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**EVALUATION OF POLYBENZIMIDAZOLE AS
A SELECTIVE METAL SORBENT AND
CONTROLLED RELEASE AGENT**


by

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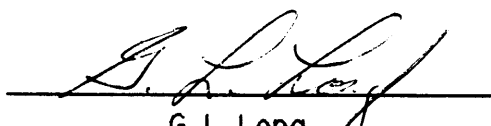
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Abstract

Polybenzimidazole (PBI) is a high performance, high thermal stability, new generation polymer that has excellent resistance to acids, bases, organic solvents, and fuels.

The imidazole functionality suggests, however, that PBI should exhibit strong affinity for certain metal ions, and could be useful for solid phase extraction of metal ions. PBI's potential as an SPE has been assessed based upon its adsorption and desorption of metal ions from aqueous and organic environments.

Factors affecting metal adsorption and desorption, including pH, temperature, and metal cation versus anionic metal complex will be discussed. Adsorption chromatography with PBI will be evaluated, also.

Acknowledgements

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1.0 INTRODUCTION

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (commonly known as Polybenzimidazole or PBI) is a high performance, new generation polymer. The inherent imidazole functionality of PBI is believed to provide the potential for many novel applications such as separation, isolation, adsorption, and catalysis. In this regard, the extent of metal interaction with the two nitrogen sites associated with each imidazole may be significant. The affinity each site has for metals will be different and should vary with the hydrogen ion concentration of the medium in which the PBI resides.

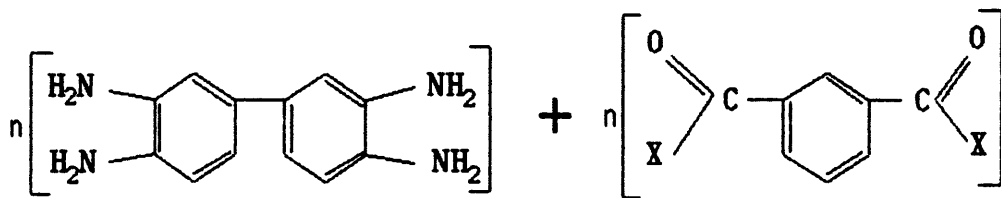
The primary goal of this research was to investigate the interaction of PBI with metallic species under a variety of conditions for the purpose of

· defining new applications for PBI which would be superior to existing commercially available polymeric materials. A secondary goal, if PBI exhibited sufficiently high affinity for metal, was to establish the potential of PBI as a stationary phase for effecting the on-line chromatographic separation of different metallic components in a mixture.

The following sections will discuss PBI's reported properties and applications to date, followed by several chapters on PBI's potential as a solid phase extractant and as an adsorption chromatography stationary phase.

1.1 SYNTHESIS OF PBI

In 1959, K. C. Brinker and I. M. Robinson reported the synthesis of aliphatic PBI (1), where n-alkanes connected the benzimidazole ring systems. These polymers were easily synthesized, but they offered only a low thermally stable product. In 1961, H. Vogel and C. S. Marvel reported the synthesis of an entirely aromatic PBI by melt condensation (2). This polymer was found to exhibit greatly increased thermal stability versus the n-alkane PBI. They found that the totally aromatic PBI could be synthesized



260°C
inert environment
10 hours

↓

-2n HX
-2n H₂O

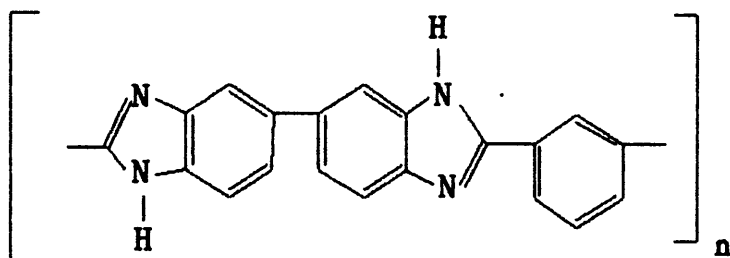


Figure 1: The Synthesis of Polybenzimidazole

(Figure 1) with several different starting reagents. By using the ligand X = NH₂ rather than OH, Cl, OCH₃, or OC₆H₅, the reaction proceeded more easily (3). These totally aromatic PBI's showed increased thermal stability and high molecular weight. In 1964, W. Wrasidlo and H. H. Levine reported a proposed condensation mechanism(4) for the synthesis of PBI. The proposed mechanism is shown in Figure 2.

The PBI that was used in our study was produced by Celanese. In their manufacturing of the product they use the reaction scheme where X = OC₆H₅. However, little information is known about their procedure due to its being proprietary information. But their bead production process is known. PBI "dope" is prepared by dissolving PBI polymer into N,N'-dimethylacetamide (containing < 2% LiCl), at approximately 5% PBI in DMAC the PBI dissolves to form a thick solution. The PBI "dope" is then spun to produce small droplets of PBI that can escape fine holes in a "centrifuge like machine". The small droplets then fall into a methanol bath and are collected. The beads then are heated to remove the solvents.

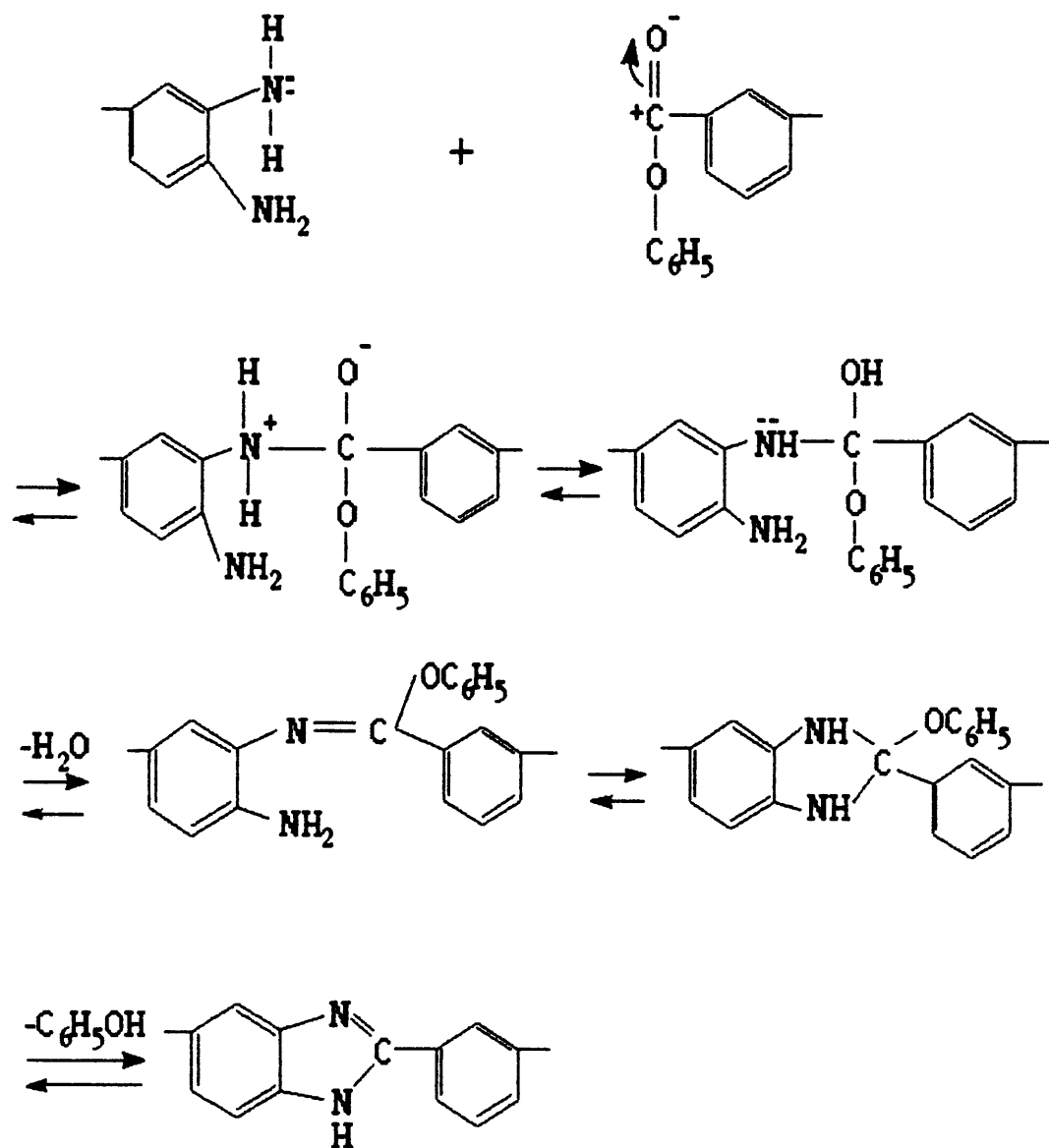


Figure 2: Condensation Mechanism for PBI

1.2 PROPERTIES

Some of PBI's physical properties are tabulated in Table 1. The most significant physical property of PBI is its outstanding thermal stability. PBI is stable in air up to 550⁰C and up to 650⁰C in an inert atmosphere like nitrogen. In addition PBI, like many other polymers, has a wide pH working range which extends from 1 to 14. A picture of a PBI bead that illustrates the bead's very porous structure is shown in Figure 3. The very porous structure of the beads leads to a high surface area, but it also leads to a very mechanically unstable polymer with respect to pressure. This is discussed in more detail later. The high surface area along with PBI's chemical structure leads to a large percent moisture up-take. If the PBI beads were exposed to air they would pick up at least 15% water and if they were stored in water they picked-up almost 75% water.

1.3 APPLICATIONS FOR PBI

Since Celanese has only been commercially producing the PBI beads since about 1980 and has only had the product for sale through a national chemical supplier (Fisher Scientific) for one year, there are rather few applications developed. However, two applications where PBI has shown excellent promise will be discussed briefly. These are a PBI-Metal catalyst for

Table 1: PHYSICAL PROPERTIES OF PBI

Theoretical Capacity (meq/g)	6.5
Physical Structure	Microporous Spherical
Specific Surface Area (m ² /g)	35
Average Pore Diameter (Å)	80
Bulk Density (g/ml)	0.2
% Swelling in H ₂ O	<10
Particle Size (µm)	75 - 150
Operable pH Range	1 - 14
Maximum Operating Temperature (°C)	
in Liquid	300
in N ₂ Gas	650
in Air	550

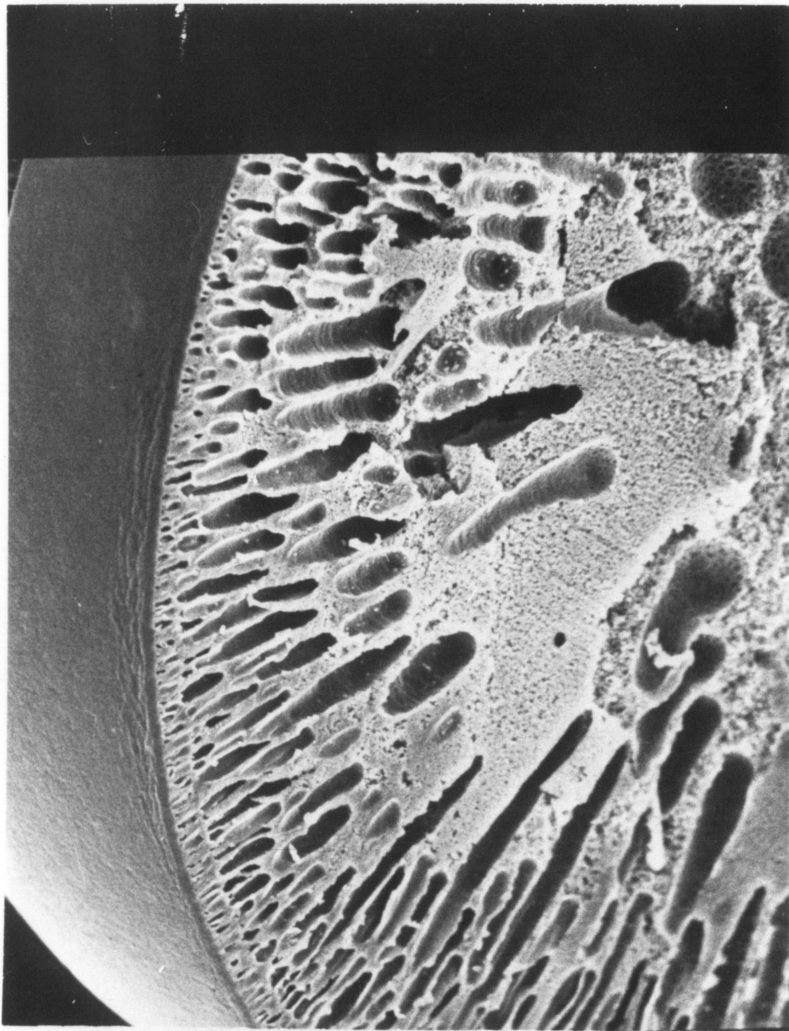


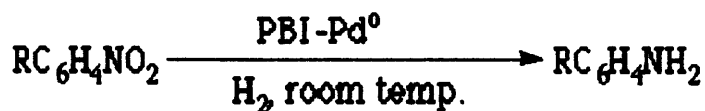
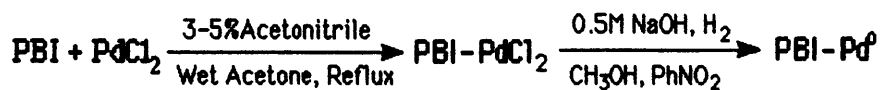
Figure 3: Photomicrograph of the Cross-section of a PBI Bead

organic reactions, and PBI fabric as a fire retardant material for airplane seats as well as other potentially high temperature environments.

