Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of beryllium from aqueous solutions by zeolite 4A and bentonite

A. Ramesh[a]; K. Rama Mohan[a]; K. Seshaiah[a]; N. Venkateswarlu Choudary[b]
[a] Department of Chemistry, Sri Venkateswara University, Tirupati, India [b] R and D Division, Indian Petro Chemicals Limited, Vadodara, India

To cite this Article Ramesh, A. , Mohan, K. Rama , Seshaiah, K. and Choudary, N. Venkateswarlu(2002) 'Removal of beryllium from aqueous solutions by zeolite 4A and bentonite', Separation Science and Technology, 37: 5, 1123 — 1134

To link to this Article: DOI: 10.1081/SS-120002245

URL: http://dx.doi.org/10.1081/SS-120002245

SEPARATION SCIENCE TECHNOLOGY, 37(5), 1123–1134 (2002)

REMOVAL OF BERYLLIUM FROM AQUEOUS SOLUTIONS BY ZEOLITE 4A AND BENTONITE

A. Ramesh,[1] K. Rama Mohan,[1] K. Seshaiah,[1,]* and
N. Venkateswarlu Choudary[2]

[1]Department of Chemistry, Sri Venkateswara University,
Tirupati 517 502, India
[2]R and D Division, Indian Petro Chemicals Limited,
Vadodara 391 346, India

ABSTRACT

The adsorption and desorption of beryllium on zeolite 4A and bentonite has been studied using batch sorption studies. Parameters such as time of equilibrium, effect of pH, and effect of adsorbent dose on adsorption were studied. The adsorbents exhibited good sorption potentials for beryllium with a peak value at pH 5.0. The adsorption followed the Freundlich and Langmuir adsorption models. About 75% and more removal occurred within 20 min, and an equilibrium was attained at around 90 min for both adsorbents. Beryllium adsorption by zeolite 4A is higher than zeolite 13X and bentonite. The desorption studies were carried out using sodium chloride solution, and the effect of NaCl concentration on desorption was studied. Maximum desorption of 87% occurred with 10% NaCl.

---

*Corresponding author. Fax: (918) 574-48499; E-mail: kallurusn2001@yahoo.com

Key Words: Beryllium; Zeolite 4A; Zeolite 13X; Bentonite; Removal; Aqueous solutions

INTRODUCTION

Addition of beryllium through waste discharges into natural bodies of water poses serious environmental hazards due to its high toxicity. Beryllium is used in x-ray tubes, in nuclear weapons and nuclear reactors, inertial guidance components, space optics, and microelectronics (1). Some of the industries discharging beryllium in their effluents are manufacturer of nuclear reactors, aircraft, and rockets. Inhalation of soluble compounds of beryllium dust or aerosols is a serious health hazard. Beryllium, as other carcinogenic metals, is geneotoxic in several in vitro mammalian cell assays (2) and decreases the fidelity of DNA synthesis in many other test systems (3). Acute pulmonary beryllium disease involving bronchitis, pneumonitis, and alveolar interstitial oedema is produced following inhalation of soluble beryllium compounds. Retention of beryllium within the lungs leads to the development of a disease condition called “berylliosis”. It causes heart diseases, non-healing ulcers, and lung cancer and could increase the occurrence of bone tumors (4). Consequently, removal of beryllium from water and waste water assumes importance.

The conventional methods for heavy-metal removal from water and waste water include reduction, precipitation, ion exchange, and adsorption. Among all the methods, adsorption is highly effective and economical. The use of various adsorbents such as cellulose (5), coal and peat (6), and silicagel-morin (7) have been reported for the removal of beryllium from aqueous solutions.

In this article, the authors studied the removal of beryllium from aqueous solutions using zeolite 4A, zeolite 13X, and bentonite. Zeolites are complex inorganic polymers based on an infinitely extending three-dimensional, four-cornered network of AlO_4 and SiO_4 tetrahedra. The structure can be considered to arise from the isomorphous substitution of Si by Al in the crystal lattice of SiO_2. The tetrahedra are linked to each other by sharing of oxygen atoms to give rise to building blocks of cubic, hexagonal, octagonal, and polyhedra (8,9). The AlO_4 in the structure gives rise to an anionic charge in the framework. This is balanced by the cations that occupy nonframework positions, which can be exchanged with other ions. Zeolites may be represented by the empirical formula $M_{n/2}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ (10), where generally x is equal to or greater than 2 because AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, and n is the cation valence. The ion-exchange capacity of the zeolites therefore depends on their framework Si/Al ratio and decreases with increase in Si/Al ratio. Bentonite is a clay mineral in which Na replaces Ca in montmorillonite clay. The clays carry a

