Removal of Heavy Metal Ions from Aqueous Solutions by Adsorption on Magadiite

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Removal of Cd(II), Zn(II) and Cu(II) from aqueous solutions using the adsorption process on magadiite has been investigated. It was found that the removal percentage of metal cations at equilibrium increases with increasing temperature, and follows the order of Cd(II)>Cu(II)>Zn(II). Equilibrium modeling of adsorption showed that the adsorptions of Cd(II), Cu(II), and Zn(II) were fitted to Langmuir isotherm. Kinetic modeling of the adsorption showed that first order reversible kinetic model fitted to experimental data. From kinetic model and equilibrium data, the overall rate constant (k) and the equilibrium constant (K) for the adsorption process were calculated. The overall rates of adsorption of metal ions follow the order of Cd(II)>Cu(II)>Zn(II). From the results of thermodynamic analysis, standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) of adsorption process were calculated.

Introduction

It is well known that heavy metals are very toxic elements and their discharge into receiving waters causes detrimental effects on human health and environment. So, it is necessary to remove these metals from industrial effluents. The technologies for removal of metal ion from wastewater such as precipitation, oxidation, reduction coagulation, ion exchange and solvent extraction, and adsorption have been studied. The well-known process is to remove heavy metals by precipitating hydrous oxides by CaO addition. Although this method is relatively simple and inexpensive, it has the disadvantages: 1) it generates a large volume of sludge which is difficult to dispose; 2) it does not produce an effluent sufficiently low in heavy metals content. Also, the removal of metals by ion exchange using zeolite was studied by many researchers.[1-5] Zeolite is an aluminosilicate cation exchanger which has been widely studied for its use in aqueous wastewater. But, the removal of heavy metal in acidic solution is reduced, because the structure of zeolite destroys. Recently, layered silicates such as magadiite ($Na_2Si_{14}O_{29}\cdot 9H_2O$), kenyaite ($Na_2Si_{22}O_{45}\cdot 10H_2O$) and kanemite ($Na_2Si_4O_9\cdot 5H_2O$) have growing interests due to their catalytic and adsorptive properties. Their basic structures are composed of duplicate SiO_4 tertrahedral sheets and are similar to clay minerals with no aluminum. Magadiite and kenyaite were primarily found by Eugster[6] in the lake bed of the lake Magadi in Kenya. Afterward, other occurrence of these deposits was found in sodium carbonate-rich alkaline lake waters.[7,8] Also, they have been successfully synthesized under a hydrothermal condition by many researchers.[9,10,11] However, there is few report about the removal of heavy metals ions in wastewater using the adsoprtion property of synthetic layered silicate.

We previously reported the syntheses of Na-magadiite and Na-kenyaite.[10] In the present study, the removal of Cd (II), Cu(II), and Zn(II) from aqueous solutions by adsorption of magadiite was primarily investigated. Adsorption isotherm, kinetics and thermodynamic parameters of adsorption are also presented.

Experimental

Synthetic magadiite was prepared by the reaction of SiO_2-Na_2O-H_2O system under hydrothermal conditions. Materials used were sodium silicate solution (SiO_2/Na_2O=3.2, 50.7%, Shinheung-Gyusan Chemical Co.) and amorphous silica (Zeosil 155, 92%, Hanbul Chemical Co.) of industrial grades. Experiments were carried out in Teflon-sealed autoclave with stirring at 150-160 ℃ under autogenous pressure during 24-72 hours, using various mole ratios of SiO_2, Na_2O, and H_2O. The products were filtered, and washed with deionized water in order to remove excess Na ion, and then dried at 40 ℃. Identification of samples was carried out by X-ray diffraction (Rigaku Rotaflex diffractometers equipped with CuKα radiation) and scanning electron microscopes (Jeol, JSM-840A). Heavy metal solutions of Cd (II), Cu(II), and Zn(II) were prepared by dissolving $Cd(NO_3)_2\cdot 4H_2O$, $Cu(NO_3)_2\cdot 3H_2O$ and $Zn(NO_3)_2\cdot 6H_2O$ in distilled deionized water. The pH values of the solutions were adjusted to pH=4 by addition of 0.1N HCl or 0.1N NaOH. Batch adsorption experimentals were conducted by using 0.05-1.5 g of adsorbent with 50 mL of solutions containing heavy metal ions of about 1000 mg/L in shaking water bath at different temperatures. After the desired contact time elapsed, suspensions were filtered. The filtered solutions were analyzed for heavy metal ions by atomic adsorption spectrophotometer (Varian Spectra 220 FS). The amount of metal ions retained by the adsorbent was calculated by the difference between the initial and final concentrations of ions in each solution.