1.3.1 CATALYSIS WITH PBI-METAL

Many polymer supports for metals have been used as catalysis in organic reactions (5,6,7). However many of these reactions require that the solution be heated. Upon heating many of these polymer-metal catalysts thermally degrade. A catalyst can lose its catalytic properties by either the loss of the metal when the polymer-metal bond breaks or the polymer can thermally degrade or break-up to collapse the metal catalyst support. Having seen reports of PBI's high thermal stability and predicting that the Nitrogen-Metal bond should be strong in PBI like it is with imidazole, Nai-Hong Li and Jean M. J. Frechet proposed using PBI as a polymeric support for metal catalyst. They studied the reductions of nitroaromatic compounds to primary amines with PBI-Pd (8) and the oxidation of alcohols to carbonyl compounds with PBI-Cr (9). The synthetic preparation of the catalysts and a summary of the catalyzed reactions are summarized in Figure 4. They were amazed that the PBI catalyst could continually be regenerated and used repeatedly without loss of reactivity. In fact the reactivity of the catalyst improved slightly after the first few runs. The

Reduction of Nitroaromatic compounds to primary amines



All reactions studied gave 100% yield at 25°C

Oxidation of alcohols to carbonyl compounds

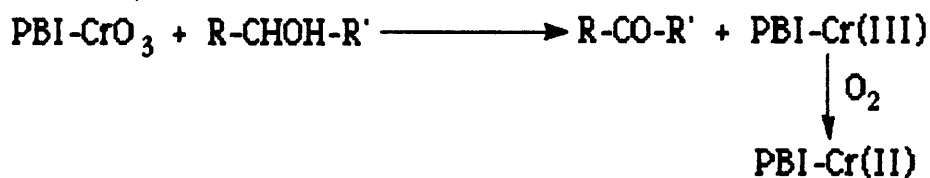
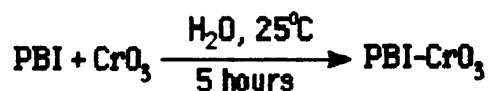


Figure 4: PBI Catalyst Reactions

reactions could also be carried-out under much milder temperatures than they had expected. With much lower temperatures, secondary reactive sites on the compound were not thermally stressed, thus preventing unwanted reactions at secondary sites. Several authors have studied Pd-Carbon catalyst for the $\text{RNO}_2 \rightarrow \text{RNH}_2$ reaction (10,11,12). These reactions proceeded with yields ranging from 49 to 92%, and usually required temperatures greater than 50°C . The PBI-Pd catalyst always proceeded with 100% yield at room temperature and no degradation of the catalyst. The oxidation of alcohols to carbonyl compounds by PBI-Cr catalyst is less understood than the previous catalyst case. It appears that if the catalyst is prepared at room temperature and at -6°C an entirely different catalyst is prepared. These two catalyst will catalyze the same reaction but the catalyst is not as recycleable as in the previous example. If the catalyst is prepared at -6°C then the catalyst retains its structural integrity and can be recycled more than five times. The catalyst made at room temperature is very brittle, can only be recycled 1 or 2 times, and is less reactive than the room temperature catalyst. They concluded that PBI as a metal catalyst support was very good and that further work would have to be done to fully utilize PBI's high thermal stability in a catalyst reaction that will only

proceed at high temperatures.

1.3.2 FIRE RETARDANCY OF PBI

PBI has been studied extensively as a fire retardant material (13,14,15,16). The first reported discussion of PBI's thermal stability was in 1961 (17). The article reported the thermal gravimetric analysis (TGA) of PBI in a nitrogen environment (heating a sample and monitoring the percent weight loss). The TGA of PBI was performed by measuring the weight loss at 400, 450, 500, 550, and 600⁰C, consecutively for 1 hour at each temperature. They found that after exposure of PBI to 400⁰C and 450⁰C only 0.4% of the PBI was thermally degraded. After being exposed to the complete test only a combined 4.5% of the PBI was lost.

In 1980-1985 several thermal studies were again performed on PBI. These studies determined whether PBI had sufficient thermal insulation and fire retardation properties to allow its use for aircraft passenger seats or other potentially high temperature exposure environments. In summary, they found that PBI fabrics were better than most Aramid fabrics (general class of polymers that are produced by the formation of amide linkages between aromatic rings), used in many applications, but fabrics made from

either 100% Kynol or 70% Kynol and 30% Nomex (poly-m-phenoleneisophthalamide) were superior. The major reason some other fabrics were considered superior was because when PBI fabrics were subjected to intense heat, some toxic gases were emitted. However, they found that these toxic gases were the result of impurities in the PBI fabric. They concluded that if the PBI synthesis could be cleaned-up, the PBI could be the best fire retardant material available today.

1.4 SOLID PHASE EXTRACTION

Solid phase extraction (SPE) is when a solid material is used to adsorb or extract unwanted materials from a gas or liquid (18). SPE's have been used in numerous applications: air conditioning (19), dehydration (20), solvent recovery (21), petroleum refining (22), and water purification (23). In all these cases, the SPE is used to clean up the sample. In general, once the SPE has done its job it is discarded. However, if the SPE is used for metal recovery, the SPE has to adsorb the metal and then the metal(s) will usually be collected in a desorption process. This relates to the work done in this thesis to determine PBI's adsorption and desorption properties for metal cations.

2.0 EXPERIMENTAL

Polybenzimidazole (PBI) which was obtained from Celanese Corporation (PBI Business Unit, Charlotte, NC) and used throughout this study was unwashed and termed "dry" even though it still contained approximately 15% water. This is the condition the PBI beads were received. The percentage of water in the PBI was determined by thermal gravimetric analysis. The particle sizes, used in all the experiments, ranged from 75 - 150 μm , these sizes were obtained by separation with a sieve (100 mesh = 150 μm and 200 mesh = 75 μm).

The metal species used throughout the study are as follows. The aqueous metal solutions were made up by dissolving the appropriate amount of either the metal chloride or nitrate in the appropriate pH deionized distilled water to result in 10mg of the metal cation in solution. The organic solutions

were prepared by diluting a high concentration standard of the metal-dialkylbenzene sulfonate to the appropriate concentration (i.e. 10mg metal in 100ml solvent with xylene). The experimental procedures of the adsorption, desorption and chromatography will follow.

2.1 ADSORPTION

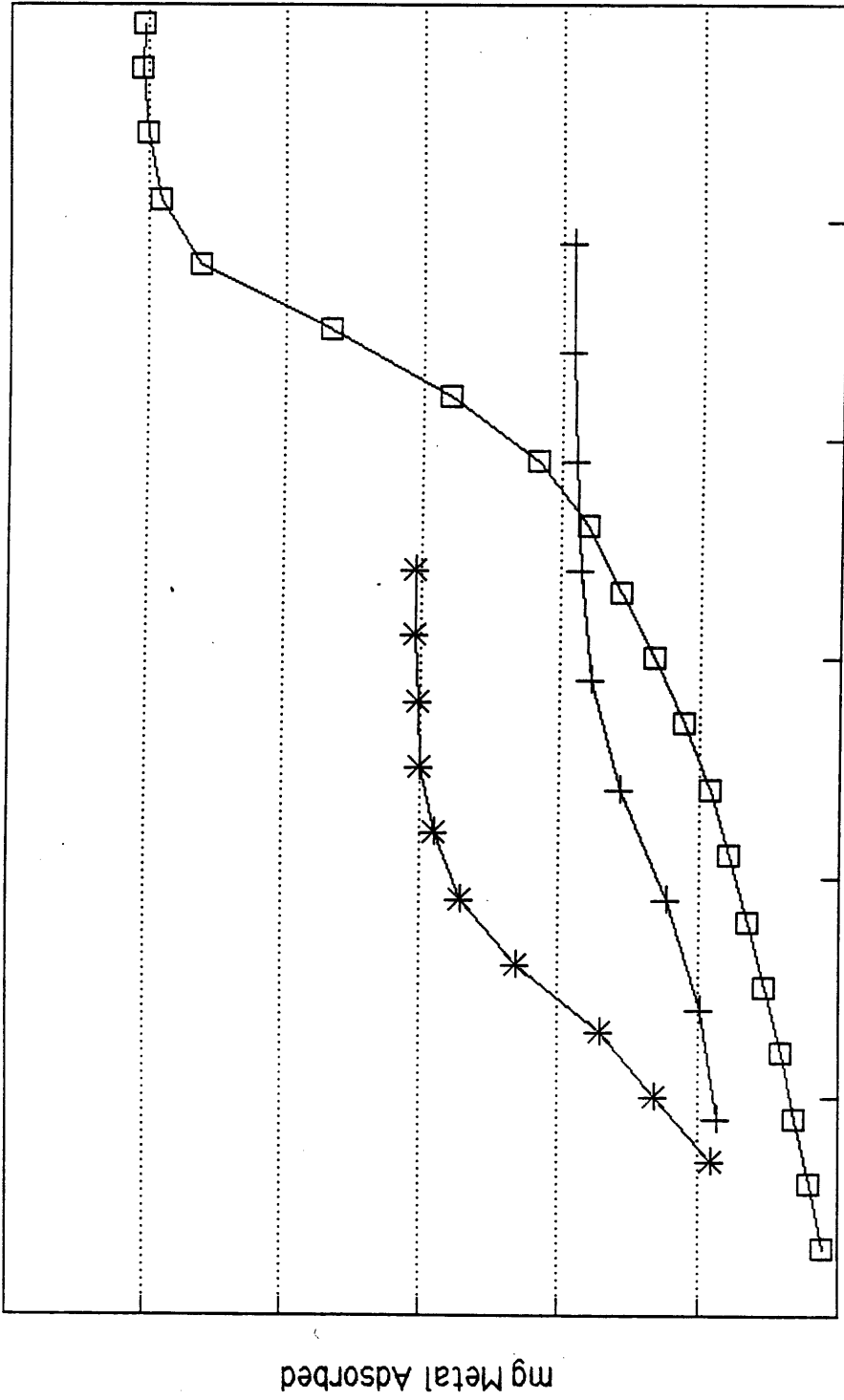
The experimental procedure for all the adsorption experiments was as follows:

1. 10mg metal was added to 1.0g of polymer (PBI or PV4P) in 100 ml of solvent (water or xylene).
2. sample was equilibrated for three hours in closed erlenmeyer flasks which were not agitated, but were temperature controlled by a water bath.
3. mixture was vacuum filtered with 0.5 μ m filter paper.
4. filtrate was analyzed for metal content by either Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Atomic Absorption (AA). See Appendix 1. The difference between initial (10mg) and final amounts of metal in solution indicate the amount of metal removed from solution.
5. Two replicate sorption experiments were carried out for each metal.

This procedure was developed based on two experiments. The first experiment studied the amount of metal adsorbed versus the amount of metal initially in solution. The general relationship between the initial concentration of metal in solution versus the amount of metal adsorbed usually appears to look like a titration curve (24), figure 5. In this figure, the adsorption curves for three polymers are shown to emphasize the various adsorption curve trends.

When the polymer is reacted with only a small amount of metal initially in solution (beginning part of the adsorption curve), the adsorption data is very erratic. If the initial concentration of metal in solution is greater than or equal to the value at which the maximum metal is adsorbed (the plateau on the adsorption curve), the polymer would have fully reacted with the metal. In this case there should be little error due to variations in adsorption. However, with PBI, it appears that this plateau could only be reached by using such high concentration of metal that the analytical measurement of the differences between initial and final concentration of metal is impossible. Keeping in mind that too much metal and too little metal initially in solution lead to large errors, a compromise ratio of 10mg metal to 1g PBI was chosen.

The second set of experiments optimized the time for equilibration.

