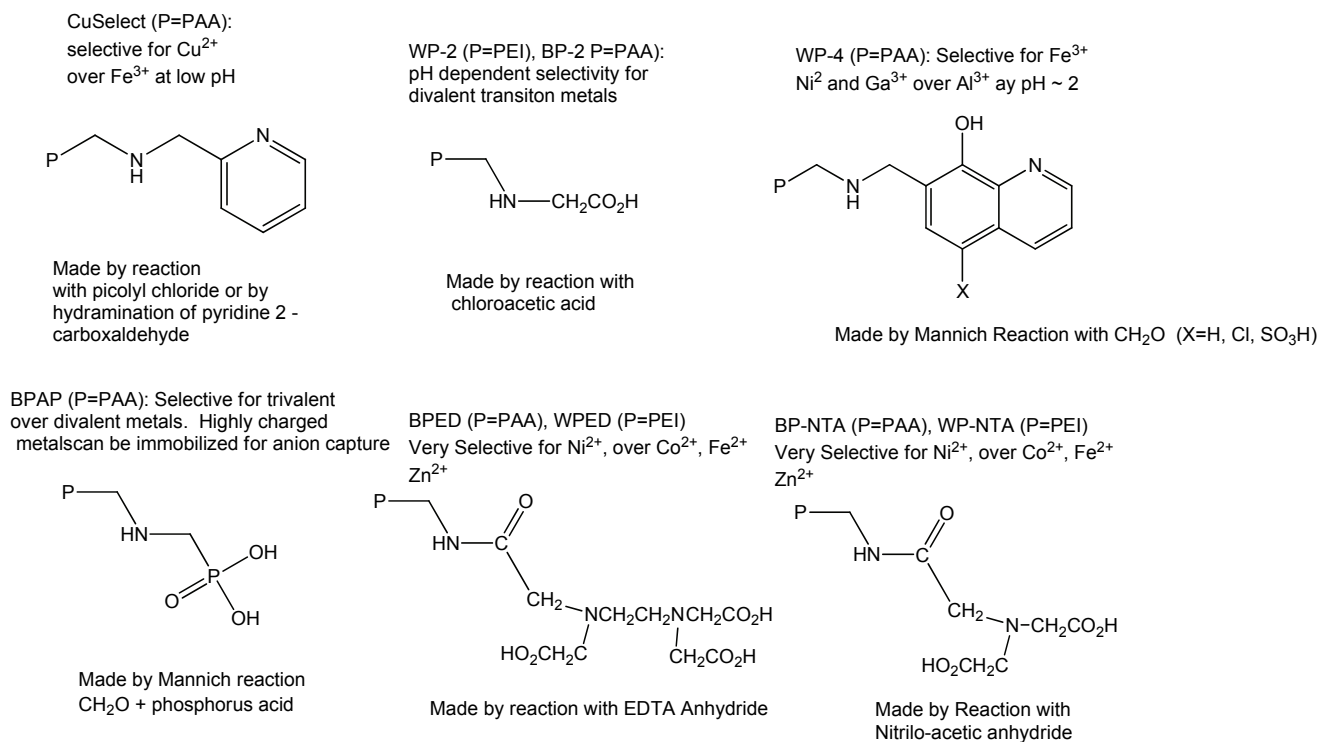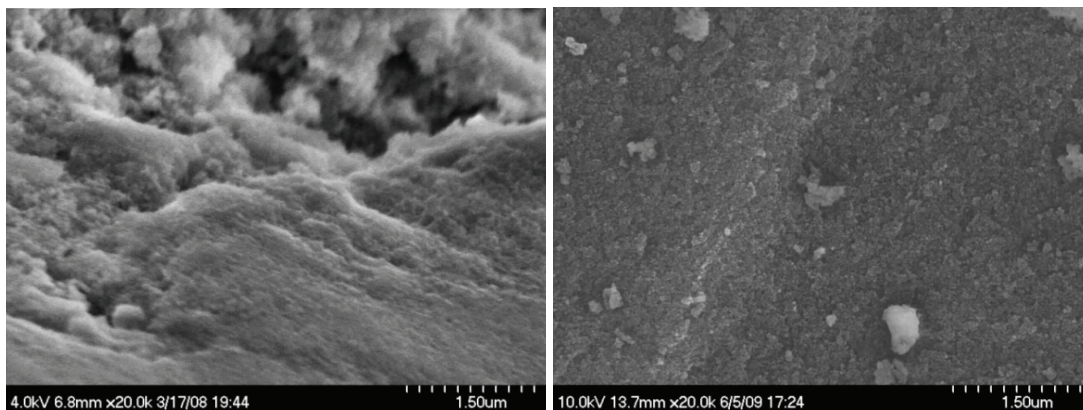
Figure 1

