A Novel Sorbent (MCM-41 Immobilized with N-Methylglucamine) for Removal/Preconcentration of Boron from Waters. Synthesis, Characterization and Applications to Water Samples

by

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A Dissertation Submitted to the
Graduate School in Partial Fulfilment of the
Requirements for the

MASTER OF SCIENCE

Department: Chemistry
Major: Chemistry

Izmir Institute of Technology
Izmir, Turkey

July 2004

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ACKNOWLEDGEMENTS

I wish to first, and most importantly, thank my advisor Assoc. Prof. Dr. Ahmet Eroglu for his guidance, care and freedom that he provided me throughout the study. Sometimes we could not understand to each other but still working with him for past three years has been an awesome experience for me. No matter how crazy (or often ridiculous) my ideas were, Dr. Eroglu would let me try them out or offered keen advice on how to turn a mediocre idea into something great. This taught me how to be a researcher.

I am also grateful to my co-advisor Prof. Dr. Levent Artok for valuable discussions and giving me opportunity to study in his laboratory.

It is an honour to work with two of the best researcher in IYTE for me.

I should extend my thank to Assist. Prof. Dr. Talal Shahwan for his contributions and to Prof. Dr. Emür Henden, Prof. Dr. Tamerkan Özgen for their criticisms and suggestions.

Special thanks are extended to Prof. Dr. Durmus Ali Demir for his encouragement and understanding and to Rsch. Scientist Oya Altungöz for her patiance and friendship during the ICP-OES measurements.

Very special thanks go to my dear friends Müge Açikel and Türker Pasinli. They were always with me whenever I needed help for anything. I'll never forget our works lasting all night. Also thanks to Betül Öztürk for computer works and friendship.

Many other friends have provided support along the way, in particular (my room mates) Bahar, Zeynep, Aytaç, Mustafa, Ayça and all other friends in IYTE. They have made my school life much more enjoyable than it would have otherwise been.

And last, but by certainly no means least, I wish to thank all of my family for the support they have given. I know without the support and confidence of my parents I would never have been able to achive what I have.

ABSTRACT

Determination of boron has become an important task in a variety of analytical applications because of the increasing use of boron compounds in various industrial fields. Its concentration is generally low in many samples and this necessitates either the use of very sensitive analytical techniques or the application of suitable preconcentration methods prior to instrumental determination.

In the present study, a novel sorbent was prepared by the functionalization of an inorganic support material, MCM-41, with N-methylglucamine for the uptake of boron from aqueous solutions prior to its determination by ICP-OES. Characterization of the newly synthesized material was performed using elemental analysis, XRD, DRIFTS, and BET analysis. Sorption behavior of the novel sorbent for boron was also investigated and found to obey Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The maximum amount of B (as H_3BO_3) that can be sorbed by the sorbent was calculated from the D-R isotherm and was found to be 0.8 mmol of B per gram of sorbent. The applicability of the new sorbent for the removal/preconcentration of boron from aqueous samples was examined by batch method. It was found that the sorbent can take up 85 % of boron in 5 minutes whereas quantitative sorption is obtained in 30 minutes. Any pH greater than 6 can be used for sorption. The desorption from the sorbent was carried out with 1.0 M HNO_3. For method validation, spike recovery tests were performed at various concentration levels in different water types and were found to be between 85-95 and 75-90 percent for ultra pure water and geothermal water, respectively.

ÖZ

Endüstriyel uygulamalarinin artmasi bor ve bor bilesiklerinin tayininin önemini artirmistir.Bor derisiminin genellikle düsük olmasi ya yüksek duyarliga sahip analitik teknikler kullanimini yada enstrümental tayin basamagindan önce uygun ön-deristirme metotlarina basvurmayi gerektirir.