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

net negative charge due to the broken bonds around the edges of the silica–alumina units that would give rise to unsatisfied charges, which would be balanced by the adsorbed cations. Substitutions within the lattice structure of trivalent aluminum for quardrivalent silicon in the tetrahedral sheet and of ions of lower valence particularly magnesium for trivalent aluminum in octahedral sheet result in unbalanced charges in the structural units of clay minerals (11). The above factors dictate largely that zeolite 4A, zeolite 13X, and bentonite are good adsorbents for the removal of beryllium in aqueous solutions.

In view of the environmental significance, the authors have studied the adsorption of beryllium on zeolite 4A, zeolite 13X, and bentonite under different experimental conditions in order to ascertain their use as adsorbents to remove the beryllium from effluents before they are discharged into water bodies.

MATERIALS AND METHODS

All the chemicals used were of analytical reagent grade. Deionized double distilled water was used throughout the experimental studies. Stock beryllium solution (1 mg/mL) was prepared by dissolving 19.6543 g of $BeSO_4{\cdot}4H_2O$ in 1000 mL of deionized double distilled water. Working standards were prepared by progressive dilution of stock beryllium solution using deionized double distilled water. Adsorbents zeolite 4A, zeolite 13X, and bentonite were obtained from Indian Petro Chemicals Limited, Vadodara, India. The chemical composition of adsorbents are shown in Table 1.

Table 1. Chemical Composition[a] of Zeolite 4A and Bentonite

	Adsorbents	
Constituents	Zeolite 4A	Bentonite
SiO_2	34.1	44.0
Al_2O_3	28.3	16.0
Na_2O	17.0	2.2
Fe_2O_3	—	12.5
TiO_2	—	1.0
MgO	—	2.4
CaO	—	2.6
H_2O	20.7	—

[a] All the values are in percentage by weight.

A varian spectrAA, atomic absorption spectrometer with beryllium hollow cathode lamp and nitrous oxide–acetylene flame was used for determining beryllium concentrations. This technique offers a detection limit of 0.05 μg/mL for the determination of beryllium. An Elico model LI-129 pH meter was used for pH measurements. A mechanical shaker (Macro Scientific Works®, Delhi, India) was used.

Procedure

Adsorption Studies

A number of stoppered reagent bottles containing equal volumes (100 mL) of beryllium solution of varying concentrations were taken, pH was adjusted to the desired value by adding ammonia solution (1:1) or HCl (1+1). A weighed amount (5.0 g) of the adsorbent was introduced into each reagent bottle. The bottles were shaken at room temperature (30 ± 1°C) using a mechanical shaker for a prescribed time to attain equilibrium. The adsorbent was then removed by filtration. The concentration of beryllium in aqueous solution was determined according to the standard method (12). Blank solutions were treated similarly (without adsorbent) and the recorded concentration by the end of each operation was taken as the initial one.

Effect of Counter Ions on the Adsorption of Beryllium

Ions like Ca, Mg, and Fe are the common ions that are present in water generally. The effect of these ions on the adsorption of beryllium on zeolite 4A and bentonite are studied. This is accomplished by adding 10 mg each of Ca, Mg, and Fe to 10 and 20 mg/100 mL of beryllium solution, and the adsorption studies were carried out as described in the previous section.

Desorption Studies

The desorption studies were carried out with varying concentrations of NaCl solution. The adsorbents, which are removed from filtration, were taken in stoppered reagent bottles. To this, 100 mL of NaCl solution was added. The bottles were shaken at room temperature (30 ± 1°C) using a mechanical shaker. The adsorbent was then removed by filtration. The above-mentioned method was used to determine the concentration of beryllium desorbed in the aqueous solution.

ADSORPTION ISOTHERM MODEL

To quantify adsorption capacity of zeolite 4A, 13X, and bentonite for the removal of beryllium from water, the data were fitted into the Freundlich and Langmuir adsorption isotherm models (13) as given below.

Freundlich model:

$$\Gamma = KC_{\mathrm{e}}^{n}$$

Langmuir model:

$$\Gamma = \mathrm{Ce}_{\mathrm{m}} b \mathrm{C}_{\mathrm{e}}/(1 + bC_{\mathrm{e}})$$

where Γ (mmol/g) and C_{e} (mmol/L) are the concentrations of beryllium in the adsorbed and liquid phases, respectively at equilibrium, K and n are the Freundlich constants, Ce_{m} and b are the Langmuir constants.

