

Immobilized *N*-Methyl-D-glucamine as an Arsenate-Selective Resin

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Immobilization of *N*-methyl-D-glucamine (NMDG) on poly-(vinylbenzyl chloride) beads yields an effective and highly selective sorbent for arsenate ions. Three important parameters in the resin's high As(V) affinity and selectivity are the structure of the ligand, its ionic form, and the cross-link density of the polymer. The NMDG resin cross-linked with 2 wt % divinylbenzene is far more selective than commercially available analogues, especially when sulfate and chloride ions are present in solution at high concentrations. Selectivity studies at neutral pH indicate that the protonated tertiary amine moiety is an important component of the complexation mechanism. The NMDG resin also has a high affinity for the un-ionized As(V) species at pH 1.

Introduction

Arsenic is a toxic and ubiquitous element that can be found above the maximum contaminant level of 10 $\mu\text{g/L}$ recommended by the World Health Organization in groundwater (1). Geogenic contamination has been reported in many countries, including India and China (2). The situation is particularly severe in Bangladesh with 30 million people being exposed daily to high concentrations of arsenic. (3) The U.S. Environmental Protection Agency has decreased the arsenic limit in drinking water from 50 to 10 $\mu\text{g/L}$ (4). The new standard must be complied with by January 2006.

Arsenic occurs mainly as arsenate (As(V)) and arsenite (As(III)) in groundwater. The distribution of As(III)/As(V) varies significantly (5, 6). Among the sorption technologies available to remove arsenic, most have a greater affinity for As(V) than As(III), thus requiring a preoxidation step to convert arsenite to arsenate. In the pH range typical of water in the environment, As(V) but not As(III) can be removed by ion exchange since the latter is present as the un-ionized H_3AsO_3 . The principal disadvantage of strong base ion-exchange resins is their lack of selectivity in the presence of sulfate (7) and chloride ions (8, 9). The use of a nitrate-selective resin (Mitsubishi A-490) allowed an increase in the number of bed volumes treated to breakthrough in the presence of sulfates as compared to a trimethylbenzylammonium resin (Purolite A-505) (10), but selectivity still requires improvement.

The *N*-methyl-D-glucamine (NMDG) ligand has been immobilized onto cross-linked polystyrene beads and de-

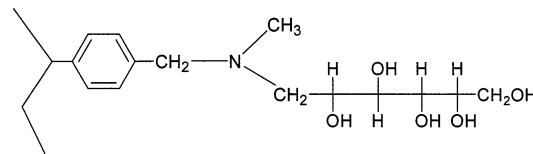


FIGURE 1. Polymer-supported *N*-methyl-D-glucamine.

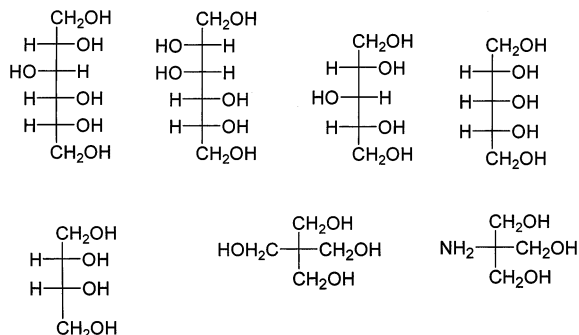


FIGURE 2. Polyol structures: D-sorbitol, D-mannitol, xylitol, adonitol, meso-erythritol, pentaerythritol, and tris(hydroxymethyl)aminomethane.

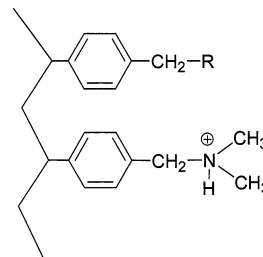


FIGURE 3. Bifunctional polyol-amine resins (R = sorbitol, mannitol, adonitol, xylitol, erythritol, pentaerythritol).

veloped in 1957 for boron removal from irrigation water (11, 12). Several macroporous NMDG resins are available: Amberlite IRA-743 (Rohm and Haas), Purolite S-108 (Purolite), Diaion CRB-02 (Mitsubishi Chemical), and Lewatit MK-51 (Bayer). The NMDG ligand consists of tertiary amine and sorbitol moieties (Figure 1). Along with boron removal, the NMDG resin has been studied for its affinity for the oxyanions of Ge(IV), V(V), Mo(VI), As(V), As(III), W(VI), Se(IV), Se(VI), and Sn(IV) (13, 14); neither As(III) nor As(V) sorption was observed. In a study with the free base form of commercially available NMDG resins, no arsenate sorption was observed in experiments with As(V) and an additional series of oxyanions (15).

This research reports the first extensive study on arsenate sorption by the NMDG resin. Its performance will be compared to available sorption technologies identified by the U.S. EPA. To fully explore the arsenate interaction with the ligand, a series of monofunctional polyol resins (Figure 2) and bifunctional resins, in which the amine moiety was separated from the polyol group (Figure 3), were also synthesized and studied.