Results and Discussion

Na-Magadiite synthesis

Na-magadiite was synthesized from sodium silicate solution and amorphous silica of industrial grades in order to apply to commercial process. Compared to the previous

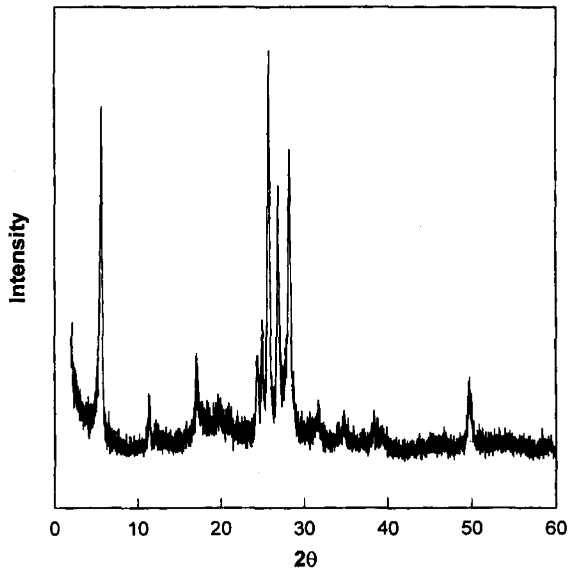

Figure 1. XRD of synthetic Na-magadiite.

method,[10] current method does not need to add to NaOH solution because sodium silicate includes sodium content, and these raw materials are supplied easily and cheaply. Therefore, the synthetic method is very economical because the cost of raw materials can be reduced remarkably.

Figure 1 shows the development of crystalline magadiite with 60 hours of reaction time at 150 ℃ in the reaction compositions of $SiO_2:Na_2O:H_2O=11:1:160$. The XRD pattern of synthetic magadiite exhibited 00L X-ray reflections of film sample corresponding to a basal spacing of 15.6 Å. The peak positions for synthetic magadiite agree well with values reported previously for synthetic and natural magadiite.[7,8,10,11] Figure 2 shows the scanning electron micrographs of the synthetic magadiite. Na-magadiite shows a particle morphology composed of silicate layers intergrown to form spherical nodules resembling rosettes.

Removal of heavy metals

Effect of contact time on the adsorption of the Cu(II), Cd (II) and Zn(II) ions on magadiite are illustrated in Figure 3-5, respectively. Removal of these cations increased with time and then become constant. The equilibrium reached within 30 min. for all heavy metal cations. The removal percentage increases with increasing temperature for all heavy metal cations. The maximum removals of 78.8% for Cu(II), 95.6% for Cd(II), 63.3% for Zn(II) were observed at 50 ℃ when 0.5 g of the amount of magadiite was used. The removal percentage of metal ion at equilibrium follows the order of Cd(II)>Cu(II)>Zn(II). An increase in uptake of heavy metal cations with the rise in temperature was observed for all heavy metal cations. This was due to the increasing tendency of adsorbate ions from solution to the interface with increasing temperature.

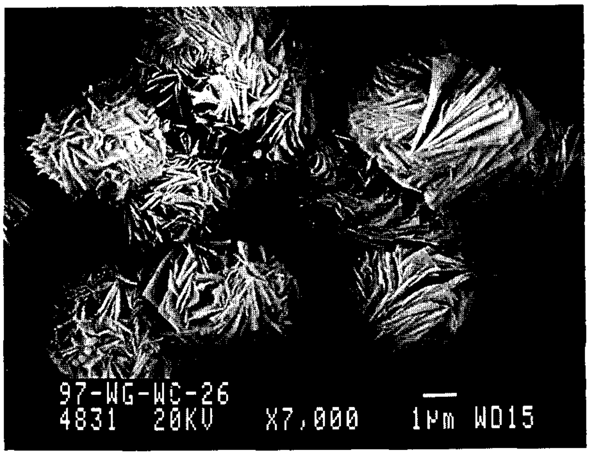

Figure 2. Scanning electron micrograph of synthetic Na-magadiite.