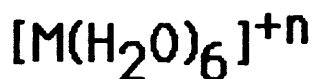


mg Metal Initially in Solution

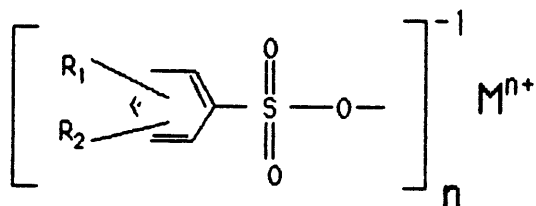
Figure 5: General Adsorption Curve

When the time dependence on the amount of metal adsorbed was studied, see Figure 6, it was found for copper(II) at 25°C and pH 4, that within 1 hour the maximum amount of copper was adsorbed. However, three hours was chosen to ensure that the sample would reached equilibrium with all the metals to be studied.

The nature of the metal species in the aqueous and organic systems differed dramatically. The aqueous metals were derived from the chloride or nitrate; however, once in solution all metals became the hexaaquo species



The organic metals were dialkylbenzene sulfonates which in xylene were believed to maintain their integrity.



2.2 DESORPTION

The experimental procedure for all the desorption experiments was as follows:

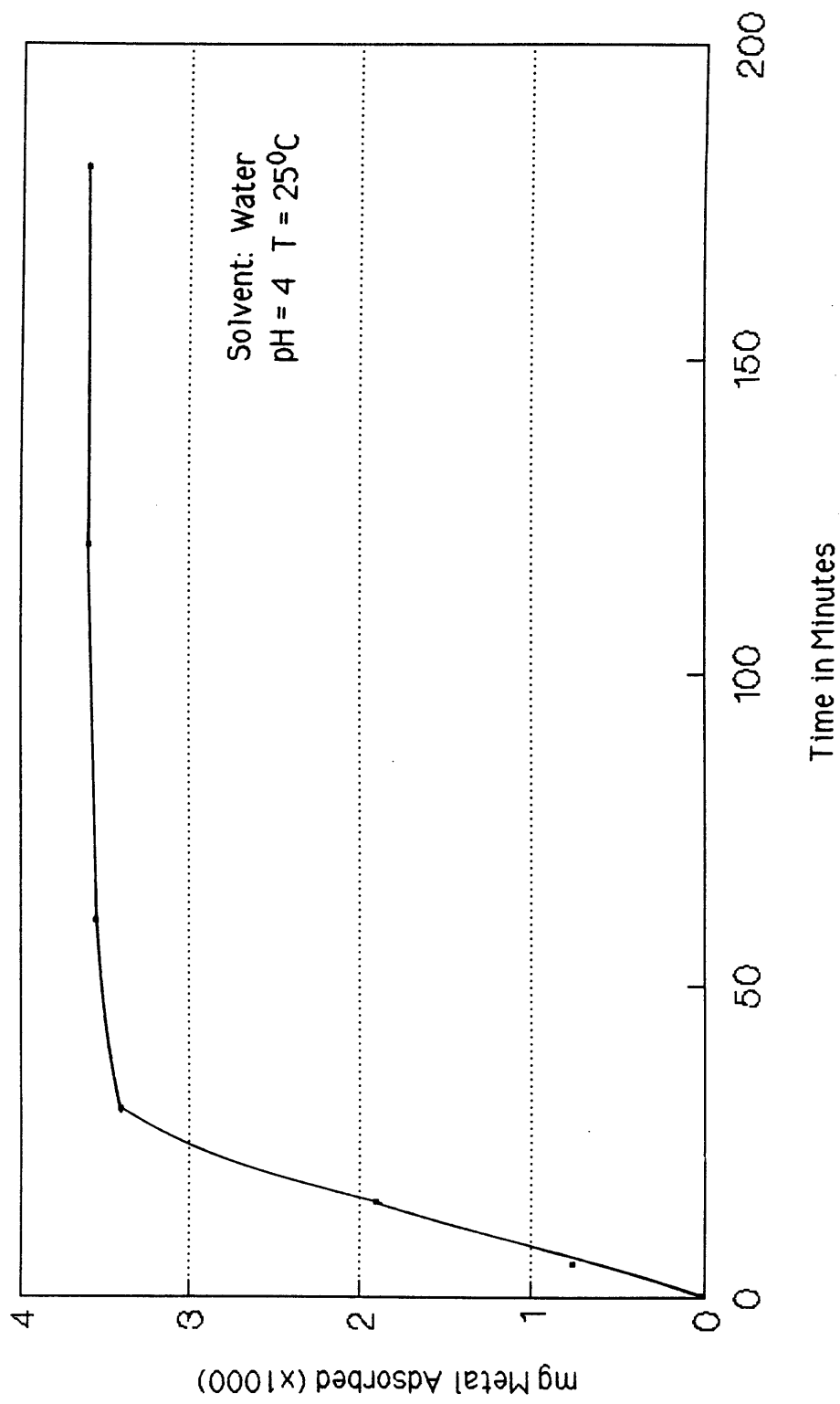


Figure 6: Time Dependence of Copper Adsorption

1. Adsorption procedure was followed except 10 times the initial quantities were used to produce 10g of PBI-Metal for desorption.
2. Dry the moist PBI-Metal at room temperature for 24 hours.
3. Place 10g of PBI-Metal in 500ml deionized-distilled water acidified or basified to the appropriate pH.
4. Mixture is equilibrated for 3 hours at room temperature without agitation.
5. Mixture is vacuum filtered with 0.5 μ m paper.
6. Filtrate was analyzed for metal by either Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Atomic Absorption (AA).

This procedure was again devised based upon one experiment. A time study of the desorption of metals found that within one hour the maximum amount of metal was released (see Figure 7); however, to ensure equilibrium was reached, the sample was equilibrated for 3 hours rather than only 1 hour.

2.3 CHROMATOGRAPHY

The procedure for the column chromatography experiments was as follows:

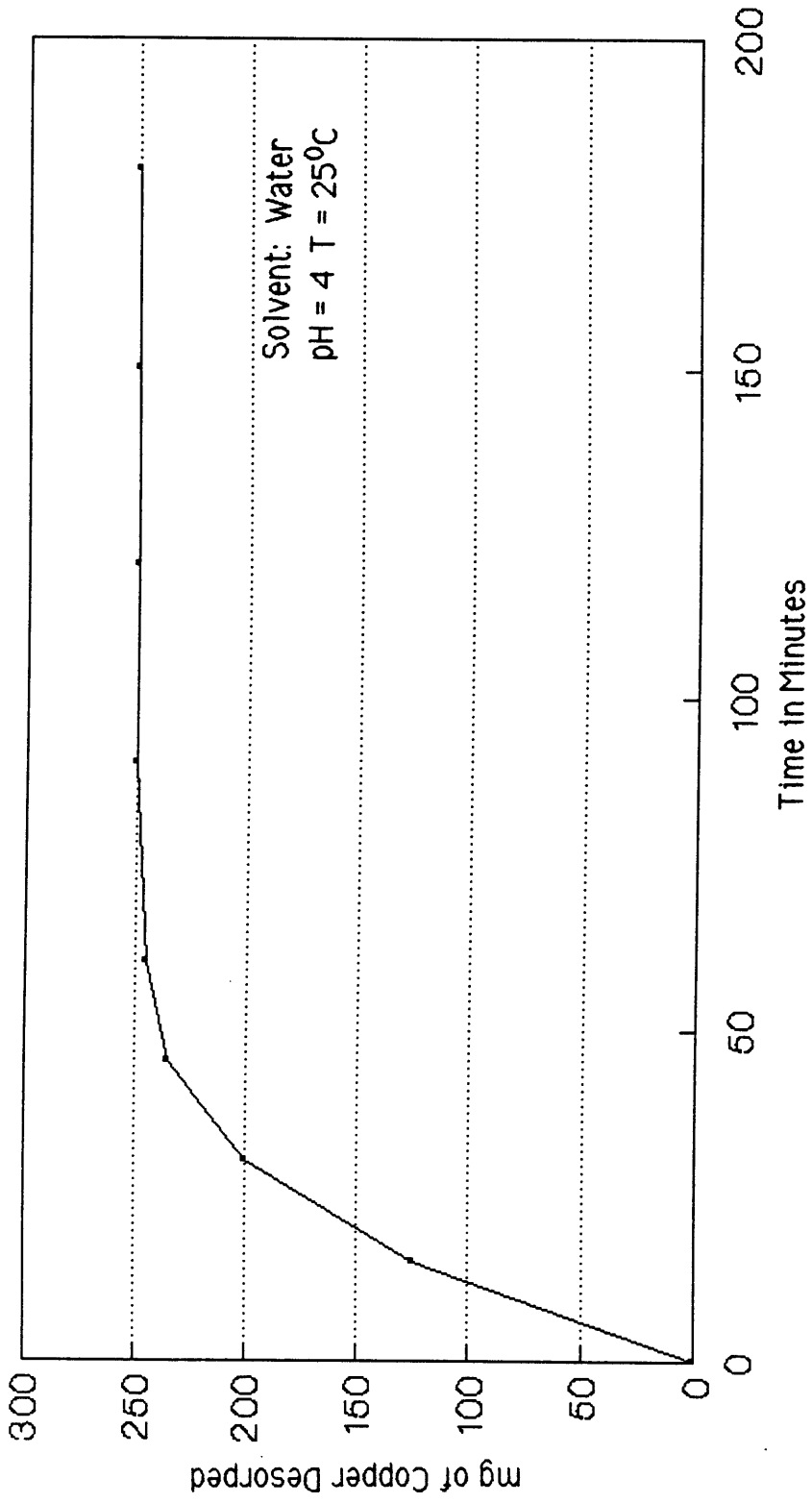


Figure 7: Time Dependence of PBI-Copper Desorption

1. Wet (slurry) pack¹ a buret with PBI in water
2. Place the metal containing sample solution on top of packing material.
3. Run mobile phase, gravity feed, at 1ml/min. The mobile phase was water which was acidified to the appropriate pH.
4. Collect samples in test tubes for analysis by either ICP-AES or AA.

¹Slurry packing a column consists of hydrating the PBI in water to insure that the maximum amount of water has been absorbed. Then a buret is filled with water and plugged with a small piece of cotton. Then the wet PBI is slowly added to the buret as the buret is slowly drained, making sure that the packing material never dries, to prevent the formation of voids.

3.0 RESULTS and DISCUSSION

This chapter will be divided into three primary sections: 1. Adsorption of metals from both aqueous and organic solution. 2. Desorption of metals from PBI in aqueous solvent. 3. aqueous adsorption chromatography.

3.1 ADSORPTION

Adsorption is the process where a material removes certain materials from solution. In this study, the adsorbent was the PBI beads and the adsorbates were the metal cations (aqueous) or metal sulfonates (organic).

Adsorption has been described (25) as a combination of one chemical and two physical processes. These are adsorption, precipitation, and co-precipitation of the adsorbent and adsorbate from solution. Adsorption is the chemical phenomenon, where the solid phase chemically reacts with

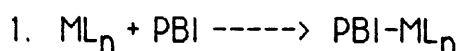
the adsorbate. The materials being extracted are removed from solution by the formation of a chemical bond with the adsorbent. This will be discussed in more detail in section 3.1.1. Precipitation is when the metal cation bonds to enough anions to form a neutral compound that will then fall-out of solution as a solid (often as the metal hydroxide or oxide). It has been reported that at very near the solid-liquid interface (inside the electrochemical double-layer), many compounds have a reduced K_{sp} and are therefore more easily precipitated onto the solid (26). Co-precipitation is when the adsorbate and the adsorbent are co-precipitated, this only occurs when the adsorbent is soluble in the solvent, however since the extractant dealt with here (PBI) is insoluble in the solvents used, there can be no co-precipitation.

The adsorption experiments that were performed on PBI could not distinguish between adsorption and precipitation of the metal ions. This is because only the difference between the initial and final concentrations of the metal was measured. However, for a solid phase extractant the important data are the bulk extraction ability of a material. This means that whether the adsorbate was adsorbed or adsorbed and precipitated by the solid phase extractant does not matter because an SPE is used simply to

remove a material. However, for obtaining chemical knowledge of the reactivity of the solid phase extractant, true adsorption data are necessary to deduce the stabilities of the metal-SPE bonds. Reports have stated that the reactivity can be very different for adsorption versus the combination of adsorption and precipitation. Usually the amount of metal precipitated versus adsorbed is very low, but the incorporation of the precipitation with adsorption has been reported to result in many reversals or oddities in the reactivity order of metals (27).

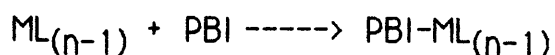
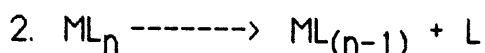
3.1.1 POSSIBLE ADSORPTION REACTIONS

The interaction of metal species with PBI can be envisioned to occur by at least two routes.