Experimental Section

The suspension polymerization of vinylbenzyl chloride (VBC) (16) has been described. The beads were sieved, and unless otherwise indicated, a particle size of 250–425 μm was used. Chemicals were reagent grade. All glassware was acid-washed in Nochromix solution and rinsed thoroughly with Nanopure water (Millipore Direct-Q 5 system). As(V) solutions were

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prepared with Na₂HAsO₄·7H₂O (Alfa Aesar). Anhydrous Na₂SO₄ (Mallinckrodt) and NaCl (Fisher Chemicals) were used for the selectivity studies. The following polyols were immobilized: D-sorbitol (Acros Organics), D-mannitol (Acros Organics), adonitol (ICN Biomedicals), xylitol (Avocado Research Chemical Ltd.), meso-erythritol (Acros Organics), pentaerythritol (Acros Organics), 2-amino-2-methyl-1,3-propanediol (Acros Organics), 3-amino-1,2-propanediol (Acros Organics), and tris(hydroxymethyl)aminomethane (Acros Organics).

Arsenate was analyzed by the molybdenum blue method (17) using a Spectronic 21D spectrophotometer. The reagent was prepared by mixing 5 mL of ammonium heptamolybdate solution (1 g in 100 mL of 6.0 N sulfuric acid) with 5 mL of hydrazine sulfate solution (0.15 g in 100 mL of water) and diluting to 50 mL with water. A 5 mL aliquot of the reagent was added to the sample (containing at least 0.1 µg of arsenic) in a 25 mL volumetric flask, and color developed over 15 min at 60 °C. After the sample was cooled, Nanopure water was added to the 25 mL mark, and the absorbance was read at 840 nm. The calibration curve was determined between 0.16 and 0.96 mg/L (the limit of detection was estimated to be 20 µg/L). At lower concentrations, and in the presence of phosphate, solutions were analyzed by ICP-MS (Hewlett-Packard 4500 series).

Sorption Experiments. Sorption experiments were done in 60 mL nalgene bottles rinsed with Nanopure water after being washed with a 10% HNO₃ solution. The isotherm was determined by increasing the amount of sorbent at a fixed volume of arsenate solution. A 3-d contact time ensured equilibrium.

In studying the effect of pH, periodic microadditions of concentrated HCl or NaOH solutions controlled the pH. Rate determinations with 2 L of 1 mg/L As(V) solutions contacting 100 mg of resin were done in a 5 L beaker from which 20 mL aliquots were removed at each of six time periods (15 min, 30 min, 1 h, 2 h, 4 h, 8 h, and 24 h). Stirring was by overhead stirrer set to 200 rpm. Rate determinations with 40 mL of 1 mg/L As(V) solutions contacting 25 mg of resin were done in six separate 60 mL nalgene bottles that were placed on a shaker. Each of the six bottles was shaken for a different period of time (5 min, 15 min, 30 min, 1 h, 2 h, and 24 h).

Synthesis of Monofunctional Resins. PolyVBC beads (1.6 g) were placed in a 250 mL round-bottom flask equipped with a condenser and overhead stirrer and refluxed for 17 h with (a) 150 mL of 40% aqueous dimethylamine (DMA) to give the DMA resin; (b) 150 mL of diethylamine (Acros Organics) to give the diethylamine resin; (c) 20 mL of diethanolamine (DEA, Acros Organics) and 100 mL of dioxane to give the DEA resin; (d) 20 g of *N*-methyl-D-glucamine (NMDG, Acros Organics), 10 mL of water, and 100 mL of dioxane to give the NMDG resin; or (e) 10 g of tris(hydroxymethyl)aminomethane (Tris), 25 mL of water, and 200 mL of dioxane to give the Tris resin. After washing, the beads were conditioned with 1 L each of water, 1 M NaOH, water, 1 M HCl, and water, then vacuum-dried at 70 °C for 17 h and characterized by FTIR and nitrogen elemental analysis (18).

Synthesis of Bifunctional Polyol–Amine Resins. Bifunctional resins were prepared by first grafting a polyol (sorbitol, mannitol, adonitol, meso-erythritol, or Pentaerythritol) via a Williamson ether synthesis on polyVBC beads. In a typical experiment, 6 g of sorbitol was added to 150 mL of *N*-methyl-2-pyrrolidinone (NMP) in a 250 mL round-bottom flask equipped with a condenser and overhead stirrer. (The mixture was heated to 70 °C if necessary to dissolve the sugar.) NaH (0.300 g, 60% dispersion) was then added under a nitrogen sweep and allowed to react for 2 h, followed by the addition of polyVBC beads (2 g) swollen in 50 mL of NMP. The mixture was stirred for 17 h at 70 °C, after which time the beads were

TABLE 1. Nitrogen Elemental Analysis of *N*-Methyl-D-glucamine Resins

polymer support	N content (mmol/g)
2% DVB gel polyVBC	2.62
3% DVB gel chloromethylated polystyrene	2.68
5% DVB macroporous polyVBC	2.58
12% DVB macroporous polyVBC	1.81

TABLE 2. Nitrogen Elemental Analyses and Surface Areas of Commercial *N*-Methyl-D-glucamine Sorbents

resin	sorbent type	manufacturer	N content (mmol/g)	BET surface area (m ² /g)
IRA-743	MR beads	Rohm and Haas	2.24	20.84
CRB-02	MR beads	Mitsubishi	2.26	27.91
S-108	MR beads	Purolite	2.27	20.58
GCP	cotton fibers	Chelest	1.37	0.26
GRY	cotton fibers	Chelest	1.05	0.27
GRY-L	cotton fibers	Chelest	1.13	0.20

TABLE 3. Effect of NMDG Ionic Form on Percent of As(V) Sorbed^a

ionic form	20 mg	30 mg	50 mg	100 mg
NMDG (protonated) (%)	73.5	96.1	99.4	99.9
NMDG (free base) (%)	8.71	9.03	10.5	22.0

^a Resin (20, 30, 50, and 100 mg) contacted for 22 h with 20 mL of As(V), 100 mg/L, pH 6.

recovered, washed with NMP, and further reacted with 200 mL of DMA, diethylamine, or DEA at reflux for 24 h. After being washed, the beads were treated as above.