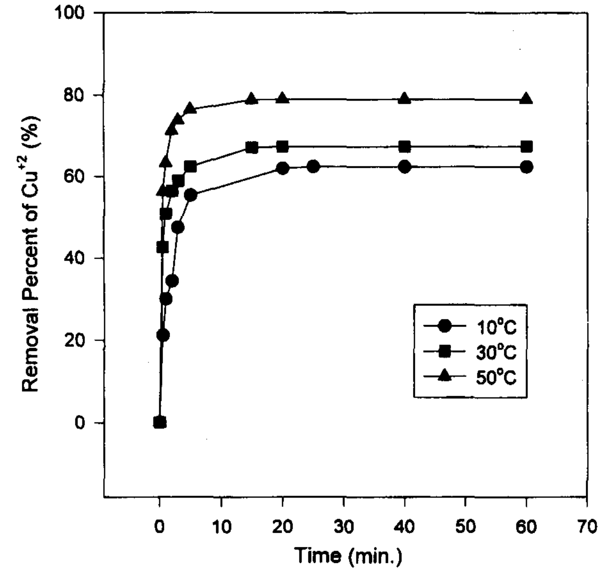

Figure 3. Percentage removal of Cu(II) on magadiite at different temperatures, the amount of magadiite: 0.5 g.

Kinetic studies. Adsorption of heavy metal cations from the liquid phase to the solid phase can be considered as a reversible reaction with an equilibrium being established between the two phases. Therefore, a simple first order reversible kinetic model is used to establish the rate of reaction. The first order reversible kinetic equation is

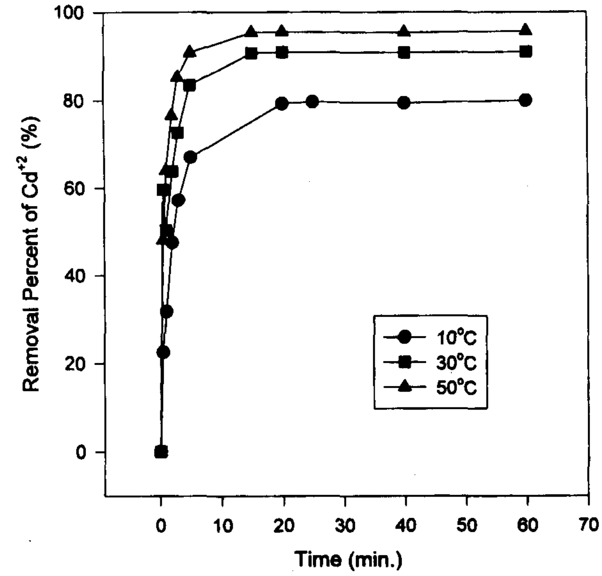

Figure 4. Percentage removal of Cd(II) on magadiite at different temperatures, the amount of magadiite: 0.5 g.

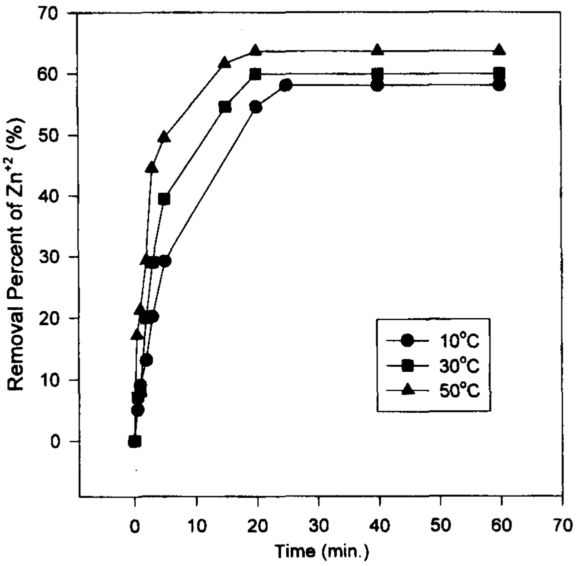

Figure 5. Percentage removal of Zn(II) on magadiite at different temperatures, the amount of magadiite: 0.5 g.