Diffusion constant (D/r^2):

Adsorption uptake was used to calculate the apparent diffusivity, D/r^2, using the well-known equation (10)

$$M_t/M_\infty = 1 - 6/\pi^2 \sum 1/n^2 \exp(-Dn^2\pi^2 t/r^2)$$

where M_t and M_∞ are the amount adsorbed at time t and infinity, D the diffusivity constant, and r the zeolite crystallite size or bentonite particle size. The diffusion constant D/r^2 was calculated from the uptake data using the above-mentioned equation by a nonlinear regression.

RESULTS AND DISCUSSION

Sorption Isotherms

Adsorption isotherms of beryllium on the three adsorbents measured at 30°C are shown in Fig. 1. The shape of the isotherms on the three adsorbents is identical indicating a similar type of adsorption process. It is expected that in all the three adsorbents the process of adsorption is through ion exchange. The adsorption capacity for the three adsorbents fall in the order zeolite 4A > 13X > bentonite. Zeolite 4A with its lowest Si/Al ratio of 1 has got the highest theoretical ion-exchange capacity. Zeolite 13X with Si/Al ratio of 1.25 has got lower theoretical capacity than zeolite 4A. The adsorption data was analyzed in terms of the Freundlich and Langmuir isotherm models. The data is well represented by Freundlich model as shown in Fig. 1(a) and Langmuir model

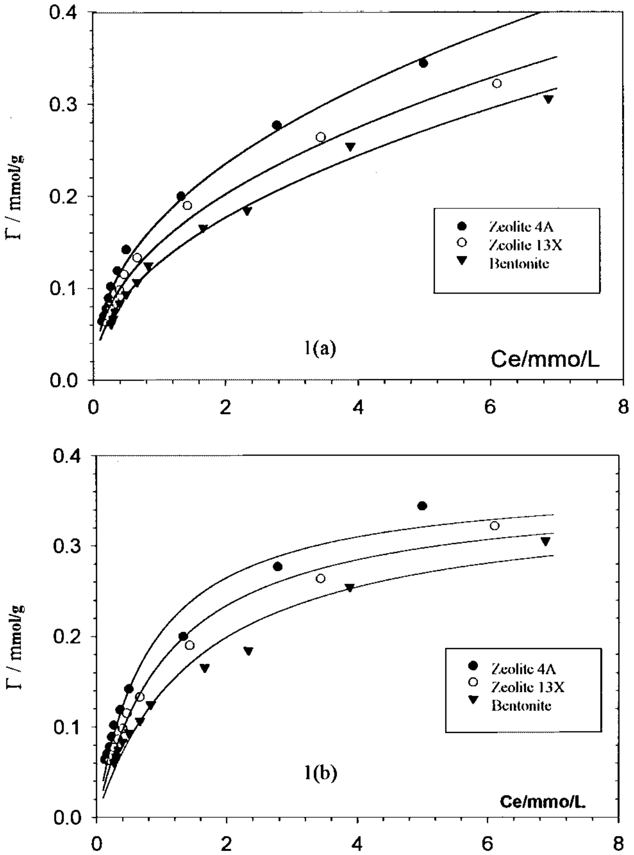

Figure 1. (a) Freundlich adsorption isotherms of beryllium at pH 5.0. (b) Langmuir adsorption isotherms of beryllium at pH 5.0.

in Fig. 1(b). The fitted constants for Freundlich and Langmuir models are summarized in Table 2.

The theoretical exchange capacity of hydrated zeolite powders of Type A and X are 5.5 and 4.7 meq/g, respectively. The ion-exchange capacity of bentonite clay as reported by the supplier is 0.8 meq/g. The observed beryllium adsorption capacity for zeolite 4A and 13X are lower than those of theoretically estimated substantially. The observed beryllium adsorption capacity obtained by Langmuir fit (0.37 and 0.36 mmol/g for 4A and 13X, respectively) are only 12 and 14% of their theoretical capacity. Beryllium with its smaller ionic size (radius 0.31 Å) and high charge density ($e/r = 6.5$) compared to other group II