CuSelect (P=PAA):
selective for Cu^{2+}
over Fe^{3+} at low pH

Made by reaction
with picolyl chloride or by
hydramination of pyridine 2 -
carboxaldehyde

WP-2 (P=PEI), BP-2 P=PAA):
pH dependent selectivity for
divalent transiton metals

Made by reaction with
chloroacetic acid

WP-4 (P=PAA): Selective for Fe^{3+}
Ni^2 and Ga^{3+} over Al^{3+} ay pH ~ 2

Made by Mannich Reaction with CH_2O (X=H, Cl, SO_3H)

BPAP (P=PAA): Selective for trivalent
over divalent metals. Highly charged
metalscan be immobilized for anion capture

Made by Mannich reaction
CH_2O + phosphorus acid

BPED (P=PAA), WPED (P=PEI)
Very Selective for Ni^{2+}, over Co^{2+}, Fe^{2+}
Zn^{2+}

Made by reaction with EDTA Anhydride

BP-NTA (P=PAA), WP-NTA (P=PEI)
Very Selective for Ni^{2+}, over Co^{2+}, Fe^{2+}
Zn^{2+}

Made by Reaction with
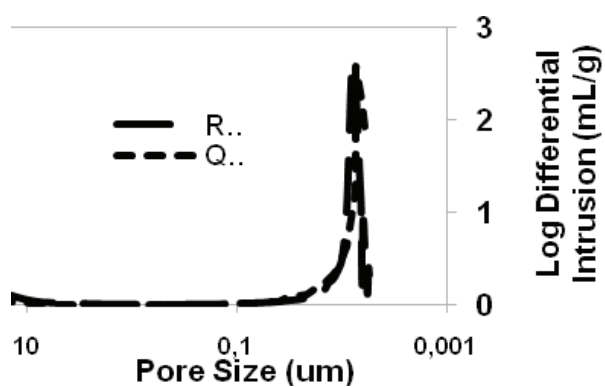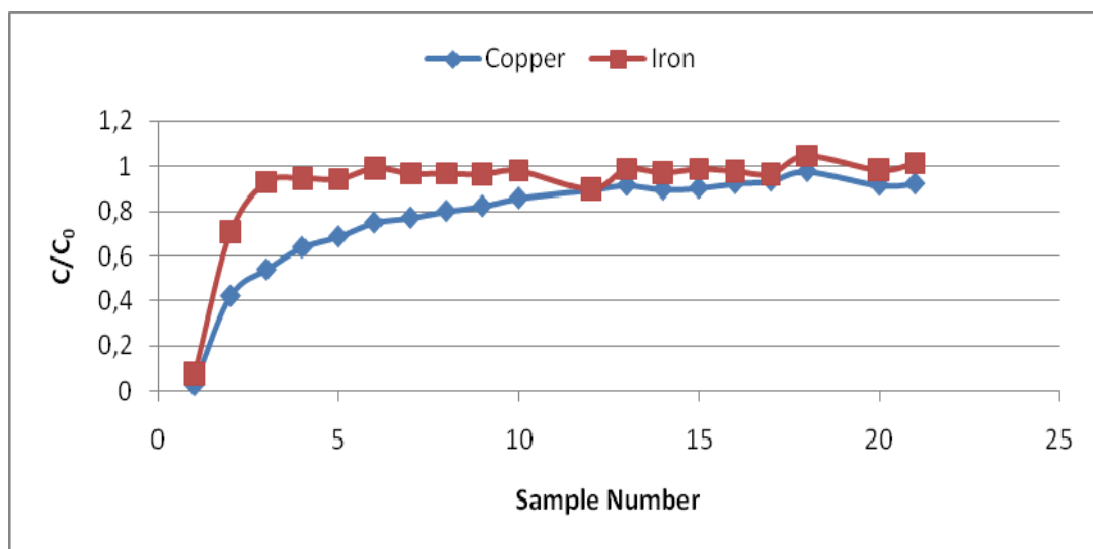Nitrilo-acetic anhydride