Synthesis of NMDG–DMA Resin. PolyVBC beads (2 g) preswollen in 50 mL of dioxane were placed in a 250 mL round-bottom flask equipped with a condenser and overhead stirrer. A solution of 1 g of NMDG, 10 mL of water, and 150 mL of dioxane was prepared and added to the beads. The mixture was refluxed for 3 h. After washing with dioxane and water, the beads were dried on a buchner funnel and refluxed with 150 mL of DMA for 17 h. After being washed again, the beads were treated as above.

Results and Discussion

The nitrogen elemental analyses of the NMDG resins prepared for this study are summarized in Table 1. In each case, the experimental nitrogen analysis is >90% of the theoretical value, indicating complete (or almost complete) substitution. Table 2 summarizes the nitrogen elemental analyses and Brunauer–Emmett–Teller surface areas of commercially available NMDG sorbents used in this study.

Effect of Conditioning on the NMDG Resin. The ionic form of the NMDG resin (i.e., free base or protonated) is determined by whether elution with 1 M NaOH/H₂O follows the conditioning sequence given in the Experimental Section. It is found to be a critical factor in the affinity of the resin for As(V): arsenate sorption is significantly higher when the ligand is in the protonated form (Table 3). With 50 mg of the protonated resin contacting 20 mL of solution at pH 6 containing 100 mg of arsenate ions/L, 99.4% of the arsenate is complexed; this compares to 10.5% being complexed when the ligand is initially in the free base form. (At pH 6, the amine moiety may be partially protonated, and this may account for the low level of sorption observed when the resin is in the nominally free base form; weak base resins have a low level of counterion uptake at pH levels greater than 7; 19.)

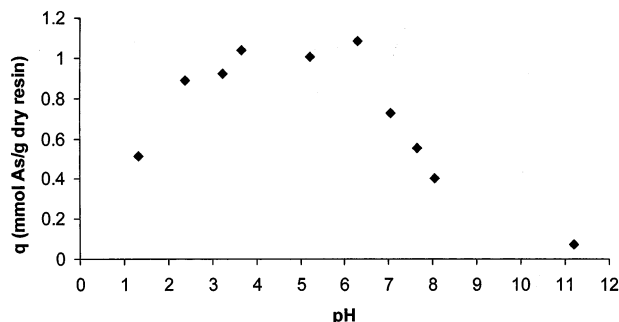


FIGURE 4. Sorption of As(V) on NMDG resin as a function of pH. NMDG resin (20 mg) contacted with 20 mL of As(V) solution (97.74 mg/L). pH periodically adjusted with concentrated HCl or NaOH. Contact time of 3 d.

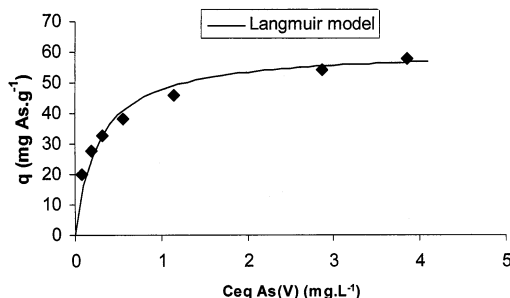


FIGURE 5. Isotherm of the NMDG resin (protonated form).

Effect of Solution pH. Arsenate sorption by the NMDG resin was quantified from solutions at pH values of 1–11 (Figure 4). Maximum sorption occurs between pH 4 and pH 6.5 when H_2AsO_4^- and HAsO_4^{2-} are the predominant species in solution (20) and the tertiary amine on the resin is protonated. Sorption decreases sharply starting at pH 7 where HAsO_4^{2-} predominates and the ligand is mostly in the free base form. Sorption at pH 1.25 is still significant (capacity of 0.5 mmol As/g_{resin}). At this pH, H_3AsO_4 is the main species present in solution (approximately 85%), which may preclude ion exchange as a significant component of the sorption mechanism. However, approximately 15% of the arsenate is present as H_2AsO_4^- ; it is thus possible that ion exchange is occurring, but the high level of sorption would require a rapid displacement of the $\text{H}_3\text{AsO}_4/\text{H}_2\text{AsO}_4^-$ equilibrium.

NMDG Sorption Isotherm. Arsenate complexation by the NMDG resin is characterized by an isotherm where the sorption sites are saturated at low residual solution concentrations (Figure 5). The data fit the Langmuir isotherm with the equation:

$$q_{\text{eq}} = (60.5)(3.74C_{\text{eq}})/(1 + 3.74C_{\text{eq}})$$

where q_{eq} and C_{eq} represent the equilibrium uptake capacity (mg/g) and solution concentration (mg/L), respectively (correlation coefficient = 0.97). The saturation capacity is calculated to be 60.5 (± 1.5) mg/g (0.808 mmol/g), and the binding constant is 3.74 (± 0.09) L/mg (280 L/mmol). The sorption capacity at low solution concentrations is significant: at $C_{\text{eq}} = 0.5$ mg/L, the sorption capacity is 39.4 mg/g (0.526 mmol/g). For comparison, at $C_{\text{eq}} = 5$ mg/L, Alcoa F-1 activated alumina has a capacity of 20 mg/g (0.27 mmol/g) (21), and iron oxide-coated sand has an As(V) capacity estimated to be 0.16 mg/g (0.0021 mmol/g) (22).