Bu çalismada ICP-OES ile tayininden önce sulu çözeltilerdeki boru tutturmak için yeni bir tutucu yüzey gelistirilmistir. Bu amaçla inorganik bir adsorbanin yüzeyine borat iyonuna seçimli bir kelatlayici olan N-metilglukamin baglanmistir. Sentezlenen tutucu yüzeyin karakterizasyonu X-isini difraktometri (XRD), difüze yansimali Fourier dönüsümlü infrared spektrometri, BET izoterm ve elemental analiz metotlari ile yapilmistir. Yeni tutucu yüzeyin bor tutma becerisi çesitli tutunma izotermlerine uygunlugu açisindan incelenmis, Freundlich ve Dubinin-Radushkevich (D-R) izotermlerine uydugu belirlenmistir. Adsorbanin gram basina 0.8 mmol maksimim bor (H_3BO_3 formunda) tutma kapasitesi oldugu D-R izoterminden hesaplanmistir. Adsorbanin çesitli çözeltilerdeki borun uzaklastirilmasi ve ön-deristirilmesi çalismalarina uygunlugu kesikli (batch) metot tutturma deneyleri ile test edilmistir. Adsorbanin çözeltideki borun % 85'ini 5 dakikada tutabildigi fakat kantitatif tutunmanin 30 dakikada gerçeklestigi ve tutunmanin 6 dan büyük pH'larda oldugu belirlenmistir. Metodun geçerliligini saptamak için çesitli derisim seviyelerinde katma (spike) geri kazanim denemeleri saf su ve jeotermal su örneklerine uygulanmis ve sirasiyla % 85-95 ve % 75-90 arasinda degistigi bulunmustur.

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CHAPTER 1

INTRODUCTION

Boron is widely distributed in the environment, from natural or anthropogenic sources. It can be found mainly in the form of boric acid or borate salts. It is an important micronutrient for plants, animals and humans. The adequate level (the range between deficiency and excess) is narrow. In recent years use of boron compounds in metallurgy, microelectronics, glass products and in fertilizers has been increasing; so that boron compounds are released into the environment from these sources. (Welz and Sperling, 1999)

Although boron and boron compounds are widely distributed in nature, their concentrations are generally low in most of the surface and ground waters except in the vicinity of borate mines or some industrial discharges. These low concentrations necessitate either the use of very sensitive analytical techniques or the application of suitable preconcentration methods prior to instrumental determination.

Turkey is known to have the largest boron reserve (~60%) in the world. This large boron reserve can be of great importance, especially when the increasing use of boron compounds in high technology applications is considered. On the other hand, it might be necessary to develop efficient boron removal procedures from the environmental waters due to possibility of contamination especially around borate mines.

Some sample matrices can be problematic in boron determination. High salt concentration may affect the boron signals in many detection systems, whereas the presence of Fe in the sample solution (e.g., soil extracts, iron metal extracts, biological fluids etc.) may cause spectral interference especially in inductively coupled plasma optical emission spectrometry (ICP-OES) determinations. (Sah and Brown, 1997) For these types of samples, there is a need to apply a matrix separation step prior to instrumental determination.

In this context, the aim of this thesis is to develop a new sorbent for the matrix separation/preconcentration purposes in the determination of boron by ICP-OES.

1.1. Boron, Occurrence and Properties

Boron has high affinity for oxygen; therefore always occurs in nature bound to oxygen in the form of inorganic borates. Borates can be present at high concentrations in a few commercially exploitable deposits (mainly as sodium or calcium borate minerals), but their concentrations are usually low in rocks (15-300 mg/kg), soils (<10-20 mg/kg), freshwater (<1 mg/L) and sea water (5 mg/L) (ECETOC, 1995).

Boron is an essential micronutrient for many plants, and apparently controls their calcium metabolism; in case of boron deficiency the pectin-lipids ratio is shifted in favour of the pectin. It has also been reported that boron deficiency results in growth disturbances of plants; hence boron is added to many fertilizers (Nowka et al., 2000). However, when optimal doses are exceeded, boron becomes toxic to plants and animals. Boron toxicity symptoms may range from necrosis of some plant organs to death of the whole plant depending on the extent and severity of the toxicity. The tendency of boron to accumulate in animal and vegetable tissues constitutes a potential hazard to the health of those consuming food and water with high boron content (Sah and Brown, 1997 and the related references therein).

Boron is also an important mineral for human nutrition; it functions closely with calcium and vitamin D in the preservation of bone mass and the prevention of bone demineralization. However, high doses of boron are known to cause atrophy and degeneration in testicles (Chapin, 1994). Amounts greater than 500 mg/day may cause nausea, vomiting and diarrhea. World Health Organization (WHO) has established a 1-13 mg/day safe and adequate range of boron intake for healthy individuals.

Boron is placed on the grey list of the European Union (EU) with some other metals such as Pb, Se, As, U, Zn, Cu, Ni, Cr, Mo, Ti, Sn, Ba, Be, V, Co, Th, Te, Au. The EU recognizes two lists; a large number of toxic chemicals on the ‘black list’ and less toxic compounds are placed on the ‘grey list’. The reason for placing these compounds on the lists was their toxicity and carcinogenicity, and in many cases these compounds are persistent as they are difficult to degrade (Scragg, 1999).