This general reaction involves the direct interaction of PBI with the intact metal species. If the metal is coordinatively unsaturated, the PBI may associate directly with the metal in its primary coordination sphere. If the metal is coordinatively saturated, as is to be expected in this work, the PBI interaction will take place in the outer metal coordination sphere which

will constitute a weaker type of association than the former. Aqueous metal cations will have six water molecules in their outer sphere, but their interaction even through the outer sphere may be significant with the PBI. For organically-bound metals in xylene, this outer sphere interaction may be extremely weak since the species are expected to be non-charged.



This reaction will be most prevalent for metals which are substitutionally labile wherein the coordination groups on the PBI favorably compete with H₂O (aqueous) or dialkyl benzene sulfonate (xylene) ligands for sites on the metal in its primary coordination sphere. This reaction is most probable for the aqueous phase. It should be less probable for the organic metals since xylene cannot stabilize the charged species resulting from the pre-equilibrium ligand dissociation.

Sorption studies have been carried-out at variable pH. Many metals will precipitate as oxides or hydroxides at high pH. If no precipitation occurs, certainly hydroxy species will be common rather than hydrated cations. PBI has three pH dependent forms based upon the degree of protonation of the benzimidazole functional group, Figure 8. Each of these forms should have

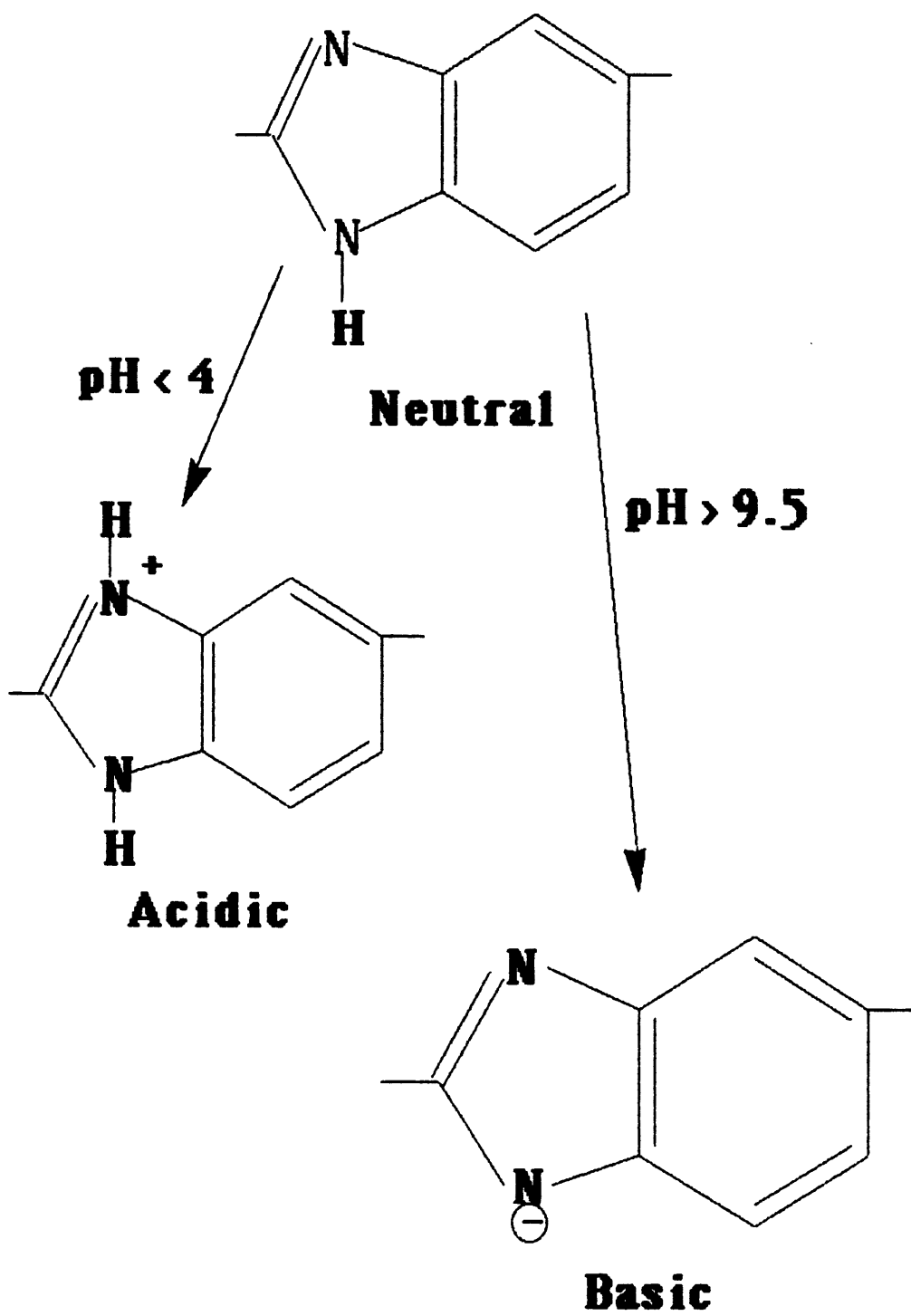


Figure 8: pH Dependent Variations of PBI

distinctively different adsorption coefficients. The basic form will be most prevalent above $\text{pH} = 9.5$. The deprotonated nitrogen should have high affinity for positive metal species because of the greater coordinating ability of the benzimidazole anion and the attraction between negative group and positive metal ion. In water, however at pH's this high, most metals will have unfortunately either precipitated out of solution or be present as soluble anionic species. The acidic form will begin to dominate if the pH is lowered below 4. This form has the trigonal nitrogen protonated leaving a positive charge on the imidazole ring system. With a positive charge on the nitrogen, this form of PBI should have its strongest affinity for negatively charged species. However, metals in an acidic environment should be positively charged aquo species and should therefore not be very strongly adsorbed. If the acid contained a strongly coordinating anion (e.g. HCl), negatively charged metal complex ions (e.g. $[\text{MCl}_4]^{2-}$) would exist and therefore be strongly attracted to the positively charged PBI. The neutral form of PBI is the most versatile. It should be able to adsorb both positively and negatively charged species but probably not to the extent of either the acidic form for positive ions and the basic form for negative ions.

In the aqueous adsorption studies, pH's of 4 and 7 were employed. These

two pH's give rise to predominately the acidic and neutral forms, respectively. In the organic phase, only the neutral form need be probably considered.

3.1.2 AQUEOUS ADSORPTION

The aqueous adsorption experiments studied PBI's affinity for various metals under changes in both pH and temperature. The tabulated adsorption data for these experiments are found in Tables 2 - 11. The data are presented on a mass of metal/mass of polymer basis as well as on a millimoles (milliequivalents) of metal per Kg of polymer basis in order to allow a valid comparison between metals. The metal systems investigated were aluminum(III), cobalt(II), copper(II), gold(III), iron(II), iron(III), manganese(II), nickel(II), and zinc(II).

Adsorption experiments with $[Zn(H_2O)_6]^{2+}$ proved fruitless. At both pH 4 and 7, the zinc ion did not remain in solution but precipitated as $Zn(OH)_2$. Efforts to solubilize the zinc with a chelating agent were not attempted because the chelating agent would most likely affect the metal's reactivity. Assuming that one of the two reaction pathways postulated before are correct, then the nature of the ligands will affect the metal's reactivity

Table 2: **Aluminum Adsorption Data**

<u>POLYMER</u>	<u>SOLVENT</u>	<u>TEMPERATURE</u>	<u>pH</u>	<u>mg Metal</u> <u>Kg Polymer</u>	<u>mmoles Metal</u> <u>Kg Polymer</u>
PBI	water	25 ⁰ C	4	580 600	22
PBI	water	25	7	490 510	19
PBI	water	63	4	1030 1100	40
PBI	water	63	7	1020 1080	39
PBI	xylene	25		390 410	14.6
PBI	xylene	55		330 370	13.0
PV4P	xylene	25		15 25	0.8
PV4P	xylene	55		175 205	7.1

Table 3: Calcium Adsorption Data

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ⁰ C	4	175	4.5
				195	
PBI	water	63	4	360	9.5
				400	
PBI	water	25	7	150	4.3
				190	
PBI	water	63	7	310	8.3
				350	
PBI	xylene	25		580	14.8
				600	
PBI	xylene	55		740	19.3
				800	
PV4P	Xylene	25		585	14.8
				595	
PV4P	xylene	55		280	7.7
				340	

Table 4: Chromium Adsorption Data

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	xylene	25 ^o C		1000	19.4
				1020	
PBI	xylene	55		970	19.3
				1030	
PV4P	xylene	25		115	2.5
				125	
PV4P	xylene	55		140	2.9
				160	

Table 5: Cobalt Adsorption Data

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ⁰ C	4	0	0
				0	
PBI	water	25	7	0	0
				0	
PBI	water	63	4	0	0
				0	
PBI	water	63	7	0	0
				0	
PBI	xylene	25		795	13.6
				805	
PBI	xylene	55		810	13.7
				810	
PV4P	xylene	25		0	0
				0	
PV4P	xylene	55		0	0
				0	

Table 6: **Copper Adsorption Data**

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ^o C	4	3500 3690	57
PBI	water	63	4	4150 4245	66
PBI	water	25	7	***INSOLUBLE***	
PBI	water	63	7	***INSOLUBLE***	
PBI	xylene	25		895 905	14.1
PBI	xylene	55		990 1010	15.8
PV4P	xylene	25		0 0	0
PV4P	xylene	55		90 130	1.7

Table 7: **Gold Adsorption Data**

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ⁰ C	4	10500 10500	54
PBI	water	63	4	10500 10500	54
PBI	water	25	7	11000 11000	54
PBI	water	63	7	11000 11000	54
PBI	xylene			***UNAVAILABLE***	

Table 8a: **Iron Aqueous Adsorption Data**

<u>POLYMER</u>	<u>SOLVENT</u>	<u>TEMPERATURE</u>	<u>pH</u>	<u>mg Metal</u> <u>Kg Polymer</u>	<u>mmoles Metal</u> <u>Kg Polymer</u>
Iron +2					
PBI	water	25 ⁰ C	4	3420 3580	63
PBI	water	25	7	4100 4300	75
PBI	water	63	4	5250 5350	95
PBI	water	63	7	5880 5920	106
Iron +3					
PBI	water	25	4	730 770	13
PBI	water	25	7	470 530	9
PBI	water	63	4	1075 1125	20
PBI	water	63	7	685 715	13

Table 8b: Iron Organic Adsorption Data

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	xylene	25		570	10.3
				580	
PBI	xylene	55		565	10.2
				575	
PV4P	xylene	25		305	5.7
				335	
PV4P	xylene	55		355	6.4
				365	

Table 9: Manganese Adsorption Data

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ⁰ C	4	55	1.1
				65	
PBI	water	25	7	40	0.9
				60	
PBI	water	63	4	0	0
				0	
PBI	water	63	7	0	0
				0	
PBI	xylene	25		705	12.9
				715	
PBI	xylene	55		710	13.1
				730	
PV4P	xylene	25		125	2.5
				155	
PV4P	xylene	55		270	5.3
				310	

Table 10: **Nickel adsorption Data**

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ^o C	4	50	1.1
				80	
PBI	water	25	7	200	3.7
				230	
PBI	water	63	4	50	1.0
				70	
PBI	water	63	7	130	2.5
				160	
PBI	xylene	25		470	8.2
				490	
PBI	xylene	55		620	10.9
				660	
PV4P	xylene	25		135	2.4
				145	
PV4P	xylene	55		205	3.7
				235	

Table 11: Zinc Adsorption Data

POLYMER	SOLVENT	TEMPERATURE	pH	<u>mg Metal</u>	<u>mmoles Metal</u>
				Kg Polymer	Kg Polymer
PBI	water	25 ⁰ C	4	***INSOLUBLE***	
PBI	water	25	7	***INSOLUBLE***	
PBI	water	63	4	***INSOLUBLE***	
PBI	water	63	7	***INSOLUBLE***	
PBI	xylene	25		1475 1485	22.5
PBI	xylene	55		1640 1640	25.1
PV4P	xylene	25		125 125	2.0
PV4P	xylene	55		480 500	7.4

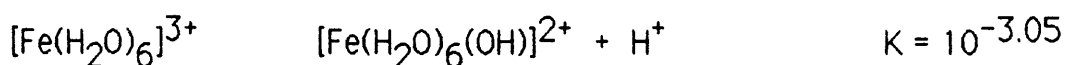
because the coordination sphere of the metal will be drastically different. Thus, resulting in data that could not be justifiably compared to the other aqueous data.