Figure 2

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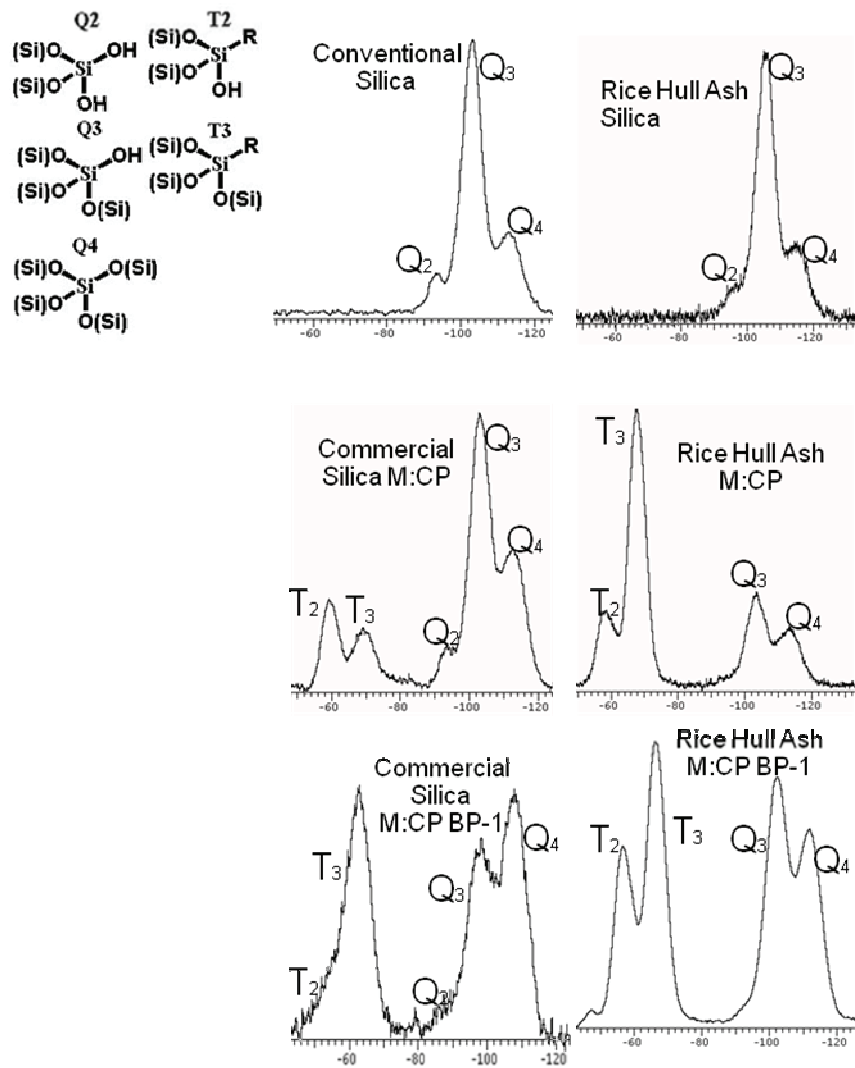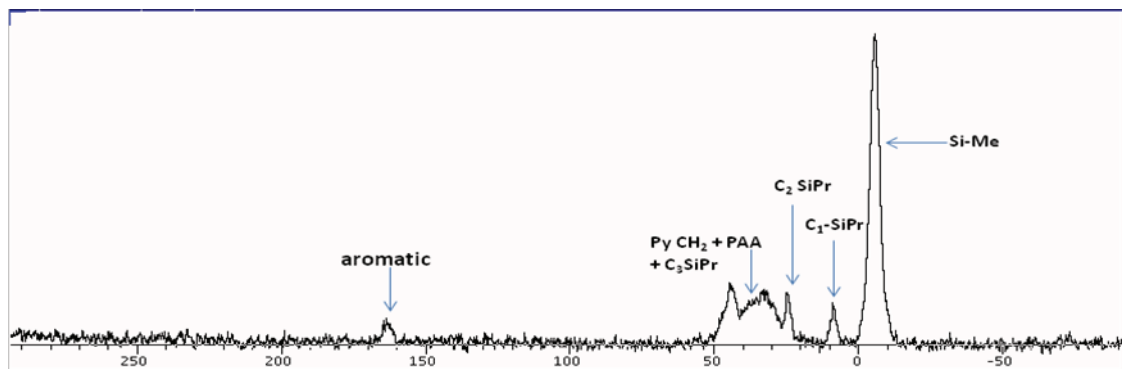a   Figure 3   b

Figure 4

Figure 5

Figure 6

Figure 7