The concentration of boron (as borates) in fresh waters is under scrutiny because the World Health Organization (WHO, 1993) published a guideline value of 0.3 mg/L for boron in drinking water (ECETOC, 1995).

1.2. Environmental Distribution

1.2.1. Aquatic Environment

Boron, with an electronic configuration of $1s^2$ $2s^2$ $2p^1$, has 3 valence electrons and forms planar, trivalent derivatives. These derivatives are electron deficient, and, similarly to Lewis acids, accept two electrons from bases to complete the boron outer-shell octet and give tetrahedral adducts (Ooi et al, 1998).

Boric acid is a weak acid with an acid dissociation constant of 5.81×10^{-10} at 25^oC (pK_a=9.24) and is slightly stronger than silicic acid (K_a of 2.2×10^{-10}, pK_a=9.66). At a pH lower than 7, boron is present in its undissociated form (boric acid) and at a pH greater than 11.5, it is present in the dissociated borate form (Darbouret and Kano, 2000). Between these pH values, both forms exist (Figure 1.1).

The undissociated acid (H_3BO_3) is the predominant species in aqueous solution at physiological pH. The conversion into undissociated boric acid applies also to boric oxide and the sodium borates. As a consequence, the ecotoxicology of all these substances is likely to be similar to the case of boric acid (ECETOC, 1995).

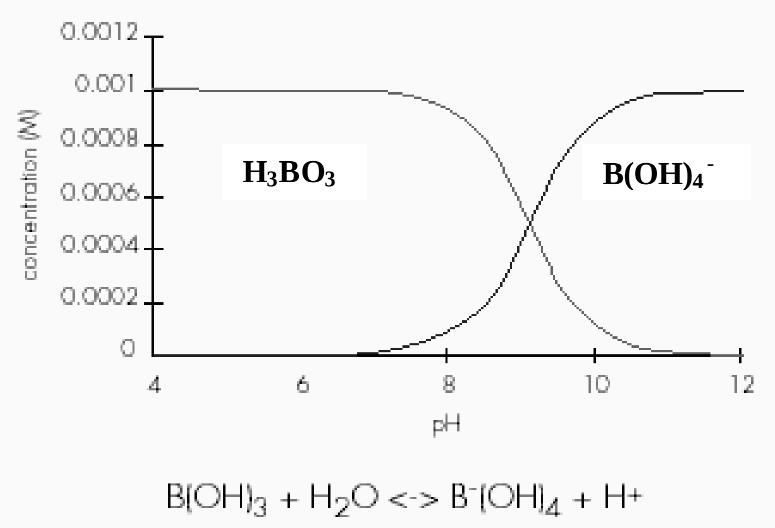


Figure 1.1. Behaviour of boric acid (1 mM) in aqueous solutions.

1.2.1.1 Seawater

Seawater is the largest destination for the water-soluble inorganic borates. Most of the boron is present in seawater as boric acid and as inorganic borates. The inorganic borate concentration in seawater is indirectly related to the salinity. The average concentration of borate in all oceans is 4.6 mg/kg water, but can vary from 0.5 mg/kg as in the Baltic Sea to 9.6 mg/kg as in the Mediterranean Sea (ECETOC, 1995).

Borate is continually being added to sea by weathering of rocks and soils, by rivers, springs, marine volcanoes, rain and dust eruptions (Mellor, 1980, page 76); but also continuously removed, maintaining a constant boron:salinity ratio. Hydrous clay-mica ilite is known to adsorb borate from seawater and thus to remove it in the form of sediments. The boron content of the world's oceans is given as approximately $7x10^{12}$ tonnes (ECETOC, 1995). The high boron content of the seawaters has some environmental significance. The presence of small quantities of boric acid vapour observed in the atmosphere probably arises from its evaporation from seawater.