given below.[12]

$$-\mathrm{Ln}(1-X_A/X_{Ae})=(k/X_{Ae})\,t \qquad (1)$$

in which k is the overall rate constant, X_A is the conversion factor of heavy metal ion from the liquid phase to the solid phase, X_{Ae} is the conversion factor of heavy metal at equilibrium. In order to confirm the kinetics scheme, the typical plots of $-\mathrm{Ln}(1-X_A/X_{Ae})$ *vs.* time are given for Cu (II), Cd(II) and Zn(II) in Figure 6-8, respectively. A relatively straight line was generally observed for all heavy metals, indicating that adsorption reaction approximately fits to first order reversible kinetics. The value of correlation coefficient is a relative indicator of the fit of the model to the data. As can be seen, a good fit is found for this reaction scheme. Table 1 represents the overall rate constants and correlation factors at different temperatures. The overall rate constants increase with the increase in temperature, as is the case with most chemical reactions. The rates of ad-

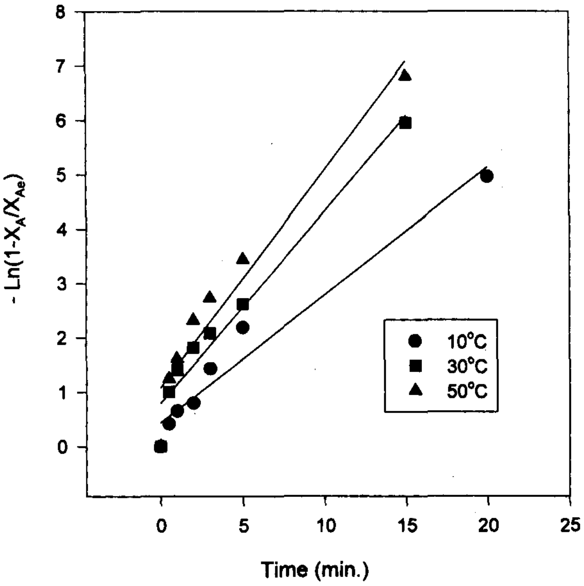

Figure 6. Typical first order reversible kinetic fit of Cu(II) adsorption data on Magadiite.

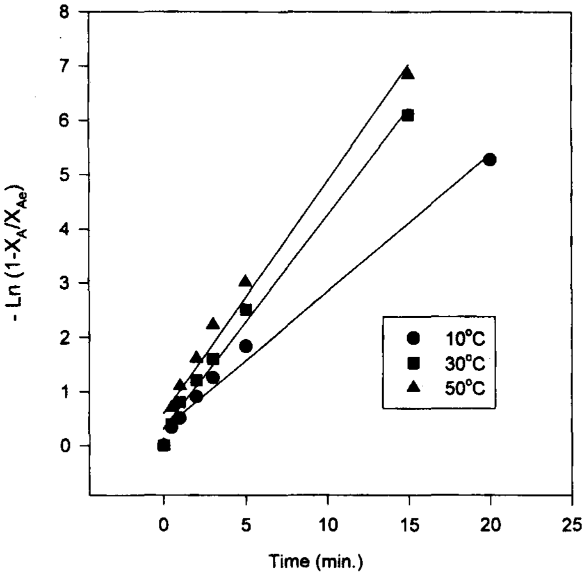

Figure 7. Typical first order reversible kinetic fit of Cd(II) adsorption data on Magadiite.

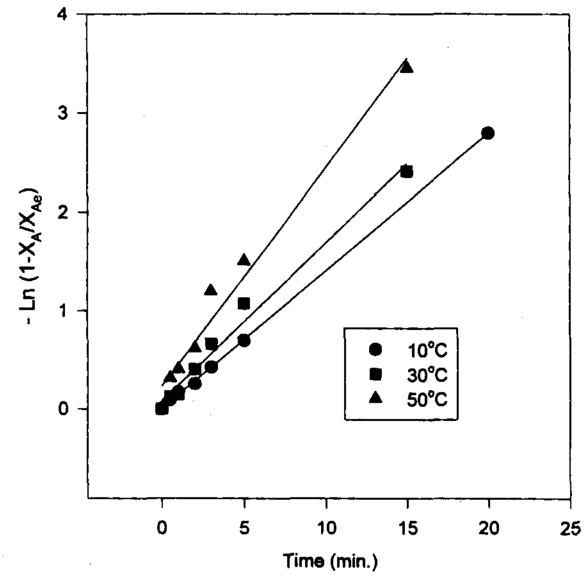

Figure 8. Typical first order reversible kinetic fit of Zn(II) adsorption data on Magadiite.

Table 1. Kinetic parameters of the adsorption of Cd(II), Cu(II), and Zn(II) ions on magadiite.