While $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ proved to be stable at pH's 4 and 7, surprisingly negligible amounts of metal were adsorbed by PBI under these conditions. Experiments performed at several temperatures gave identical results for cobalt (II). At $\text{pH} > 6$, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ was found to precipitate as $\text{Cu}(\text{OH})_2$ or CuO . The same results were obtained if the source of copper was changed from $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ to $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$. Data at pH 4 with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ were obtainable, and will be discussed later.

As mentioned previously, the PBI used was 'as received' from Celanese. Late in the work we were told that the PBI beads may be contaminated with ionic impurities. For example, it was suspected that LiCl added in one of the processing steps may have remained in the PBI beads. To determine the effects these ions may have on adsorption, the adsorption of copper was compared with 'dirty' PBI versus two washed PBI samples. Two washing procedures used were: 1. 20 bed volumes of deionized distilled water. 2. 10 bed volumes ethanol, then 10 bed volumes deionized distilled water. The adsorption of copper (pH 4 and 25°C) on 'dirty' versus washed PBI showed no

difference. 'Dirty' PBI adsorbed 3600 mg Metal/ Kg of polymer and procedure 1 and 2 washed PBI adsorbed 3580 and 3550, respectively. The error of these measurements is greater than the differences in these numbers. It was concluded that since PBI had the same adsorption whether it was clean or not, the experiments could continue to use 'as received' PBI.

An overview of the aqueous data is graphically displayed in Figure 9 for adsorption at 25⁰C and pH 4 for several of the cationic species studied. Al, Cu and Fe(II) exhibited the highest affinity for a fixed mass of PBI. A correlation between the degree of metal adsorption and the charge on the metal species does not appear to exist. Originally a tri-positive cation would have been predicted to adsorb more strongly than a dipositive cation. However, Cu(II) and Fe(II) are more highly adsorbed than either Al(III) or Fe(III). This discrepancy can easily be accounted for based upon the actual species in solution. As a first guess, one would say that the metal species in solution at pH 4 would be the hexaaquo species, which is probably true for all the divalent species studied. But, based on the equilibrium data published for iron(III) and aluminum(III) (28,29), solutions of these ions contain a mixture of metal species:



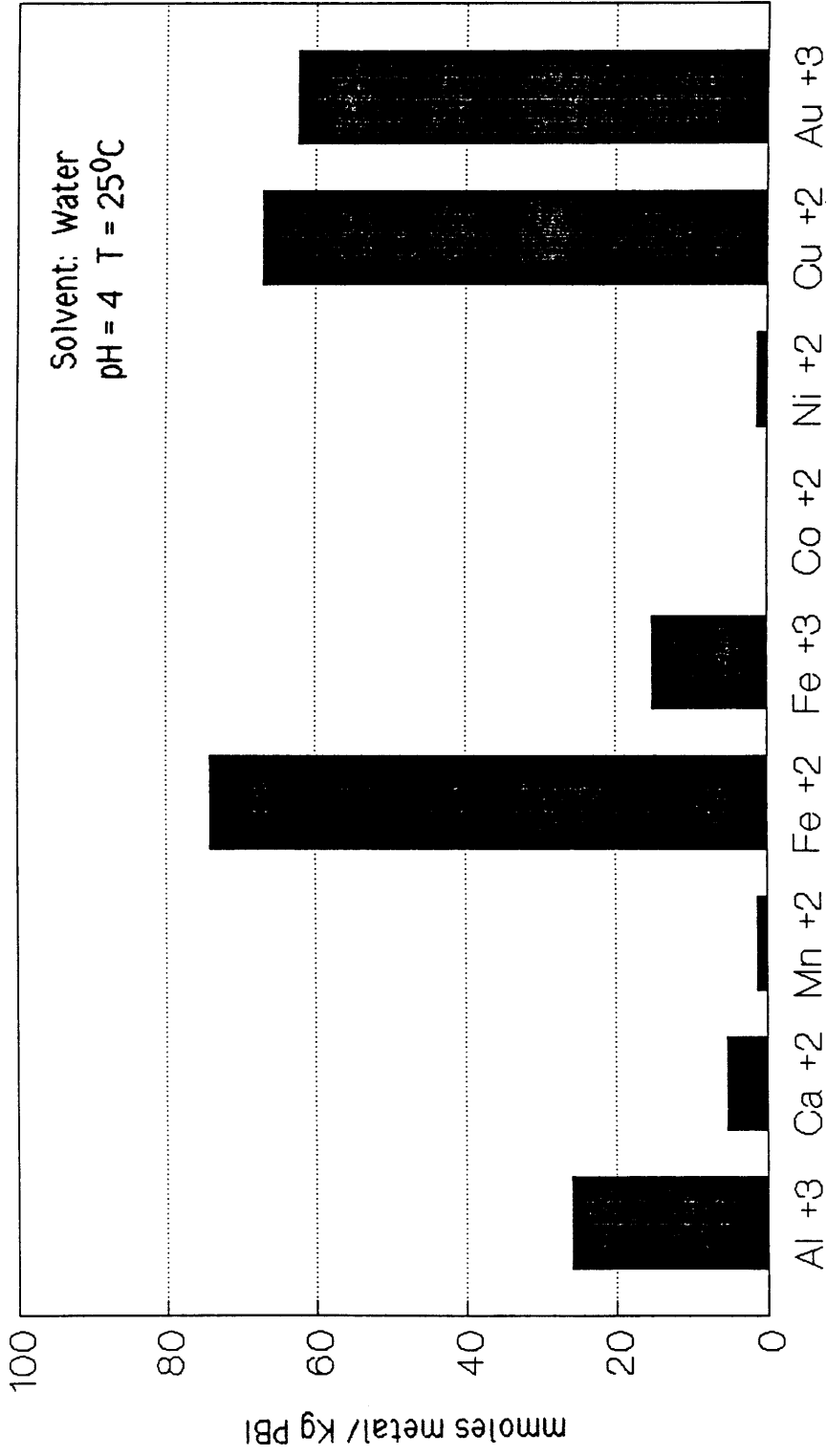
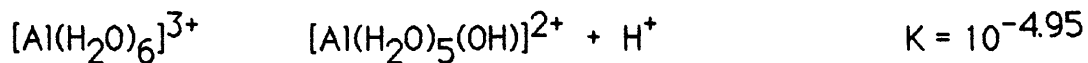
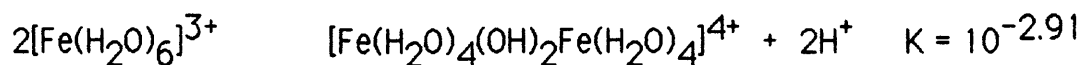
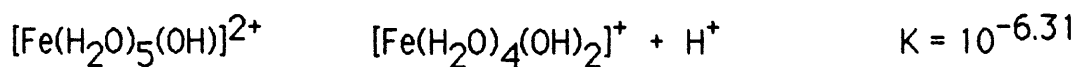


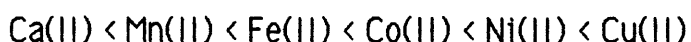
Figure 9: Aqueous Adsorption pH 4 and 25°C



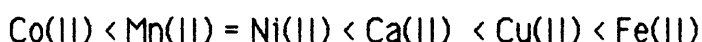
Depending on what pH the sample is at, the concentration of each species of iron and aluminum will vary. For example, at pH 4, 11% of the aluminum is the monohydroxide; whereas, at pH 7, 99% of the aluminum is the monohydroxide. Because the metal(III) is not entirely the hexaaquometal(III) species but rather to a large extent either a +2 or +1 mono- or di-hydroxy species, the adsorption should reflect a net degree of adsorption of the strongly adsorbed +3 cation, the moderately adsorbed +2 cation, and the weakly adsorbed +1 cation. This explanation seems to be validated by the experimental results. For example Al is in a higher concentration, regardless of the pH, as a +3 or +2 species and is therefore more highly adsorbed than the iron which is more likely to be found as the +1 and +2 species. This is because of the lower equilibrium constant for $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ dissociation.

A correlation of the metal uptake with the divalent metals is difficult to find. If direct metal ion-PBI interaction were the case, the order of

reactivity according to expected heats of reaction (or the order w.r.t. the second ionization potential) would be:



However the experimental order found in the study at pH = 4 and 7 and at 25⁰C and 63⁰C (Mn and Ni are very similar at all temperatures and pH's), is:



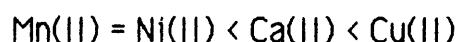
The Fe(II) and Co(II) cations show the largest deviation from the predicted reactivity order. The formation of the most stable co-ordination compound is attained by the combination of three factors (30). One, the central atom attempts to maximize the amount of interaction between metal and ligand by packing as many ligands as possible around it. However, this is limited by the greater 'interference volume' of the ligand molecules compared to the water molecules. Two, the metal's electrons will tend to remain in their most stable ground state electronic configuration. This factor is opposed by three, the tendency to make each interaction between metal and ligand as strong as possible by using the strongest possible hybrid bonding orbitals.

In the case of Fe(II), the most probable explanation for its dramatic increase in reactivity could be accounted for based on factor three. Here the iron will rehybridize an orbital to maximize its bonding strength to PBI, and

the remaining orbitals will bond to water molecules. The literature sites several cases where Fe(II) does bond abnormally strong to some nitrogens and most aromatic systems.

In the case of cobalt, the probable explanation for its nonadsorbance could be factor one. When bonding to PBI the space around the nitrogen will most likely limit the number of water molecules than can associate with the cobalt. If the cobalt does not form a very strong bond to the nitrogen of PBI it may be energetically more feasible to remain in solution with its full hydration sphere.

Now that the Fe(II) and Co(II) cation's adsorptions are accountable, the remaining cations must be considered. Their order remains



There are only two minor differences between this order and the expected order of reactivity. First, nickel and manganese appear almost identical whereas nickel is expected to be better. This is understandable because in many studies comparing the stability of coordination compounds across the first transition metal series, the difference between Mn(II) to Ni(II) show only a small difference for many ligands (31). So Ni might be expected to be very similar to Mn. Also the order of reactivity is based upon a combination of adsorption and precipitation, not simply adsorption. It was concluded by

several authors, and summarized by Anderson and Rubin (32), that if the data were not corrected for precipitation and co-precipitation effects, the data would reveal several metals interchanged in order of reactivity.

Regardless of the temperature, 25⁰ or 63⁰C, the order of adsorption is invariant; although the extent of metal adsorption is enhanced at the higher temperature except in the manganese case, Figure 10. This general observation may reflect a greater PBI surface availability for metal ion adsorption at the higher temperature, but more likely it reflects that with more kinetic energy available there will be more collisions between the PBI and metals that could result in bonding. The percentage increase for each metal on going to the higher temperature is not the same as might have been expected if the temperature was only affecting the swelling of the PBI. It is interesting to note that no measurable Co(II) was adsorbed even at 63⁰C.

The metal uptake for experiments conducted at both pH 4 and 7 does not follow an easily identifiable trend, Figure 11. Co(II) again does not adsorb. The higher pH results in less metal uptake for Al, Mn, Fe(III), Ni, and Cu. Whereas, the opposite situation occurs with Fe (II). It could be argued that if the metal remains in the cationic state at higher pH's, PBI should have exhibited a higher affinity for metal because PBI's deprotonated form becomes more favorable at higher pH.