1.2.1.2. Inland Fresh Waters

The boron levels in inland fresh waters are not expected to be very high, but especially near the borate mines higher levels of boron are measured. Turkey possesses about 60% of the world's reserves of borate ores, and the borate mines are located along the Simav Riverat the north of the Bigadiç town. The boron level in this river before it reaches the mining region is reported as 0 to 0.5 mg/L, but pollution from the discharge waters from the mine raises it to 4 mg/L, or even 7 mg/L, during the irrigation season. Such levels of 4-7 mg/L would render this river water unsuitable for irrigation purposes. Researchers have tried some measures like adsorption by Mg_2O and use of specific ion-exchange resin (Amberlite IRA 743) for the purification of the river water but their methods were not very successful (Okay et al, 1985).

1.2.1.3. Geothermal waters

Boron, expressed as boric acid H_3BO_3 or HBO_2^-, is an important diagnostic species in geothermal fluids (Nicholson, 1993). Spring and well discharges of chloride fluids usually contain 10-50 mg/kg boron, but very high concentrations of boron (~800-1000 mg/kg) can be found in waters associated with organic-rich sedimentary rocks. To indicate a common reservoir source for waters the Cl/B ratio is often used. Some caution is required, however, in applying this interpretation since waters from the same reservoir can show differences in this ratio. These differences can be due to the change in lithology at depth over a field or to the adsorption of boron onto clays during lateral flow.

As mentioned before the volatility of boric acid has environmental significance also around the geothermal power plant, because the volatility of boric acid increases with increasing temperature. Although originally derived by rock leaching and concentrated in the liquid phase, significant quantities of boron can be transported to the vapour phase around the geothermal power plant. The principal volatile boron species is boric acid (H_3BO_3 or $B(OH)_3$), although BF_3 may also be present in gases evolved from acidic, high-fluoride fluids (EPRI, 1986).

There have been some laboratory investigations about the extraction of boron from geothermal fluids especially for environmental control purposes. According to these studies, a boron specific resin which will work reversibly can be used to recover boron in addition to its removal. It is also mentioned in these studies that silica, one of the most common solutes in geothermal fluids, must be removed before boron extraction due to the detrimental effect of silica on the commercial resins (Fanelli, 1995).

The fact that Turkey possesses the greatest boron reserve worldwide in addition to a plenty of geothermal fields makes studies on boron removal, specially important. One of the most important examples is the Kizildere geothermal power plant in Denizli. The wastewater disposed away from the power plant has a capacity of 1500 tons/hour and contains boron approximately at a concentration of 30 mg/L. This very high boron concentration in wastewater precludes its use for irrigation in agricultural areas. Kabay et.al. (2004) studied the removal of boron from the Kizildere wastewater using N-glucamine type chelating resins, Diaion CRB 01, Diaion CRB 02, and Purolite S 108.

1.2.2. Atmosphere

Relatively few data are available on the content of boron in the earth's atmosphere, and these have been reviewed by Mellor (1980). Various sources for boron in the atmosphere have been suggested, and these include sea spray, volcanic and hot-spring emanations, airborne dust and industrial pollutions. The greatest source seems to be the evaporation of boric acid from sea water. The presence of even low borate content in rainfall or snow may be some significance in promoting plant growth.

The atmospheric boron content shows wide variation. For example, in France in 1955 the borate content of rain varied from 0.002 to 0.0045 mg/L, whereas 0.1 mg/L was reported from Japan in both rain and snow.

Anderson et. al.(1994) showed that, on average, 85% of the total atmospheric boron was in the gas phase at a concentration of 16 ng/m^3. The authors estimated that about 65-85% of the total borate source strength can be attributed to the oceans and 8-20% to anthropogenic activities such as coal, agricultural, fuel wood and refuse burning. Contribution of volcanic activities is 6-15%.

The atmospheric boron is removed from the air by rainfall and snow. The total global removal of boron from the atmosphere by wet and dry deposition was estimated to be 5.3 to 7.0 million tonnes per year.

1.2.3. Soil

Boron status on soil can be complicated because of the tendency of the water-soluble borates to adsorb/desorb from the soil. The boron-soil interaction has been reviewed by Keren and Bingham (1985). The authors emphasize the need to take into account the physical-chemical characteristics of the soil to explain such interactions. According to their study, overall boron content in the earth's soil may be divided into two types. The low borate content (<10 mg/kg) soils are present on most of the earth. The high borate content (up to 100 mg/kg or more) soils are found in the Great Basin and Mojave areas of Western USA and in a band across the Mediterranean through Turkey, Iran, and Kazakhstan. The average overall content of borate of all soils in the world is reported as 10-20 mg/kg (Mellor, 1980, pp 107-109). The boron content of igneous and sedimentary rocks is also found in the above mentioned study.