Cation	Temp. (℃)	k (min^{-1})	Correlation coefficient (r^2)
Cu	10	0.146	0.92
	30	0.236	0.92
	50	0.315	0.88
Cd	10	0.209	0.98
	30	0.357	0.98
	50	0.410	0.96
Zn	10	0.0807	0.99
	30	0.0957	0.97
	50	0.1399	0.95

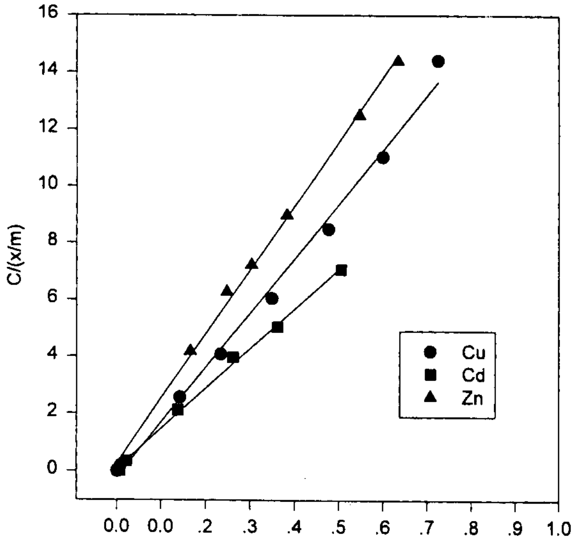

Figure 9. Langmuir adsorption isotherms of Cu(II), Cd(II) and Zn(II) at 30℃.

sorption of metal ions follow the order of Cd(II)>Cu(II)>Zn(II). Compared with the results previously reported on the adsorption of heavy metals by bentonite,[13] the rate of adsorption on magadiite is much faster than the rate of adsorption on bentonite.

Adsorption isotherm. Typical adsorption isotherms for Cu(II), Cd(II), and Zn(II) are presented in Figure 8. As seen from the figures, the experimental data of the adsorption of Cu(II), Cd(II), and Zn(II) fit to the Langmuir isotherm. In magadiite these metals seem to reach saturation which means that the metal cations fill possible available sites and further adsorption takes place at new surfaces. The adsorption isotherm equation is given below.[14]

$$C/(x/m)=1/(a\cdot b)+(1/b)\,C \tag{2}$$

where, x/m is the amount of metal ion adsorbed per unit weight of adsorbent, a and b are the Langmuir constants, and C is the equilibrium concentration of Cu(II), Cd(II), and Zn(II). From the adsorption isotherm, the Langmuir constants for Cu(II), Cd(II), and Zn(II) were calculated. These correlation coefficients related with the equations represent that this model agrees well with the experimental data. The results and the correlation coefficients are given in Table 2.

Table 2. Langmuir constants of Cu(II), Cd(II), and Zn(II) ions

Cation	Temp. (℃)	a (L/g)	b (dimemsionless)	Correlation coeffiecient (r^2)
Cu(II)	10	1.69×10^3	0.0521	0.99
	30	7.30×10^3	0.0500	0.98
	50	2.53×10^3	0.0460	0.98
Cd(II)	10	9.24×10^2	0.0713	0.99
	30	1.05×10^3	0.0614	0.99
	50	8.20×10^2	0.0532	0.98
Zn(II)	10	2.59×10^2	0.0442	0.99
	30	7.51×10^2	0.0448	0.99
	50	1.29×10^3	0.0535	0.99

Table 3. Thermodynamic parameters for the adsorption of Cd(II), Cu(II), and Zn(II) ions on magadiite

Cation	Temp. (℃)	K	$\Delta G°$ (J/mol)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol)
Cu(II)	10	1.653	−1183	−7690	−22.99
	30	2.051	−1810	−24376	−74.50
	50	3.734	−3538	-	-
Cd(II)	10	3.925	−3217	−33376	−106.6
	30	10.011	−5803	−30664	−82.0
	50	21.270	−8210	-	-
Zn(II)	10	1.386	−767	−2675	−6.74
	30	1.494	−1011	−6435	−17.90
	50	1.750	−1503	-	-