NMDG Selectivity. The high sorption capacity of a resin can decrease significantly in the presence of competing ions. Sulfate is commonly present in groundwater with a concentration exceeding that of arsenic by several orders of magnitude: in China, arsenic-contaminated groundwater has been reported to contain more than 800 mg/L of sulfate

TABLE 4. As(V) Sorption by NMDG Resin in the Presence of Phosphate Ions at pH 6^a

initial phosphate (mg/L)	% As(V) sorbed
0	99.97
20	99.99
40	99.98
100	99.96
200	99.93
400	99.89

^a 100 mg of NMDG resin contacting 20 mL of As(V) solution with increasing amounts of phosphate for 39 h.

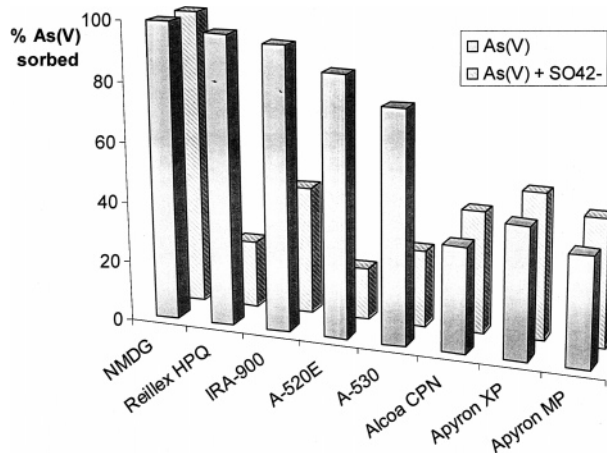


FIGURE 6. As(V) affinity and selectivity by NMDG and commercially available sorbents. 100 mg of sorbent contacted with 20 mL of [As(V), 100 mg/L, pH 6.5] or [As(V), 100 mg/L + sulfate, 560 mg/L, pH 6.8]. Contact time of 8 d.

ions (23). Ion-exchange resins have not been recommended for As(V) when the sulfate concentration exceeds 120 mg/L (24). Phosphate behaves similarly to arsenate and interferes with arsenate sorption (25–27).

The selectivity of the NMDG resin for arsenate in the presence of phosphate, sulfate, and chloride ions was investigated. As summarized in Table 4, As(V) sorption remains at 99.9% or greater even at a phosphate level of 400 mg/L (the corresponding initial molar ratio of phosphate to arsenate is 10:1). A level this high is unlikely to be found in groundwater, but it demonstrates the remarkable selectivity of the NMDG resin. This selectivity is noteworthy, especially when one considers that both phosphate and arsenate have similar pK_a values (2.2, 7.0, and 11.5 for H_3AsO_4 and 2.15, 7.20, and 12.38 for H_3PO_4) (28) and similar chemistry in homogeneous solution (29).

Sulfate selectivity was studied with the NMDG resin and its performance compared to six commercially available products (three organic resins and three inorganic sorbents). The resins were Reillex HPQ (a methylated vinylpyridine resin, reported to be effective in removing As(V)) (30), Amberlite IRA-900 (a benzyltrimethylammonium resin), and Purolite A-530 (a bifunctional tripropyl-trihexylammonium resin that selectively sorbs pertechnetate ions from water) (31). The inorganic sorbents were Alcoa CPN activated alumina, Apyron XP (a composite of aluminum (75–100 wt %) and manganese (0–25 wt %) oxides) (32), and Apyron MP (the latter two being metal oxide-based sorbents used in pilot scale studies to treat arsenic-contaminated water in Bangladesh) (33). As shown in Figure 6, the NMDG resin has the highest affinity of the organic resins; HPQ slightly outperforms IRA-900 and significantly outperforms A-530; however, despite a high level of arsenate complexation when it is the only ion present in solution, only the NMDG resin is arsenate-selective in the

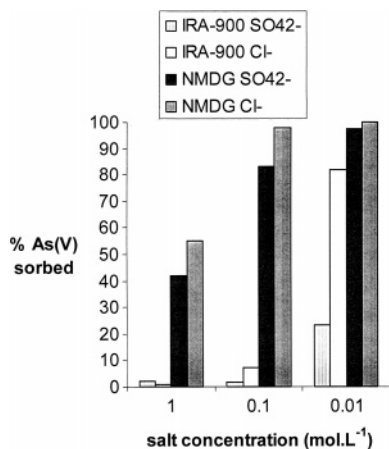


FIGURE 7. Comparative As(V) affinity and selectivity of NMDG and Amberlite IRA-900 resins. 100 mg of sorbent contacted with 20 mL of As(V), 100 mg/L, pH 6.5, in the presence of sulfate or chloride ions.