Table 2. Fitted Constants for Freundlich and Langmuir Models

Adsorbent	*K*	*n*	r^2	σ
Values of Freundlich constants				
NaA	0.1742	0.4343	0.993	0.008
NaX	0.1497	0.4399	0.989	0.010
Bentonite	0.1284	0.4645	0.993	0.007
	Ce_m (mmol/g)	*B*	r^2	σ
Values of Langmuir constants				
NaA	0.373	1.2273	0.976	0.016
NaX	0.363	0.9090	0.989	0.010
Bentonite	0.353	0.6431	0.971	0.014

metal ions is know to form $[Be(H_2O)_2]^{2+}$ ion. The enthalpy of hydration for Be^{2+} is also the highest (−2494 kJ/mol). Hence it is the hydrated Be^{2+} that is adsorbed and not Be^{2+}. The larger $[Be(H_2O)_2]^{2+}$ may not be able to enter the smaller sodalite or β-cages. The adsorption of beryllium may take place only in super cage or α-cage. For divalent ions, the reported (10) order of ion exchange selectivity is

$$\mathrm{Sr}(1.15) > \mathrm{Ba}(1.35) > \mathrm{Ca}(0.99) \gg \mathrm{Mg}(0.65)$$

It is difficult to exchange the ions with a lower ion-exchange selectivity. Be, though not reported in the literature, can be expected to have lower selectivity than Mg, which explains the lower capacity observed in the present study.

The observed beryllium capacity of 0.35 mmol/g (from Langmuir fit) for bentonite adsorbent compares well with the capacity reported by the supplier. Such an observation can be ascribed to layered structure of bentonite and its property to swell in aqueous solutions allowing free exchange of cations.

Results relating to desorption of beryllium by NaCl are given in Table 3. The results showed that with increase in concentration of NaCl the desorption also increased but attained a constant with 10% NaCl. The desorption of beryllium from zeolite 4A is more when compared to bentonite. This shows that bentonite, which expands freely, allows internal diffusion of Be^{2+} ions and hence the desorption process becomes difficult when compared to zeolite 4A. Hence the regeneration capacity of zeolite 4A is more (87%) with 10% NaCl than bentonite.

Table 3. Desorption Experiments

Adsorbent	Initial Concentration Be^{+2} mg/100 mL	Desorption[a] with 5% NaCl	Desorption[a] with 10% NaCl	Desorption[a] with 15% NaCl
Zeolite 4A	3	70	75	75
	5	73	77	78
	10	74	82	82
	15	79	86	85
	20	81	87	86
Bentonite	3	63	68	67
	5	64	67	67
	10	67	74	73
	15	72	81	82
	20	63	70	70

[a] All values are per cent (%) recovery of beryllium.

Sorption Kinetics

The kinetics of sorption describing the contact time in the removal of beryllium is one of the characteristics defining efficiency of sorption. The rates of uptake of beryllium by the adsorbents are shown in Fig. 2. The fractional uptake overlapped for all the three adsorbents. The rates of adsorption of beryllium are rapid in all the three adsorbents. For example, over 80% uptake is completed within 20 min and equilibrium is attained at around 90 min. The value of the diffusion constant, D/r^2, calculated from the fractional uptake data is therefore the same ($D/r^2 = 8.3 \times 10^{-4}$ sec^1) for all the three adsorbents. This shows that the diffusional resistance is similar in all the three adsorbents.

Effect of PH on Adsorption

The effect of pH on the adsorption of beryllium from water on all the three adsorbents measured at 30°C is shown in Fig. 3. It can be observed that the adsorption of beryllium is dependent on the pH of the solution. Adsorption of beryllium increased with increase in pH in all the adsorbents. At low pH, for example at pH = 1, the beryllium uptake is very small. It is known that mineral acids affect the structure of zeolites and clays. The extent of the damage to their structure depends on the pH of the acids. The structure of zeolites and clays particularly with low Si/Al ratio may collapse in the presence of acids with pH lower than 5, but the severity would be more at pH below 3. In fact, pH less than 5

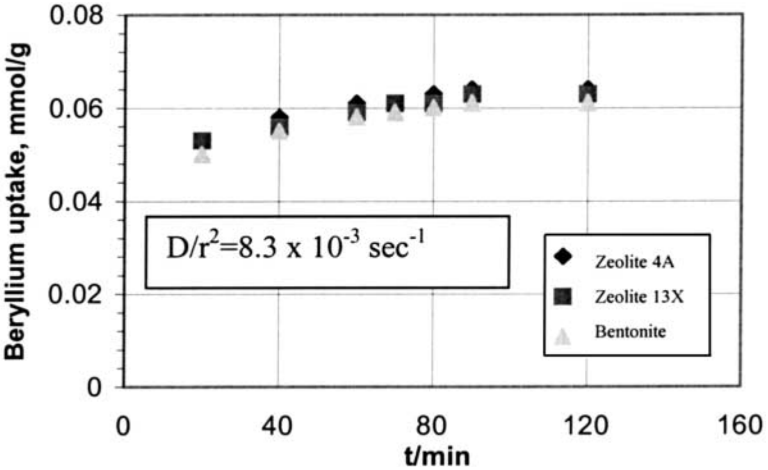

Figure 2. Effect of contact time and initial concentration of beryllium (initial concentration of beryllium 3 mg/100 mL, pH 5.0).