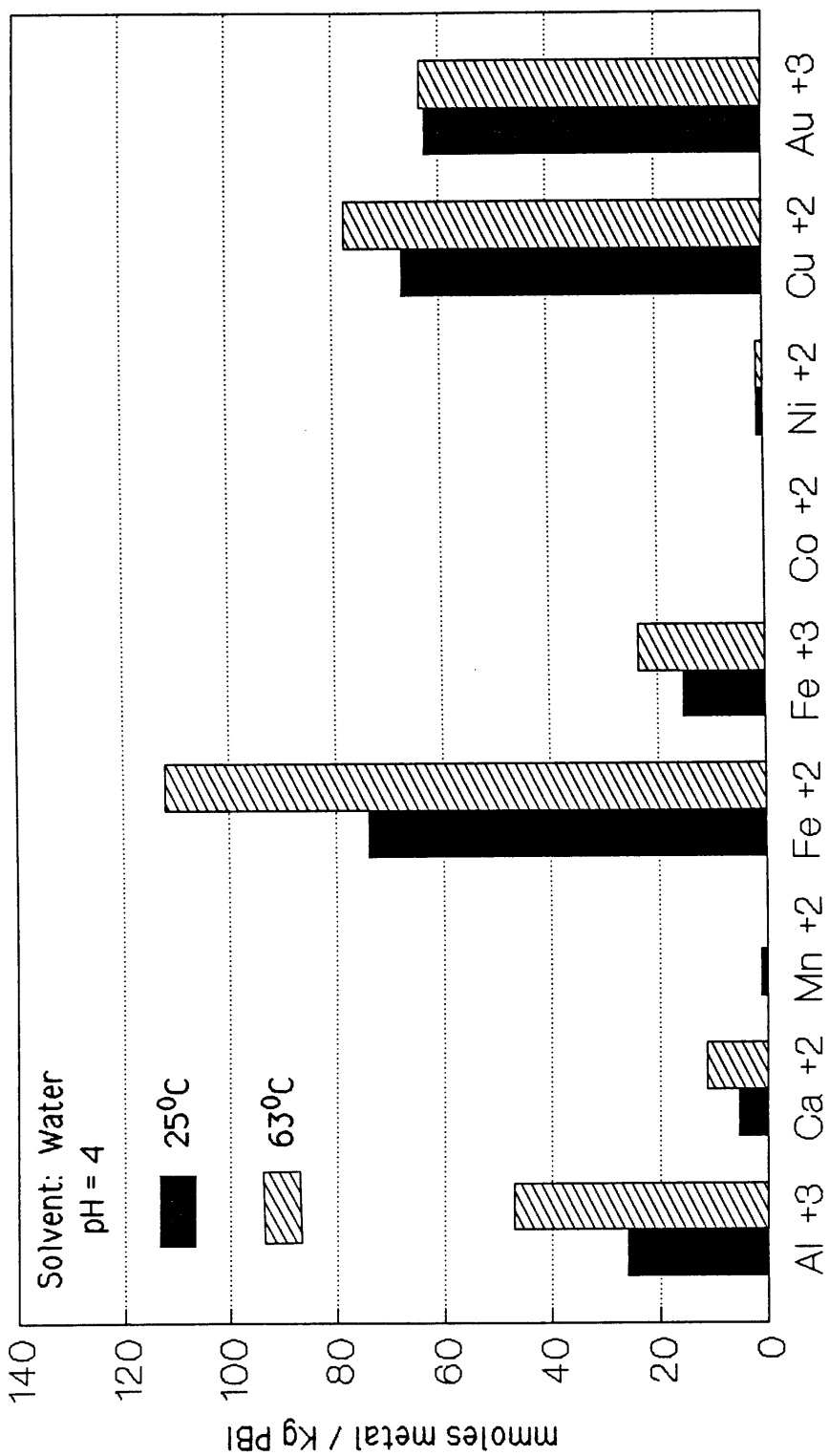


Figure 10: Aqueous Adsorption 25°C versus 63°C

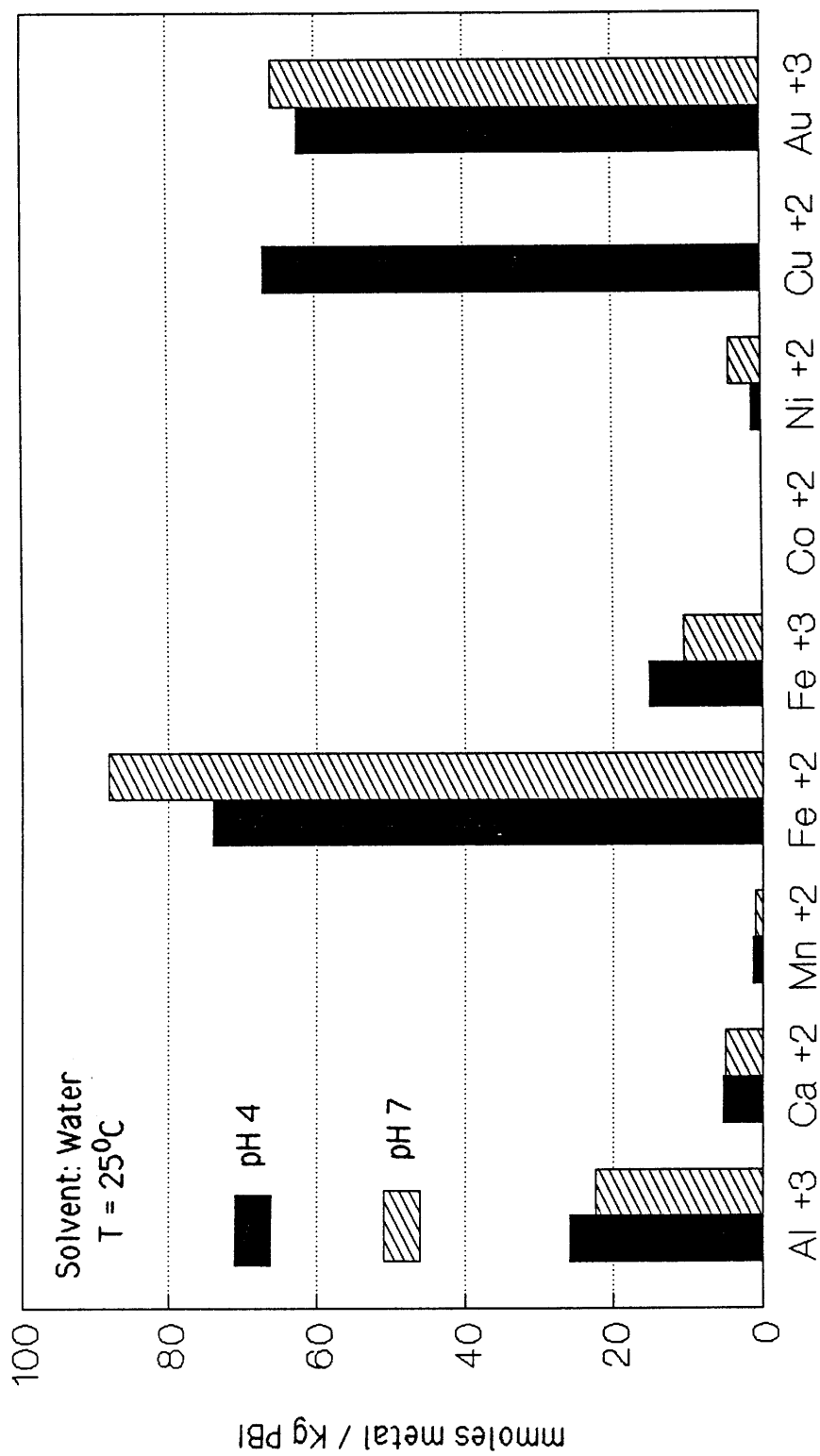
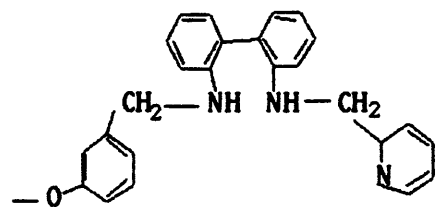


Figure 11: Aqueous Adsorption pH 4 versus 7 at 25°C

The only metal species that was dramatically adsorbed from water was the $[\text{AuCl}_4]^-$ species. We found that all 10mg of $[\text{AuCl}_4]^-$ which was originally introduced to the PBI was completely adsorbed. An upper limit in adsorption of $[\text{AuCl}_4]^-$ was not determined. The probable reasoning behind gold's strong adsorption is that this metal species is anionic rather than cationic. At lower pH's the acid form of PBI is expected to be a strong anionic acceptor and $[\text{AuCl}_4]^-$ is expected to be stable at the lower pH's. These data lead one to believe that PBI is a much better anionic acceptor at both pH 4 and pH 7 than a cationic acceptor.

With all metals studied the extent of metal adsorbed is quite low compared with the theoretical capacity of PBI. If we assume there are two reactive nitrogen sites per repeat unit (308amu), then the theoretical capacity of PBI would be 6500 mmoles/Kg of polymer. Correcting for the 15% water expected to be incorporated into the PBI yields approximately 5500 mmoles/Kg of PBI. Experimentally, we found only about 60 plus/minus 40 mmoles of metal/Kg of PBI. This means that PBI is using less than 2% of its available nitrogen sites to bond to metal cations. Commercially available ion exchange resins exhibit much higher capacities, see Table 12.

Table 12: PBI versus other Ligands for Adsorption of Metal Ions

Polymer	Cu adsorbed mmoles/g	Fe adsorbed mmoles/g	Reference
	1.70	0.007	33
PBI	0.057	0.063	
AG MP-50 Macroporous Resin Sulfonated polystyrene cation exchanger	11.7	12.0	34

3.1.3 ORGANIC ADSORPTION

Adsorption of metallic species by PBI in an organic phase (xylene) was next attempted. Numerical data are found in Tables 2 - 11 and in Figure 12 for Al, Ca, Co, Cr, Cu, Fe, Mn, Ni, and Zn at 25⁰C and 55⁰C. Several points can be made upon examination of the data. First, all adsorptions are dramatically smaller in xylene than in water at 25⁰C. For example, aqueous adsorption of Cu is over 60 mmoles/Kg of PBI (pH = 4); whereas, in xylene only 15 mmoles/Kg of PBI are adsorbed. This suggests that the nature of the metal species must be critical regarding its affinity for PBI. Second, the adsorption trends in xylene are quite different from the trends in water although the chemical state of the metal is somewhat questionable for certain metals in the xylene case. For example, Fe(III) and Co(III) are suspected in xylene rather than their divalent analogs. Third, there is much less variation (8.2 mmoles/Kg of PBI for Ni and 22.5 mmoles/Kg of PBI for Zn, at 25⁰C) in the extent of adsorption for particular metals in going from xylene to water (0 mmoles/Kg of PBI for Co and 75 mmoles/Kg of PBI for Fe(II), at 25⁰C and pH = 7), as five metals have approximately equal adsorption in xylene. Adsorption experiments were also conducted at 55⁰C for comparison. While certain metals (Ca, Mn, Co, Ni, Cu, and Zn) showed greater uptake at the higher temperature, Cr and Mn were without effect and

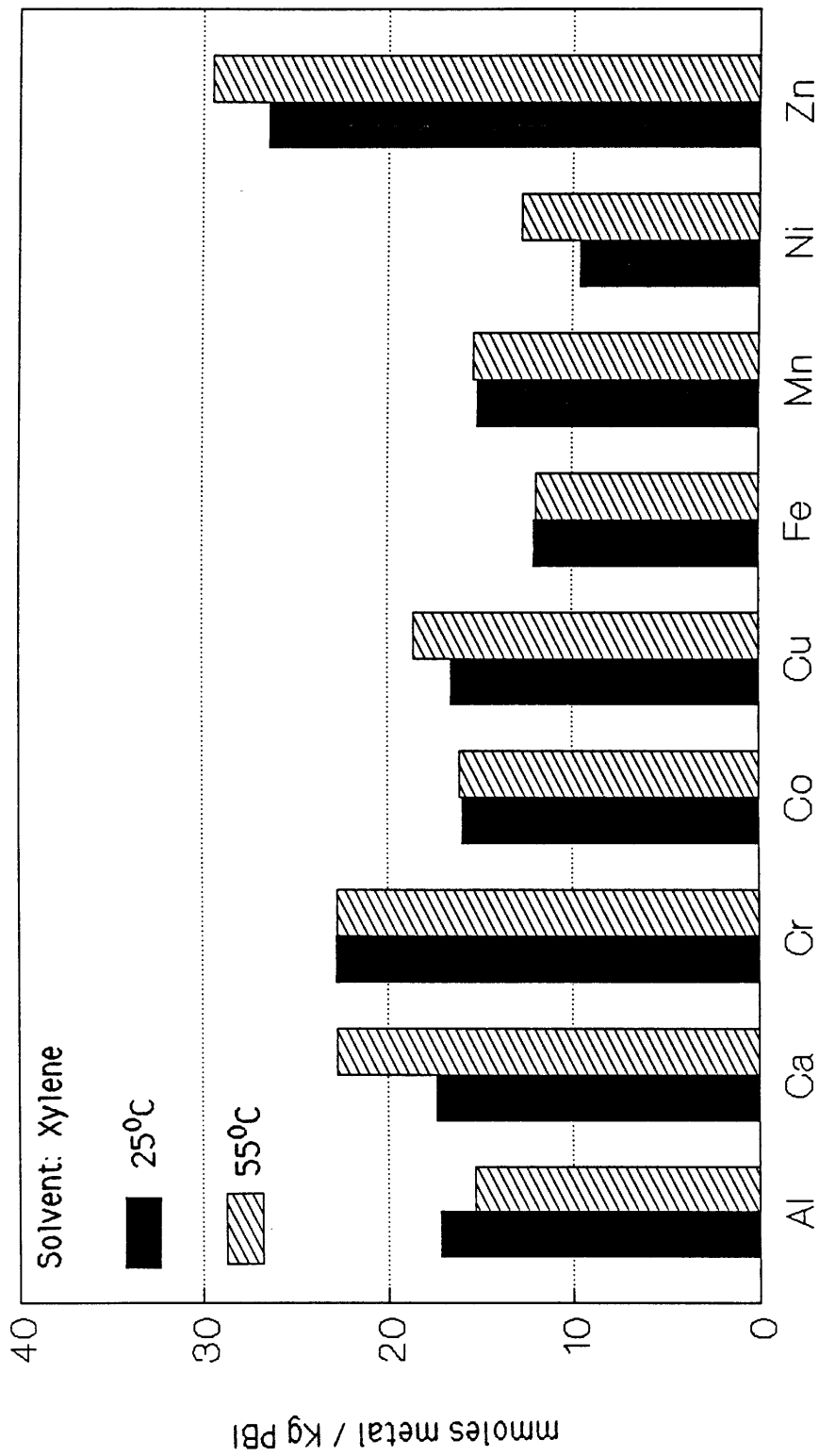


Figure 12: Organic Adsorption 25°C versus 55°C

AI actually decreased.