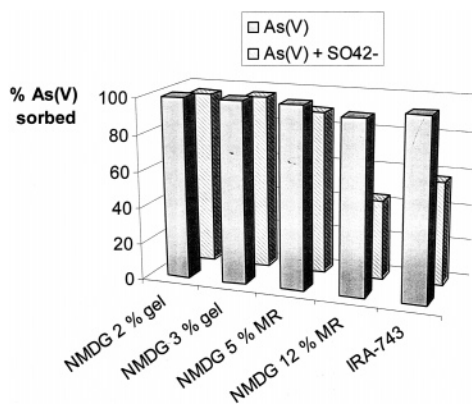


FIGURE 8. Effect of bead type and cross-linking ratio on As(V) affinity by NMDG resins. Enough resin to give 0.3 mmol of N contacted with 20 mL of [As(V), 100 mg/L, pH 6] or [As(V), 100 mg/L + sulfate, 560 mg/L, pH 6]. Contact time of 21 h.

presence of 560 mg/L of sulfate ions. The three inorganic sorbents have comparable arsenate affinity and are selective for it in the presence of sulfate, but their sorption level is significantly less than that of the NMDG resin.

The selectivity of the NMDG resin as compared to IRA-900 is evident from the data given in Figure 7 where arsenate sorption is quantified in the presence of 0.01, 0.10, and 1.0 M concentration of chloride and sulfate ions. When the resins are contacted with a solution of 100 mg As(V)/L in 0.10 M of either Cl⁻ or SO₄²⁻, the NMDG resin sorbs 96% and 83% of the arsenate, respectively, while IRA-900 sorbs less than 10% As(V) in the presence of either competing ion. The trends are identical at all three concentrations. Furthermore, sulfate ions interfere more than chloride ions, though, as seen from the results in 0.01 M solutions, the effect was much more pronounced with IRA-900 than with the NMDG resin.

Effect of Cross-Linking. The effect of the level of cross-linking within polystyrene supports on the affinity and selectivity of NMDG resins was studied at 2%, 3%, 5%, and 12% divinylbenzene (DVB). Results reported above have been with DVB at the 2% level. The 3% DVB resin was prepared from chloromethylated polystyrene through a commercial supplier who provided a sample. As shown in Figure 8, its performance is comparable to that of the 2% DVB resin, indicating that the secondary cross-linking inherent to chloromethylated beads has no effect on the resin's arsenic affinity and selectivity.

To ensure ionic accessibility, the higher cross-link levels were prepared as macroporous supports. It was determined

(Figure 8) that arsenate affinity decreased slightly when cross-linking was increased to 5% DVB and further decreased at 12% DVB, but selectivity decreased most significantly at 12% DVB. For comparison, IRA-743 performed most like the resin with 12% DVB cross-linking. It is thus concluded that the flexibility of the polystyrene chains is an important factor in the NMDG ligand's selectivity for the arsenate ion.

Comparative Study with Commercially Available NMDG Resins and Fibers. Commercially available NMDG sorbents were obtained from Rohm and Haas, Mitsubishi, Purolite, and Chelest. Nitrogen elemental analyses and BET surface areas are reported in Table 2. Before contact with arsenate solution, the resins and fibers were eluted with HCl to protonate the amine moiety and vacuum-dried.

As summarized in Table 5, the three commercial resins (IRA-743, CRB-02, and S-108) complex more than 99% of the arsenate present in a 100 mg/L solution. CRB-02 attained the lowest residual concentration of 80 µg/L, though the NMDG resin had a residual concentration of less than 50 µg/L. Selectivity, however, proved once more to be the critical feature of the NMDG resin: in the presence of 560 mg/L of sulfate ions, sorption by IRA-743, CRB-02, and S-108 dropped from 99.7%, 99.9%, and 99.1%, respectively, to 79.4%, 90.3%, and 77.9%, respectively; the NMDG had a negligible decrease (from 99.9% to 99.4%).

The NMDG fibers (GCP, GRY, and GRY-L) performed similarly to the NMDG resin with respect to affinity and selectivity. However, differences in the level of ligands on the NMDG resin and the fibers makes it important to compare the sorption capacities at a given equilibrium solution concentration. The data in Table 5 show that GRY, GRY-L, and the NMDG resin have a common solution concentration (approximately 0.04 mg/L), and at that concentration, the sorption capacities are less than half for the fibers as compared to the NMDG resin (6.92 and 7.45 mg As/g for the fibers vs 16.4 mg As/g for the resin).

Comparative Study with Bifunctional Polyol-Amine Resins. To probe the nature of the arsenate-NMDG interaction, a set of resins was prepared that had separate polyol and amine groups. In each case, enough resin to give 0.3 mmol of amine was contacted with arsenate or arsenate/sulfate solution. The results, summarized in Table 6, are given in terms of percent complexed and the amount of arsenate left in solution (as mg/L). By comparison to the NMDG resin (<1 mg/L in the absence or presence of 560 mg/L sulfate at pH 5.6), arsenate sorption by the monofunctional dimethylamine (DMA) resin shows that the amine group is important to the observed affinity (15.6 mg/L remaining in solution) but not to its selectivity (80.7 mg/L arsenate in solution in the presence of sulfate ions). On the other hand, the polyol moiety alone is ineffective: monofunctional sorbitol, mannitol, adonitol, and xylitol resins have a negligible affinity (1.5–6%) for the arsenate ion. [Based on steric considerations, it is likely that immobilization occurs through the terminal (primary) hydroxyl groups rather than the interior (secondary) groups, and this is supported by results with picolyl chlorides (34). However, some reaction at the interior sites cannot be ruled out, though this does not affect the conclusions, given the low levels of arsenate in solution.] Thus, although the polyol moiety has a critical role in the selectivity displayed by the NMDG resin toward arsenate, it is ineffective when isolated from the amine moiety.