1.3. Determination of Boron in Environmental Samples

Boron may be present in environmental samples in a variety of matrices like plants, living organisms, soils, different types of waters. Due to the presence of interfering species, borate is usually extracted from the samples prior to instrumental determinations.

The most common methods for the determination of boron are UV-Vis molecular spectrophotometric and plasma-source atomic spectrometric methods (Sah and Brown, 1997). Each technique has its limitations, but inductively coupled plasma optical emission spectrometry (ICP-OES) is one of the well-established techniques with low detection limits, good sensitivity and rapid sample analysis. Inductively coupled plasma mass spectrometry (ICP-MS) is used when more sensitive determinations are required. Although most spectrophotometric methods are based on colorimetric reactions of boron with azomethine-H, curcumin, or carmine, other colorimetric and fluorometric methods have also been used to some extent. These methods, in general, suffer from numerous interferences and have low sensitivity and precision. Application of nuclear techniques and atomic emission/absorption spectrometric (AES/AAS) methods has remained limited because these methods have poor sensitivity and suffer from serious memory effects and interferences (Sah and Brown, 1997).

Irrespective of the analytical technique used for boron determination, the quality of the results (accuracy, precision, etc.) will be dependent on the care that is taken during the sampling and the sample preparation steps. Use of borosilicate and other boron-containing glassware should be avoided because of the possibility of contamination.

1.3.1. Spectrophotometric Methods

A number of spectrophotometric methods based on the use of anionic dyes for color development are employed for boron determination. Examples of these methods are curcumin (Rand, 1975; Williams, 1979), carmine (Rand, 1975; Williams,1979), methylene blue (Williams,1979), azomethine-H, and others such as quinalizarine, arsenazo, and crystal violet. Under anhydrous acidic conditions the anionic dye is protonated and can then form a spectophotometrically-active complex with boron.

Among these, the azomethine-H is perhaps the most commonly used complexing agent in boron determinations. As stated by many researchers, the azomethine-H method is fast, simple, and sensitive and does not require concentrated acids, which make it desirable for automation (Sah and Brown, 1997 and the related references therein).

1.3.1.1. Interferences and Drawbacks of the Spectrophotometric Methods

The curcumin method is reported to be affected by nitrate, chloride and fluoride interferences, with the fluoride interference also affecting the carminic acid method. Despite this, the American Public Health Association Standard Methods includes both the curcumin and the carminic acid procedures for the determination of boron. These procedures are applicable for concentration ranges 0.1-1 mg/L and 1-10 mg/L, respectively (APHA, 1989).

The azomethine-H method is not affected by the anions generally found in raw, potable, and saline waters or sewage whereas high nitrite levels (above 9 mg/L) may interfere with the method. Some cations such as iron, copper and calcium may also cause interference in the method, but these cations can be masked by complexation with EDTA. A buffer of polyphosphate, thiourea and ascorbic acid may also be used to reduce interferences from iron, copper and calcium (Ferran *et al*, 1988)

1.3.2. Atomic Spectrometric Methods

Atomic absorption spectrometry is not widely used in boron determinations due to its poor sensitivity, presence of memory effects of previous samples, and numerous interferences (Papaspryrou et al., 1994). Due to this low sensitivity this technique often requires separation and preconcentration of boron from the sample matrix for acceptable results (Butelho et al., 1994). Castillo et al. (1985) improved the detection limit and sensitivity of the method by separating boron from the sample matrix as volatile methyl borate and measuring the atomic emission signal of BO_2^- radical at 548 nm.

Electrothermal atomic absorption spectrometry (ET-AAS) has also poorer detection limit for boron compared to its detection power for the other elements, probably due to inefficient thermal dissociation of boron-containing species and serious memory effects (Luguera et al. 1991).

1.3.3. Plasma –Source Methods

Introduction of plasmas as ionization sources and the development of plasma-source analytical instruments (plasma-source-OES and MS) have provided high sensitivity and low detection limit in boron determinations. Most commercial plasma-source instruments use an argon ICP as in inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

In most of the determinations using plasma-source instruments, liquid samples are employed. Solid samples are decomposed and solubilized prior to introduction to the plasma by a proper nebulization device. Several alternative modes of sample introduction (e.g., slurry, powder, gases, laser ablation, and electrothermal vaporization (ETV)) are used for direct analysis of solid samples for specific purposes, mainly to avoid sample preparation and reduce interferences (Jarvis et al., 1992).