Data such as these, while not impressive in terms of overall metal uptake, appear to be rather unique since a search in the literature did not reveal any analogous studies with other polymer ligands. For this reason we conducted similar studies with poly-4-vinylpyridine (PV4P) (see Appendix 2 for a brief review of PV4P's physical characteristics). These data are also found in Tables 2 - 11. PV4P was chosen because the pyridine nitrogen should also have a high affinity for positively charged metal species at pH = 7. In addition, PV4P should display an acidic form at low pH's similar to benzimidazole. PV4P was found to exhibit even less affinity for the same metal species in xylene than PBI, Figure 13. In fact, Co and Cu failed to be adsorbed by PV4P. Several reasons may account for this observation. PV4P contains less nitrogen sites per repeat unit than PBI. The PV4P which was used, in order to remain insoluble, was 2% cross-linked with divinyl-benzene; therefore at least 2% less surface area was probably available with PV4P. On the other hand, the theoretical capacity of PV4P is about 50% greater than PBI, 9000 mmol/Kg of PV4P, which could have caused one to predict higher amounts of metal uptake for PV4P relative to PBI per unit mass.

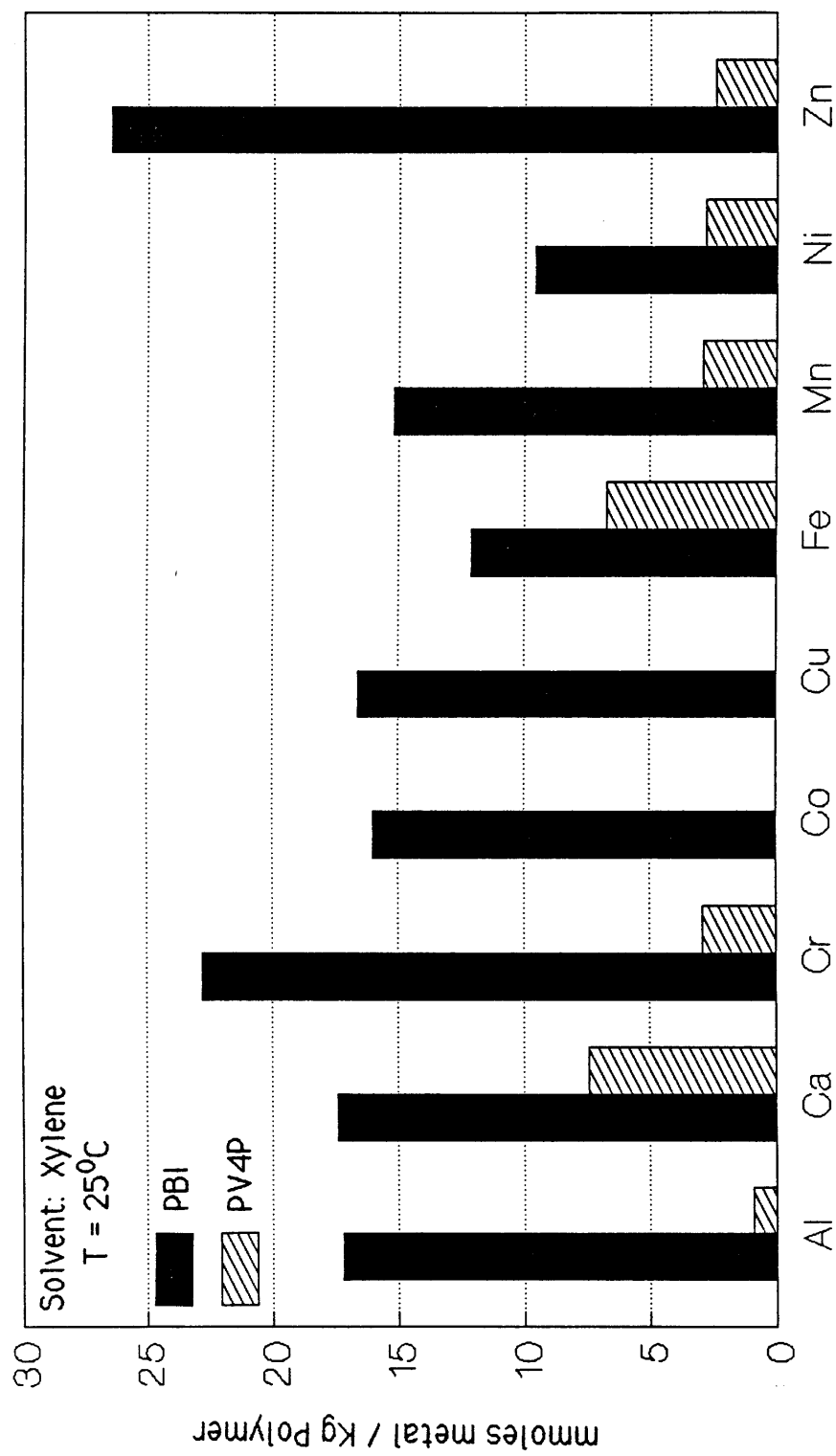


Figure 13: Organic Adsorption PBI versus PV4P at 25°C

3.2 DESORPTION

Desorption is simply the process where the extracted material bound to the extractant is released. In our case, the extracting material is the PBI and the extractants are metal ions. Desorption will probably take place in the following manner. The metal will be loosely bound to the PBI and a counter ion near-by will begin to attract the metal. As the metal is attracted away from the PBI it will again begin to re-hydrate to a full hexaaquo and the corresponding double layer of waters. Then the metal is fully released.

The desorption of metals should be very pH dependent. As stated earlier, the PBI will exist in different forms at different pH's. At pH 7, the PBI will be in the neutral form, this form presumably can adsorb and desorb. However, at pH 4 the PBI should be the protonated form, the pKa is 5.6. The hydrogen ion will result in the loss of aromaticity in the imidazole ring, thus losing all the favorable energetics by bonding to the metal. Thus the metal will easily be released by the PBI at low pH's.

The desorption data are found in Table 13 and the graphical presentation of the desorption versus the adsorption of metals is presented in Figure 14. Little metal is released by the PBI, for Fe(III) it's 490 mg metal/Kg PBI-Metal and for Ca(II) it's only 120. However, the desorption data do

Table 13: **Aqueous Metal Desorption Data**

<u>Metal</u>	<u>Desorption in mg Metal/ kg PBI-Metal</u>	
	pH 4	pH 7
Ca	120	65
Mn	60	35
Fe (II)	300	110
Fe (III)	490	210
Cu	245	140

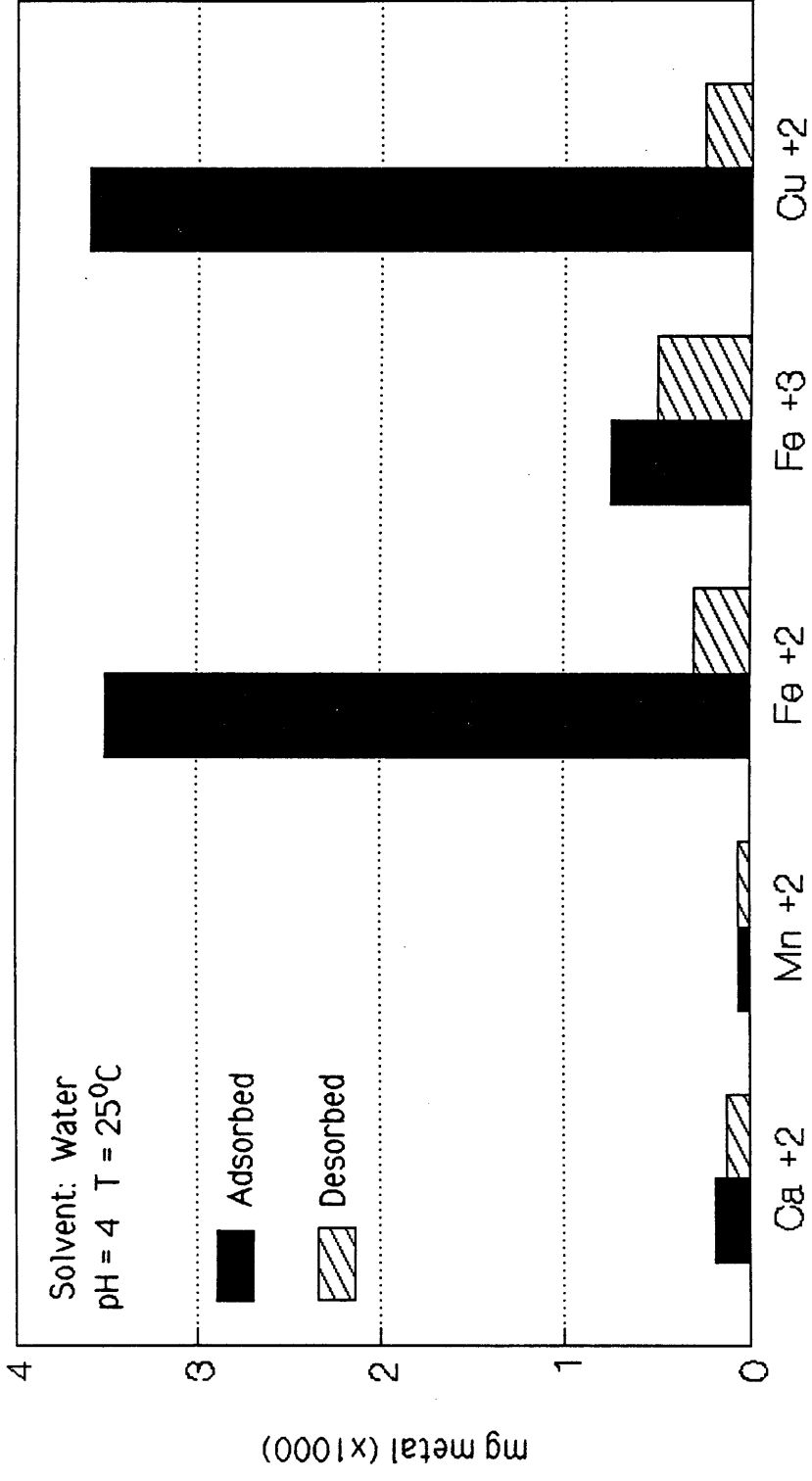


Figure 14: Aqueous Adsorption versus Desorption pH 4 and 25°C

follow a more logical trend than the adsorption data. It seems clear that the more strongly the metal is adsorbed or in other words the stronger the metal-PBI bond, the poorer the metal is released. This makes complete sense that, if the PBI-metal bond is strong then it is hard to break that bond.

The desorption of metals from PBI is also very pH dependent, Figure 15. It is easily seen that at pH 4 more metal is desorbed than at pH 7. The pH dependence of desorption even follows the predicted order. In that the desorption at pH 4 should be greater than at pH 7 because at lower pH's the imidazole ring will be protonated. Once it is protonated the energetically stable metal bond is weakened, because the aromaticity of the imidazole ring was destroyed. Since this bond is weakened, it would be easier for another H^+ to replace the metal ion.

3.3 CHROMATOGRAPHY

Inorganic adsorbent materials have been used for both thin layer (35) and column chromatography (36,37). However, open-column (classical liquid chromatography) and high performance liquid chromatography (HPLC) have been used much more extensively. In this work both HPLC and classical LC with PBI as the stationary phase will be discussed.