Combining the dimethylamine and polyol moieties on separate sites within a given polymer (entries 3–6, Table 6) shows enhancement in affinity and selectivity relative to the monofunctional DMA resin, but both are still significantly below the results with the NMDG resin. Sorbitol-DMA outperforms mannitol-DMA (residual arsenate of 5.68 vs 10.2 mg/L, respectively), the latter performing similarly to the five-carbon polyols adonitol-DMA and xylitol-DMA.

TABLE 5. As(V) Affinity and Selectivity of Commercial NMDG Sorbents^a

resin	C_{eq} As(V) (mg/L) [As only]	% As(V) sorbed [As only]	q (mg/g) [As only]	C_{eq} As(V) (mg/L) [As + sulfate]	% As(V) sorbed [As + sulfate]	q (mg/g) [As + sulfate]
NMDG	0.03	99.9	16.4	0.63	99.4	16.6
IRA-743	0.30	99.7	14.7	20.7	79.4	13.3
CRB-02	0.08	99.9	14.9	9.70	90.3	13.7
S-108	0.89	99.1	14.8	22.2	77.9	11.8
GCP	1.42	98.6	8.88	1.21	98.8	9.06
GRY	0.04	99.9	6.92	2.22	97.8	6.87
GRY-L	0.04	99.9	7.45	1.04	98.9	7.46

^a 0.3 mmol of N contacted with 20 mL of [As(V), 100 mg/L, pH 5.8] or [As(V), 100 mg/L, SO_4^{2-} , 560 mg/L, pH 6.0]. Contact time: 3 d.

TABLE 6. As(V) Affinity of Bifunctional Polyol–Amine Resins^a

	ligand	N content (mmol/g)	% As(V) sorbed [As alone]	%As sorbed [As + sulfate]
1	NMDG ^b	2.51	99.9 (0.07 mg/L) ^c	99.0 (0.95 mg/L) ^b
2	DMA	3.86	84.2 (15.6)	19.3 (79.9)
3	sorbitol–DMA	2.18	94.3 (5.68)	43.3 (56.1)
4	mannitol–DMA	2.26	89.7 (10.2)	32.1 (67.2)
5	adonitol–DMA	2.19	90.2 (9.68)	33.3 (66.0)
6	xylitol–DMA	2.06	90.2 (9.68)	35.2 (64.1)
7	erythritol–DMA	2.63	82.1 (17.7)	19.0 (80.2)
8	pentaerythritol–DMA	2.63	86.9 (13.0)	28.7 (71.6)
9	diethylamine	3.88	89.0 (10.9)	36.3 (62.5)
10	sorbitol–diethylamine	3.03	87.9 (11.9)	31.3 (67.4)
11	DEA	3.44	87.9 (12.0)	25.5 (73.7)
12	Tris	2.44	73.8 (25.9)	12.2 (86.1)
13	2-amino-2-methyl-1,3-propanediol	3.21	75.1 (24.4)	10.5 (87.9)
14	3-amino-1,2-propanediol	3.12	67.8 (31.6)	7.30 (91.0)
15	sorbitol–DEA	2.71	88.6 (11.3)	28.3 (70.9)
16	NMDG–DMA	4.51	95.2 (4.73)	50.4 (49.8)
17	sorbitol–NMDG	2.14	99.9 (0.06)	98.2 (1.78)

^a Resin (0.3 mmol N) contacted with 20 mL of [As(V), 100 mg/L, pH 5.6] or [As(V), 100 mg/L, + SO_4^{2-} , 560 mg/L, pH 6.0]. Contact time: 41 h.

^b NMDG, *N*-methyl-D-glucamine; DMA, dimethylamine; DEA, diethanolamine; Tris, tris(hydroxymethyl)aminomethane. ^c Corresponding amount in solution at equilibrium.

Decreasing the chain length to the triols (erythritol–DMA and pentaerythritol–DMA) decreases the affinity and selectivity enough to give results comparable to DMA alone. Thus, the polyol length and stereochemical placement of the -OH groups play a role in the complexation of arsenate.

Substituting diethylamine for dimethylamine results in a resin with somewhat better affinity and selectivity than the DMA resin (entry 9). This may be due to the increased size of the ethyl moieties making the positive charge on the nitrogen appear to be more diffuse (and thus softer) by preventing close contact between it and the bulky (presumably soft) arsenate ion. This phenomenon has been utilized in the preparation of a pertechnetate-selective anion-exchange resin (31). The addition of sorbitol (entry 10) does not affect the results.

Using the NMDG ligand as a model, hydroxy groups were placed in closer proximity to the amine site than is possible with the bifunctional resins by immobilizing diethanolamine (DEA), tris(hydroxymethyl)aminomethane (Tris), 2-amino-2-methyl-1,3-propanediol, and 3-amino-1,2-propanediol onto the polyVBC support. As indicated by entries 11–14 (Table 6), the DEA resin has results similar to diethylamine and the Tris, 1,3-propanediol, and 1,2-propanediol resins have a comparable performance that is lower in arsenate affinity and selectivity than the DMA resin. Adding sorbitol ligands to the DEA leads to no improvement in results (entry 15).