1.3.3.1. ICP-OES for the Determination of Boron

Development of ICP-OES has revolutionized the determination of so-called “problem elements” such as B, S, Mo, in sub mg/L to mg/L concentrations, and those trace elements which are hard to detect, owing to its low detection limits, wide linear dynamic range, and multielement detection capability. The reported detection limits for boron are 10 to 15 µg/L in soil solutions and plant digests by ICP-OES based on a linear self-scanning photodiode array (Spiers and Evans, 1990).

1.3.3.1.1 Spectral and Matrix Interferences in ICP-OES for Boron Determination

Interferences encountered in ICP-OES can be of two kinds, spectral and matrix-related. If the wavelength of the element of interest is near the wavelength of another element in the sample and if these two close wavelengths cannot be resolved, this effect is called spectral interference. For instance, iron is the most important spectral interference in boron determination by ICP-OES. It interferes with the two most sensitive boron lines at 249.773 nm and 249.678 nm in the ICP-OES method (Pritchard and Lee, 1984). If the sample has high iron concentrations (as encountered in the digests of soil, metals, geological and some biological materials) then 249.773 nm and 249.678

nm lines cannot be used because of the overlap of Fe at 249.782 nm and 249.653 with boron lines. Boron determination by ICP-OES is also affected by interferences caused by sample matrix (chemical interferences); for example, Si interferences may render low levels of boron determination unreliable (Owens et al., 1982; Din, 1984). The presence of Fe, Ni, Cr, Al, and V depressed, while Mn, Ti, Mo, and high concentrations of Na enhanced boron signals. (Sah and Brown, 1997 and the related references therein).

1.3.3.2. ICP-MS for the Determination of Boron

The ICP-MS is often the method of choice over ICP-OES and spectrophotometric methods for boron determination due to its higher sensitivity, lower detection limits, simultaneous measurement capability of boron isotopes (^{10}B to ^{11}B) and total boron concentration in a sample. The ability of ICP-MS to measure boron isotope ratios is important especially in biological boron tracer studies. The reported detection limits are at the µg/L level, e.g., 1-3 µg/L (Smith et al., 1991; Evans and Krahenbuhl, 1994) in biological materials, 0.15 µg/L in saline waters (Gregoire, 1990), and 0.5 µg/L in human serum (Vanhoe et al., 1993). The uniqueness of ICP-MS is also due to its capability to carry out boron determination by isotope dilution method which is considered the most precise method for quantitative determination.

1.3.4. Memory Effects

Boron tends to raise the baseline in spectrometric and other procedures by adhering to instrumental components, which affects subsequent readings of many determination methods. This phenomenon is called ″memory effect″ and presents a major problem in boron determination. Different mechanisms for the memory effects of boron in ICP spectrometry have been proposed. Sun et al. (1997) inferred that the memory effect comes from the reaction of boron with the sample introduction system, especially the spray chamber, which is usually made of borosilicate glass or quartz. Al-Ammar et al. (1999) considered that it originates from the tendency of boron to volatilize as boric acid from the sample solution layer that covers the inside surface of the spray chamber. Some efforts have been made for eliminating or minimizing the memory effect. (Evans and Krahenbuhl,1994; Sun et al., 1997; Al-Ammar et al., 1999). Smith et al. (1991) used a direct injection nebulizer instead of a conventional sample introduction system for fast boron cleanout. However, a commercial direct injection nebulizer is expensive and is not easy to use in routine analysis. A simple way for minimizing the memory effect of boron is to rinse the system with a flush solution. Evans and Krahenbuhl (1994) suggested the use of sodium fluoride as the flush solution, but Pros et al. (1997) indicated that 13 minutes were required to remove the memory resulting from 0.5 µg/mL of boron. Dilute nitric acid was also employed as the rinse solution for the determination of boron.

Da-Hai Sun et al.(1997) examined the memory effect of boron by using different diluent and rinse solutions, including water, nitric acid, Triton X-100, ammonia and mannitol in water, in nitric acid and in ammonia. They suggested that a mixture of ammonia and mannitol as diluent and rinse solution minimize the memory effect of boron.