is not recommended for zeolites (14). The loss in adsorption capacity at lower pH can therefore be ascribed to the collapse in the structure of these adsorbents. Both zeolites and clays are very stable at higher pH, and do not affect the adsorption of beryllium at pH above 5. Therefore, the role of pH on the

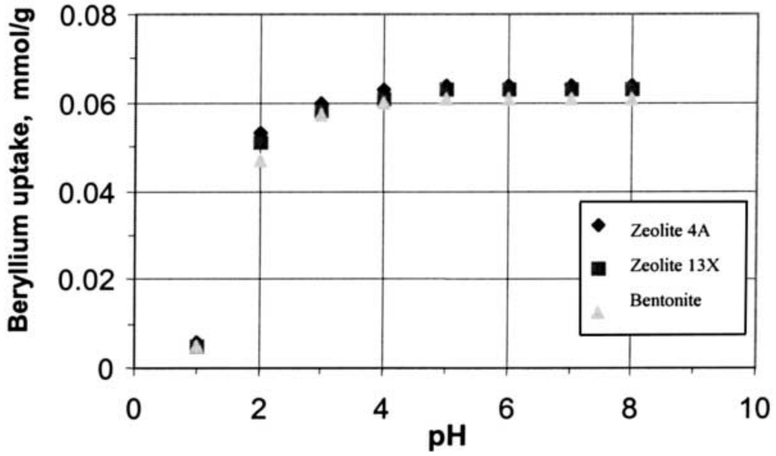

Figure 3. Effect of pH on beryllium removal at 30°C (initial concentration of beryllium 3 mg/100 mL, contact time 120 min).

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

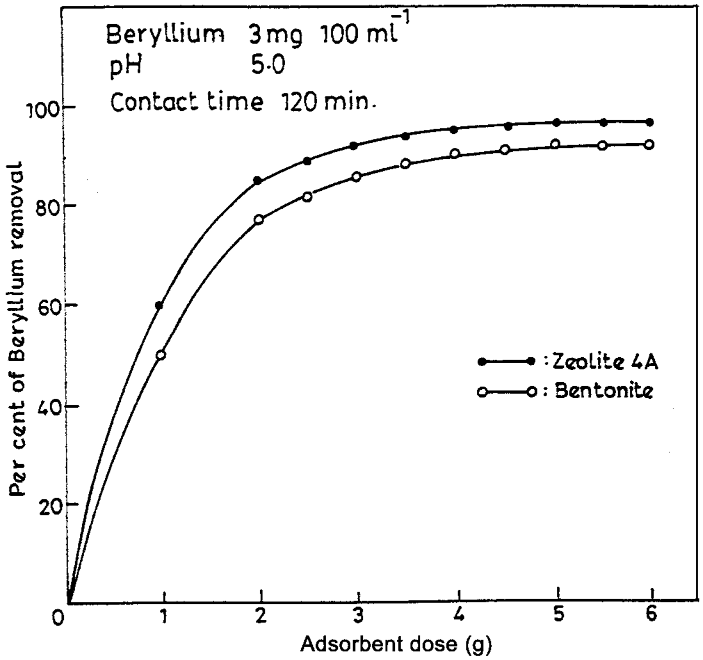

Figure 4. Effect of adsorbent dose on percentage removal of beryllium (initial concentration of beryllium 3 mg/100 mL, contact time 120 min, pH 5.0).

adsorption of beryllium, other than the damage to the structure of the adsorbent, may not be significant.

Studies on Dosage

Data relating to the percentage (%) removal of beryllium by zeolite 4A and bentonite dosage at pH 5 is shown in Fig. 4. The figure indicates that the adsorption increased with increasing adsorbent dose up to a certain value and then there was no further increase of adsorption. It is evident from these plots that a minimum of 5 g of adsorbent is required for the maximum removal of beryllium, (3 mg/100 mL) at pH 5.