Though there is no evidence that an interaction between polyol and amine moieties in bifunctional resins can give results as high as those of NMDG itself, it may be significant

that the sorbitol–DMA resin is more effective than the DMA resin. To further explore the possibility of inter-ligand cooperation between sorbitol and dimethylamine ligands, bifunctional resins were prepared by incorporating dimethylamine or sorbitol groups into partially substituted NMDG beads. It was found that the NMDG–DMA resin (entry 16) had an affinity and selectivity lower than NMDG itself and comparable to sorbitol–DMA, while the sorbitol–NMDG resin (entry 17) had results that were comparable to the NMDG resin. These last two entries may thus indicate that inter-ligand cooperation of the -OH groups is important in the arsenate affinity and selectivity displayed by the NMDG resin: replacing DMA ligands with NMDG improves the affinity and selectivity relative to results with the DMA resin but does not equal the performance of the NMDG resin while replacing NMDG ligands with sorbitol has no significant effect on either affinity or selectivity. The sorbitol–diethylamine and sorbitol–DEA resins do not perform as well as the sorbitol–DMA resin because the bulkier amines can prevent inter-ligand cooperation. The NMDG–DMA resin performs as well as sorbitol–DMA because of a comparable ability of the ligands to cooperate. Cooperativity is maximized in the all-NMDG resin. This hypothesis is consistent with results presented earlier on the effect of cross-link level: as cross-linking increases (decreasing matrix flexibility), arsenate affinity and selectivity decrease. Thus, the NMDG ligand within a flexible matrix displays unique arsenate binding properties that are not duplicated by either bifunctional resins with similar monofunctional moieties or monofunctional resins with similar bifunctional moieties.

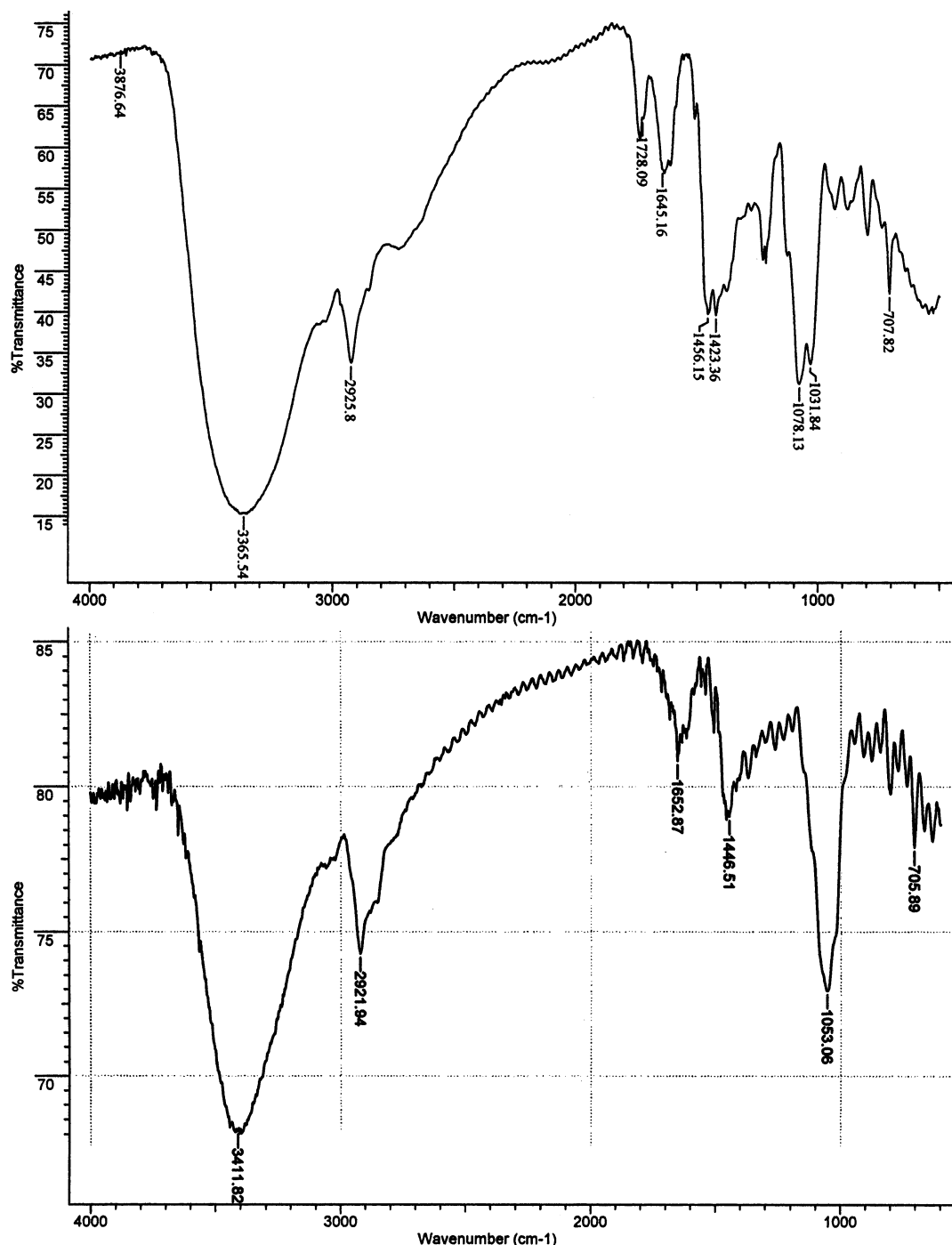


FIGURE 9. FTIR spectra of NMDG (protonated) resin before (top) and after (bottom) complexation with As(V).