Thermodynamic studies. In order to evaluate the nature of adsorption of heavy metals cations on magadiite, the adsorption thermodynamic parameters were calculated. The change in standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) were calculated using the following equations.[13,15]

$$\Delta G°=-RT\ln K \tag{3}$$

$$\Delta H°=R(\ln(K_2/K_1))\,T_1T_2/(T_1-T_2) \tag{4}$$

$$\Delta S°=(\Delta H°-\Delta G°)/T \tag{5}$$

Where, R is the gas constant. K, K_1 and K_2 are equilibrium constants at the temperature T, T_1 and T_2, respectively. Numerical values of equilibrium constants were calculated from

$$K=C_{Be}/C_{Ae} \tag{6}$$

where C_{Be} and C_{Ae} are the equilibrium concentrations of heavy metal cations on the sorbent and solute, respectively. Equilibrium constants are represented in Table 3. It is observed that K value increases as temperature increases. K values follow the order of Cd(II)>Cu(II)>Zn(II). Calculated thermodynamic parameters for the adsorption of Cu(II), Cd(II), and Zn(II) on magadiite are given Table 3. The negative values of these Gibbs free energy are indicative of the spontaneous nature of the process. Entropy has been defined as the degree of chaos of the system and the negative value of this parameter found in our investigation reflect the adsorption of Cu(II), Cd(II), and Zn(II). The negative values of $\Delta H°$ shows the exothermic nature of Cu, Cd, and Zn adsorptions.

Conclusions

Removal of heavy metals from aqueous solutions using the adsorption process on synthetic magadiite has been primarily investigated. The removal percentage of metal ions at equilibrium follows the order of Cd(II)>Cu(II)>Zn(II). In equilibrium modeling, the adsorption of Cd(II), Cu(II), and Zn(II) were fitted to a Langmuir isotherm. In kinetic modeling, first order reversible kinetic model fitted to the adsorption of heavy metals. From these results, kinetic parameters and thermodynamic data were calculated. The rates of adsorption follow the order of Cd(II)>Cu(II)>Zn(II). The rate of adsorption is much faster than the results previously found on the adsorption of heavy metals by bentonite or clay.[13,16] Also, the removal percentage at equilibrium is much higher than that of treated clay.[13,16] Magadiite is a good adsorbent for heavy metals without the need for any chemical treatment.

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A Route to Boron Nitride Via Simply Prepared Borazine Precursor

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Borazine ($B_3N_3H_6$) as an inorganic analogue of benzene was synthesized by reaction of cheap raw materials ($NaBH_4$ and $(NH_4)_2SO_4$), and by using simple glass reaction apparatus in a scale up to 20 g per run with highly improved yield over 50%. It appears that synthesis of borazine is competing with formation of poly (aminoborane) as an inorganic analogue of polyethylene. The synthesized borazine and its polymerized product were characterized by comparison with products obtained from a commercial one. Bulk pyrolysis of the borazine polymer to 1500 °C produced a pure boron nitride (BN) with 75% ceramic yield, which displayed good oxidation resistance under dry air.

Introduction

Inorganic polymeric precursors have been used for the preparation of ceramic fibers, coatings and matrices in ceramic fiber/ceramic matrix composites. It has been reported that liquid inorganic polymers could be used to utilize the processibility of polymers as well as excellence of ceramics, and to readily control the microstructure and composition of ceramic products. Polymer-derived SiC and Si_3N_4 ceramics are beginning to be commercialized in market as fibers while a variety of sol-gel processes are widely used in electronic and structural industries.[1]

However there has been little attention to extensive applications and/or related researches on preparation of BN from polymeric precursors, although BN shows the similar structure and properties, compared to graphite, but higher oxidation resistance and lower dielectrics.[1] It has been mainly caused by the limited availability of starting monomer, borazine, that has proven to be an almost ideal chemical precursor.

Recently we demonstrated the first successful preparation of carbon fiber/BN matrix composite(C/BN) by using low viscous borazine polymer prepared from borazine monomer purchased with a price of $25/g.[2] These composites displayed outstanding mechanical properties and excellent resistance to oxidation up to 850 °C, presently leading to develop airbrake materials. In addition, it was found that low temperature treatment of the polyborazine led to mesophase formation as similar to pitch mesophase.[3] It is interesting to note that chemistry of polyborazine as a BN precursor is quite similar to that of polyaromatic compounds as a graphite precursor.

It is believed that the efficient synthetic route for borazine must open its related basic studies as well as the potential applications such as coating, fiber and other specialties. Therefore, various attempts are expected to develope the convenient and less cost-consuming procedures for the synthesis of borazine. Since borazine was discovered by