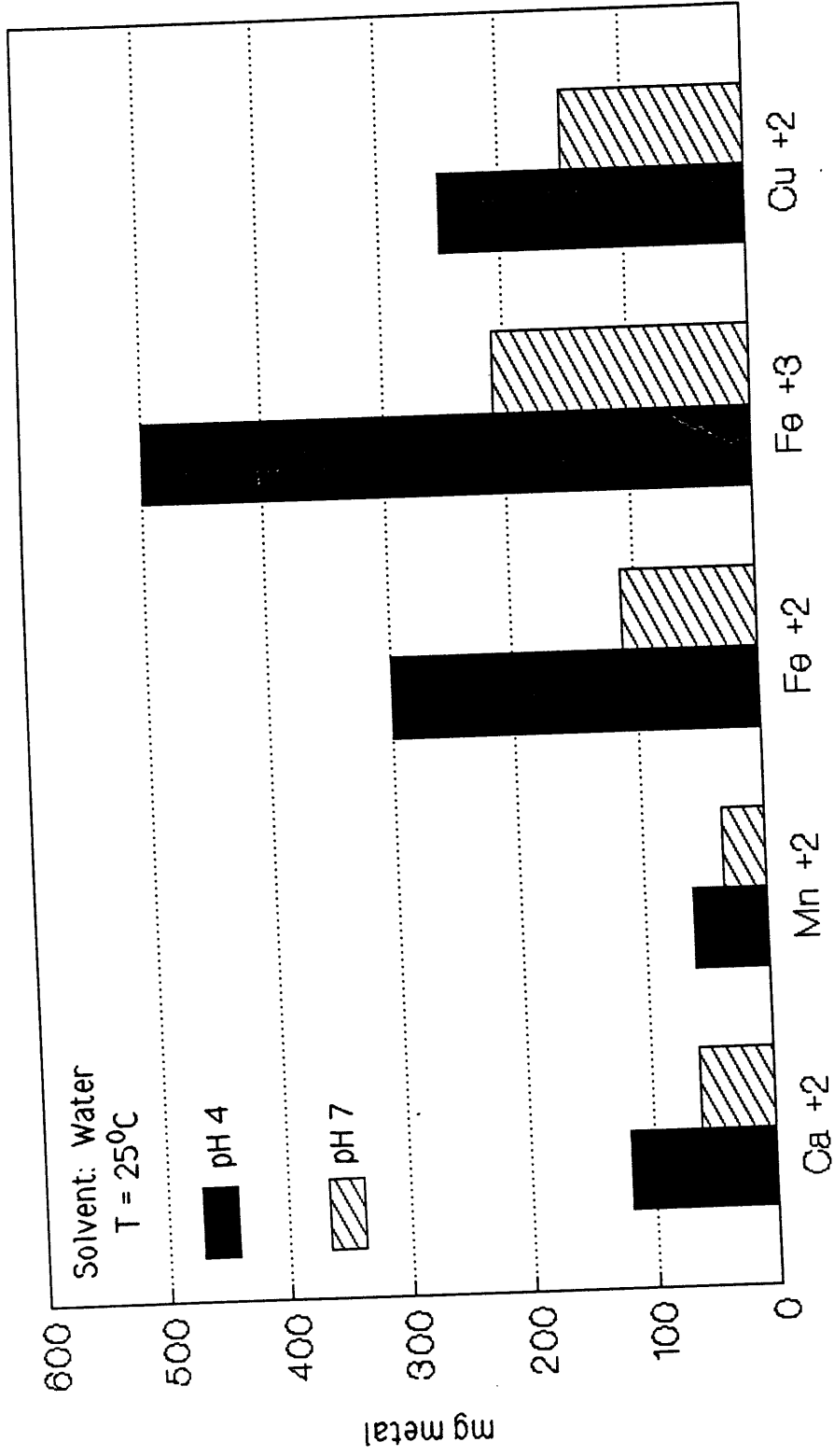


Figure 15: Aqueous Desorption pH 4 versus 7 at 25°C

To understand the later discussion regarding chromatography, it is necessary to briefly review the mechanism of separation in adsorption chromatography. Once the sample has been placed onto the column and the mobile phase is introduced, the different components begin to interact with the stationary phase. The cation will begin to be attracted by the imidazole ring and is held for a variable amount of time depending on the strength of the interaction. The cation is released because another cation approaches the imidazole ring, whether it be another cation from the sample or the abundant H^+ species. Therefore the separation of the cations is dependent on the adsorption or interaction between the cations and the polymer.

There are several characteristics that make a good stationary phase for the separation of cations. First, the stationary phase has to selectively adsorb and desorb cations, thus creating separation between cations. Second, the stationary phase should only weakly adsorb and strongly desorb the cations. This will result in well separated and well resolved peaks, that elute quickly with a moderate strength solvent. Third, the polymer itself should withstand high pressures and a wide range in pH.

Two different types of chromatography were attempted with PBI. The first was High Performance Liquid Chromatography (HPLC), which failed miserably. The second was a simple gravity feed column chromatography.

The HPLC experiment really never could be attempted. The first step for HPLC was to pack an analytical column, 4.6 mm internal diameter by 25 cm.

The procedure requires that the column be packed under high pressure. The PBI beads could not even take as little as 3,000 psi without being completely crushed. In conclusion, HPLC would be impossible with PBI beads currently available due to their pressure instability. The other possibility of HPLC with PBI would be to polymerize a very thin coating of PBI onto small glass beads. This was attempted with a procedure Celanese uses to coat glass plates with PBI. The procedure consists of making a 3% PBI solution in N,N'-dimethylacetamide (DMAC) and mixing the glass beads in the solution. After thirty minutes separate the solution and beads by filtration and immediately wash the beads with large quantities of water. Then dry the beads in a vacuum oven at 110°C for at least 10 hours. However, all attempts to produce PBI coated beads never worked. The beads and PBI would all form one very hard ball. No individual beads could ever be made.

The second chromatography experiment involved gravity feed column chromatography. The details of packing the buret for this chromatography were discussed in the Experimental chapter. The experiment consisted of placing 5 mg of Co(II), Fe(III), and Cu(II) onto the top of the column and

running the solvent (water, pH 7) through the column at 1 ml/min. The eluted mobile phase was collected with 4ml going into each testtube. Then the three components were detected first by human eye and second by AA. The cobalt came off the column in the solvent front. The iron band broaden and was still coming off the column after running over 120 ml of eluted mobile phase. The concentration of the iron was equal throughout its release from the column . In an effort to get the iron off the column the solvent was changed to pH 4 and then pH 1. However, the iron could not be totally removed. Copper was never detected as leaving the column, however it could have come off so slowly that the concentration of the copper wasn't ever noticeable. Clearly this shows that the PBI adsorbs metals but often desorbs them slowly in an irreversible fashion. In the case of cobalt, no adsorption was detected so the metal went unretained through the column. Some of the iron was left on the column because the iron forms a bond to the PBI which is too strong to break. In the case of copper, it is very tightly bond to the PBI so none of the metal could be passed through the column.

4.0 CONCLUSIONS

The extent to which PBI adsorbs positive and neutral metal species is so marginal that its use as a solid phase extractant agent is questionable. The trend in adsorption of metal species in organic and aqueous solvents is very difficult to justify. Besides PBI's poor adsorption, its desorption of metals is so low that its use as a SPE in a metal recovery process would not work. While its high thermal stability and resistance to strongly acidic and basic conditions are noteworthy, a number of commercially available cationic exchange resins yield much higher distribution coefficients between pH's 1 - 7 than PBI. As indicated previously PBI would exhibit much higher affinity for metals at low pH if the metal were in an anionic form. Unfortunately this situation is not often encountered with the possible exception of the plating industry.

The low affinity of PBI for metal species could possibly be put to advantage in the rapidly growing area of ion chromatography. However, most of the metals studied were very poorly desorbed. This would result in such extensive peak tailing, that PBI could never be used except for the crude separation of only a few metals.

Appendix 1: Analytical Techniques

The choice of using the Atomic Absorption (AA) or the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was based on two facts. First, all the organic solvent determinations had to be run on the ICP. Second, the aqueous solvent determinations could be done with either technique. But the decision was based on whether the ICP was working (only about one half of the aqueous samples could be run on the ICP).

The ICP was an Applied Research Laboratories (ARL) ICPQ 137000. Which has 1.0 meter Pachen-Runge polychrometer set to analyze 35 elements. The specific details about the spectrometer and analytical techniques for the analysis of metals can be found in Dr. D. W. Hausler's thesis, The Development of on-line Liquid Chromatograph-Inductively Coupled Plasma-Atomic Emission Spectrometer for the Analysis for Trace Organically Bound Metals and Metalliods in Coal Derived Products completed in October 1980.

The AA was a Varian 175, which Dr. Long graciously allowed me to use frequently. The procedures for the analysis of all elements determinable by AA, can be found in Analytical Methods for Flame Spectroscopy a Varian techtron Publication (printed in Australia in 1972).

Appendix 2: Polyvinyl-4-pyridine

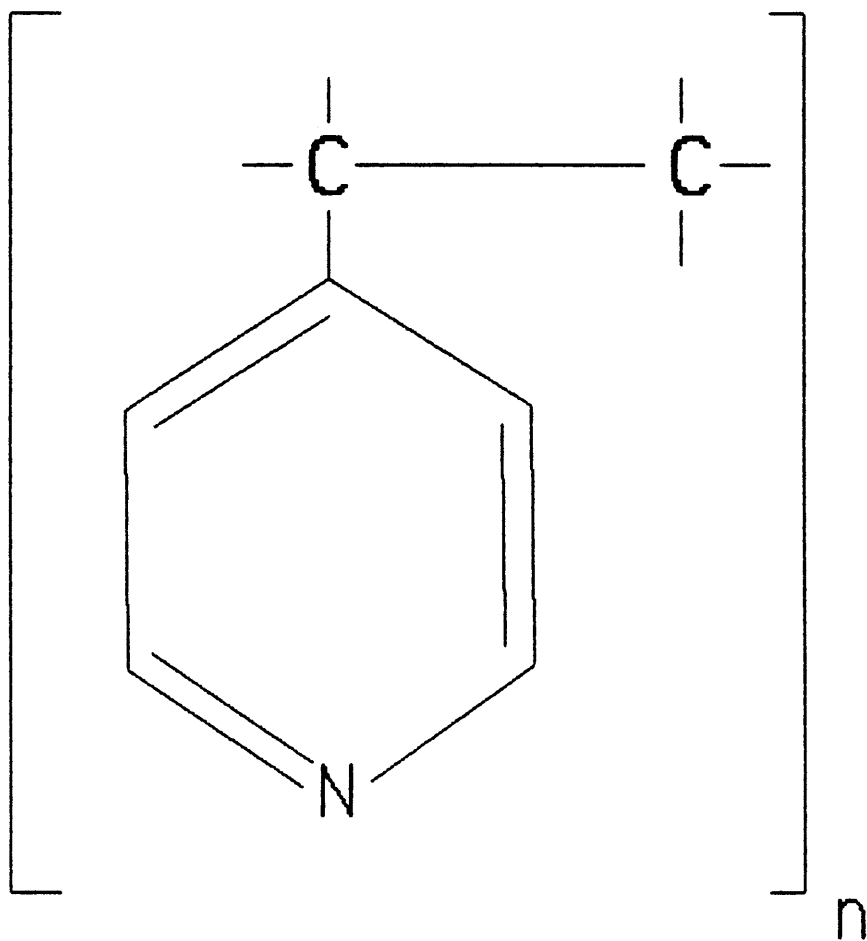
PV4P, shown on the next page, was chosen based upon the pyridine functionality on the polymer. To ideally compare PBI to PV4P, it was wished to not cross-link the PV4P. However, uncross-linked PV4P dissolves in xylene, but 2% divinylbenzine cross-linked results in a nonsoluble polymer, this polymer was used.

PV4P was supplied by Reilly Tar & Chemical Company in a wide variety of sizes. This sample was sieved to acquire a range of 75 - 150 μm size particles.

The physical properties of PV4P are summarized here:

Theoretical Capacity (meq/g)	9.5
Physical Structure	
Specific Surface Area (m^2/g)	0.4
Bulk density (g/ml)	1.154
% Swelling in Toluene	8 - 12
Particle Size (μm)	75 - 150
Thermal Stability	200 $^{\circ}\text{C}$

Poly-4-Vinylpyridine



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Vita

Peter Jonathan Walter, the son of Donald and Erdine Walter, was born October 19, 1962 in Anaheim, California. He began elementary school at Ford School in Fullerton, California. His family moved to Fairfax, Virginia in 1970. He then proceeded to attend John C. Wood Elementary, Sidney Lanier Intermediate, and graduate from Fairfax High School in June 1980.

He began his college education at George Mason University where he received his Bachelor of Science in chemistry degree in May 1984.

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In January 1987, he will continue his graduate studies towards a Ph.D. at the University of Maryland.

A handwritten signature in black ink, reading "Peter J. Walter". The signature is written in a cursive style and is positioned diagonally across the lower half of the page.