Given that the NMDG resin performed unexpectedly well at pH 1.5, the study was extended to pH 1, where un-ionized H_3AsO_4 predominates, with the DMA, DEA, sorbitol, and sorbitol–DMA resins. As shown in Table 7, the NMDG resin complexes 97.5% of the As(V) present from an initial solution of 96.5 mg/L As(V); the residual concentration was 2.42 mg/L. The DMA and DEA resins complexed no As(V) whatsoever, while the sorbitol and sorbitol–DMA resins both complexed less than 10% of the H_3AsO_4 . FTIR spectra of the NMDG resin before and after complexation with As(V) show distinct differences (Figure 9); the significance of those differences is under study.

Sorption Kinetics. To quantify the sorption kinetics of the microporous NMDG resin, 100 mg of resin was placed in 2 L of arsenate solution (1 mg/L), and aliquots were

TABLE 7. As(V) Affinity at pH 1 by NMDG and Control Resins^a

ligand	C_{eq} As(V) (mg/L)	% As(V) sorbed
NMDG	2.42	97.5
DMA	96.5	0
DEA	96.5	0
sorbitol ^b	90.4	6.42
sorbitol–DMA	88.6	8.33

^a 0.3 mmol of N contacted with 20 mL of As(V), 96.5 mg/L, pH 1. Contact time: 46 h. ^b 100 mg in 20 mL of As(V), 96.5 mg/L, pH 1. Contact time: 39 h.

analyzed at different times. The macroporous resins IRA-743 and IRA-900 were also evaluated, the latter used as a control since the rate of ion exchange between Cl^- and

TABLE 8. Percent of As(V) Sorbed as a Function of Time^a

contact time (h)	0.25	0.50	1	2	4	8	24
NMDG	5.3	11.7	14.9	25.5	44.7	70.2	97.1% (0.027 mg/L) ^b
IRA-743	4.2	8.3	11.5	21.9	37.5	61.5	88.5% (0.11 mg/L) ^b
IRA-900 (Cl ⁻)	2.1	7.3	13.5	26.0	45.8	70.8	93.8% (0.060 mg/L) ^b

^a 100 mg of resin contacted with 2 L of As(V), 1 mg/L. ^b Residual As(V) concentration at 24 h.

TABLE 9. Percent of As(V) Sorbed as a Function of Time^a

contact time (min)	5	15	30	60	120	1440
NMDG	17.5	49.0	70.8	92.7	99.0	100.
IRA-900 (Cl ⁻)	18.6	54.6	67.0	90.7	99.0	99.3

^a 25 mg of resin in 40 mL of As(V), 1 mg/L, pH 5.3.

HAsO₄²⁻/H₂AsO₄⁻ is rapid (35). (The large volume of highly dilute solution was contacted with small amounts of resin to slow the rate of sorption in order to reliably quantify any differences in resin performance.) As reported in Table 8, the NMDG resin has kinetics that are comparable to IRA-900 and faster than IRA-743, despite the macroporosity of both resins. At 2 h, the three resins sorb 22–26% of the arsenate in solution, and both the NMDG resin and IRA-900 exceed 90% sorption at 24 h. The residual arsenate concentration is lower for the NMDG resin than for either resin (0.027, 0.11, and 0.060 mg/L for NMDG, IRA-743, and IRA-900, respectively). It is therefore concluded that the cross-link level of 2% DVB for the NMDG resin, important for matrix flexibility, allows for ionic accessibility that is comparable (or perhaps better) than that for macroporous supports.

A second set of rate experiments was performed with 25 mg of resin contacting 40 mL of arsenate solution (1 mg/L). Results from the NMDG resin were compared to IRA-900 (as control). As summarized in Table 9, the NMDG resin performs similarly to IRA-900, in agreement with the results in Table 8: sorption exceeds 90% As(V) at 1 h and equilibrium is reached in 2 h. A similar amount of arsenate is sorbed by both resins at 24 h. In agreement with results presented earlier, the rapid As(V) sorption kinetics by the NMDG resin, its comparable performance to IRA-900, and the fact that boron sorption by the NMDG ligand (which occurs by diol complexation) has slow kinetics (36), one can conclude that ion exchange is an important component (but not the sole component) of the sorption mechanism.

The results indicate that arsenate selectivity is dependent upon immobilizing the NMDG on a flexible polymer support and having the amine in the protonated form. The precise nature of the binding to arsenate has yet to be established. However, a relevant study of polyols with arsenate using potentiometric titrations has shown that sorbitol forms a stable complex with As(V) in acid media and that the arsenate complex decomposes in neutral solution (37). In contrast to this, borate forms a complex with sorbitol under neutral or alkaline conditions, explaining why the NMDG resin best complexes borate when it is in the free base form. The results in homogeneous solution with arsenate are thus consistent with our results involving the protonated NMDG resin and point to a coordination of the arsenate by the hydroxyl groups within the acidic microenvironment of the resin.

The NMDG resin thus has significant promise for the selective removal of arsenate from groundwater. It combines the high sorption capacity at low concentrations of strong base resins with selectivity as well as rapid sorption kinetics. The high capacity from acidic solutions offers additional applications, including the treatment of acid mine drainage water, where it is common to have very high sulfate concentrations under acidic conditions, and the removal of

arsenate from brine. Continuing work focuses on regeneration of the resin, column studies to determine its breakthrough capacity, and spectroscopic studies to determine the exact mechanism of complexation.

Acknowledgments

We gratefully acknowledge financial support from the New York State Energy Research and Development Authority (NYSERDA) and the Pall Corporation. We are also grateful to Purolite, Chelest, Mitsubishi, and Apyron for providing commercial samples.

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Received for review January 2, 2004. Revised manuscript received August 19, 2004. Accepted August 30, 2004.

ES040312S