Effect of Counter Ion

Presence of counter ions such as Ca, Mg, and Fe can affect the adsorption of beryllium. The effect of the counter ion was studied by adding 10 mg/100 mL of

Table 4. Effect of Counter Ions on the Adsorption of Beryllium

Initial Beryllium Concentration in Solution (mg/100 mL)	Percent (%) Removal of Beryllium by Zeolite 4A in Presence of Counter Ion (10 mg/100 mL)			
	No Counter Ion	Ca	Mg	Fe
10	88	75	68	71
20	77	69	62	64
	% Removal of Beryllium by Bentonite			
10	79	78	75	76
20	70	68	64	65

the counter ion under investigation. The effect of the counter ions on the adsorption of beryllium is studied at two initial beryllium concentrations viz., 10 and 20 mg/100 mL. The data is summarized in Table 4, showing that Mg exhibited the highest effect on the adsorption of beryllium both on Zeolite 4A and bentonite. The decreasing order of the counter ion effect is Mg > Fe > Ca. However, all the counter ions exhibited lesser effect on bentonite than on zeolite 4A.

CONCLUSIONS

Adsorption of beryllium by zeolite 4A, zeolite 13X, and bentonite was found to proceed in accordance with Freundlich and Langmuir adsorption isotherm equations. The adsorption of beryllium by zeolite 4A, zeolite 13X, and bentonite follow in the order of zeolite 4A > 13X > bentonite. The adsorption capacities depend on solution pH, and the maximum adsorption of beryllium by zeolite 4A, 13X, and bentonite at concentrations up to 3 mg/100 mL/5 g of adsorbent was attained at pH 5. The maximum percentage desorption of beryllium with 10% NaCl was 87%.

ACKNOWLEDGMENTS

The authors A. Ramesh and K. Rama Mohan are thankful to CSIR (New Delhi) for providing financial assistance in the form of CSIR—Senior Research

Fellowships. The authors are thankful to M/S Amara Raja Batteries Limited, Karakambadi, Tirupati, for providing the AAS facilities.

REFERENCES

1. Kumaresan, M.; Riyazuddian, P. Chemical Speciation of Trace Metals. Res. J. Chem. Environ. **1999**, *3* (4), 59–79.
2. Sirover, M.A. Effect of Metals in In Vitro Bio Assays. Environ. Health Perspect. **1981**, *40*, 163–172.
3. Zakour, R.A.; Kunkel, T.A.; Loeb, L.A. Metal-Induced Infidelity of DNA Synthesis. Environ. Health Perspect. **1981**, *40*, 197–205.
4. Kannan, K. Metals and Metallic Compounds. In *Fundamentals of Environmental Pollution*; 2nd Ed.; S. Chand and Company: New Delhi, 1995, 151–152.
5. Burba, P.; Willmer, P.G. Cellulose: A Biopolymeric Sorbent for Heavy-Metal Traces in Waters. Talanta **1983**, *30* (5), 381–383.
6. Eskenazy, G.R. Adsorption of Beryllium on Peat and Coals. Fuel **1970**, *49* (1), 61–67.
7. Szczepaniak, W.; Szymanski, A. Sorption and Preconcentration of Trace Amounts of Beryllium from Natural Waters on Silicagel with Immobilised Morin Prior to its Determination by ETA-AAS Method. Chem. Anal. **1996**, *41* (2), 191–199.
8. Jasra, R.V.; Choudary, N.V.; Bhat, S.G.T. Separation of Gases by Pressure Swing Adsorption. Sep. Sci. Technol. **1991**, *26* (7), 885–930.
9. Flanigen, E.M. Molecular Sieve Zeolite Technology, the First Twenty-Five Years. Pure Appl. Chem. **1980**, *52* (9), 2191–2211.
10. Breck, D.W. Structure, Chemistry and Use. In *Zeolite Molecular Sieves*; John Wiley and Sons: New York, 1974.
11. Naidu, V.M.; M.Tech. Thesis, Sri Venkateswara University, Tirupati, India, 1988.
12. APHA; AWWA; WEF. Metals. In *Standard Methods for Examination of Water and Waste Water*; 19th Ed.; Washington, DC, 1995; 3-9–3-12.
13. De, A.K.; De, A.K. Heavy Metals Removal from Waste Water Using Fly Ash and Agricultural Wastes: A Review. J. IAEM **1994**, *21*, 36–39.
14. Ribeiro, F.R.; Rodrigues, A.E.; Rollmann, L.D.; Naccache, C. Science and Technology. In *Zolites*; Martinus Nijhoff Publications: The Hague, 1984; 594.

Received October 2000
Revised June 2001

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:35 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS120002245