1.4. Matrix Isolation and Removal of Boron

Boron removal has given rise to numerous works (Pilipenko et al., 1990). The main processes that have been studied are:

(1) precipitation-coagulation,

(2) adsorption on oxides (Lapp and Cooper, 1976; Choi and Chen, 1979; Okay et al., 1985; Pilipenko et al., 1990; Hayashi et al., 1991),

(3) adsorption on active carbon or cellulose (Choi and Chen, 1979),

(4) ion exchange with basic exchangers (Peterson,1975; Popat et al., 1988),

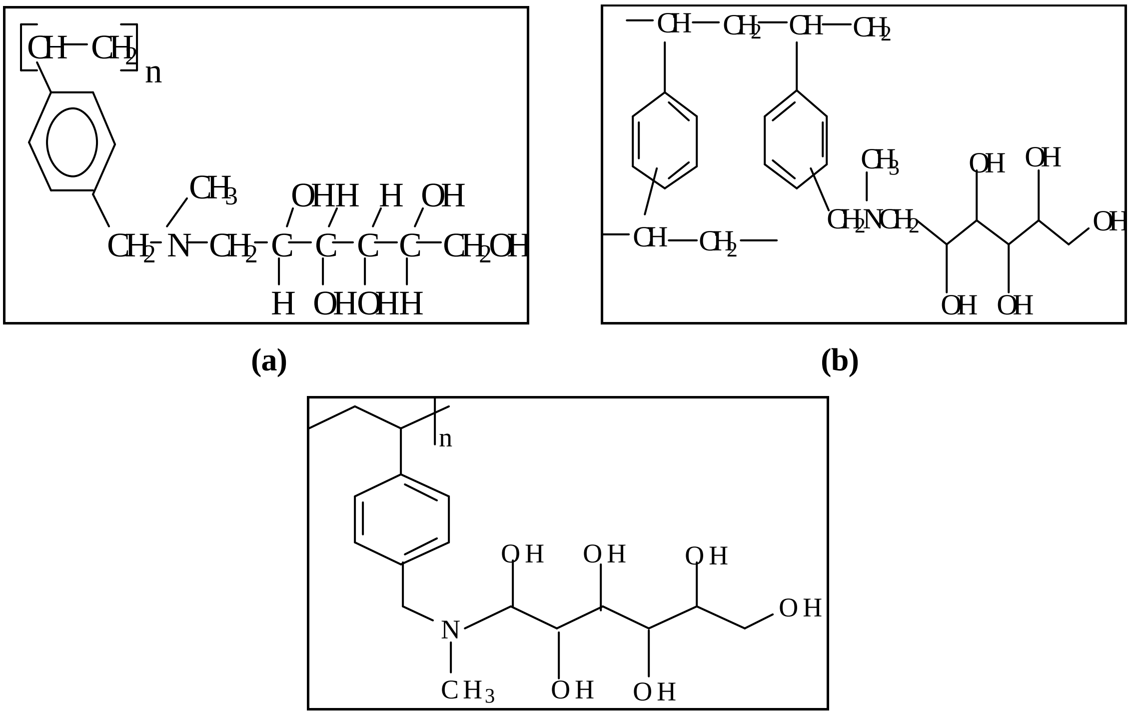
(5) solvent extraction, after complexation (Lapp and Cooper, 1976; Grinstead and Wheaton, 1971; Pilipenko et al.,1990; Matsumoto et al., 1997),

(6) membrane filtration after complexation (Smith et al., 1995),

(7) use of boron selective resins, with diols as boron-complexing agents, particularly Amberlite XE 243 (Lyman and Preuss, 1957; Kunin and Preuss, 1964; Sahin, 1996) then the macroreticular resin Amberlite IRA743 (Okay et al., 1985; Recepoglu and Beker, 1991) and some other N-glucamine type chelating resins Diaion CRB-01, Diaion CRB 02 and Purolite S 108 (Kabay et al. 2004)

Among the boron removal methods, ion exchange process is the most extensively used. It is also known that chelating resins containing functional groups in which hydroxyl groups are in the 1-2 or 1-3 position show high selectivity for boron removal through the formation of borate-diol complexes (Kunin et al., 1964; Schilde and Uhlemann, 1992). In one study, removal of boron from natural gas brines was studied by commercially available chelating resins containing N-methyl (polyhydroxyhexyl) amino groups. The resins used were Amberlite IRA 743, Diaion CRB 02, Duolite ES 371. Ooi et al. (1996) reported recently the screening results of various adsorbents for boron removal from brine. Among the adsorbents, some hydrous oxide of tetravalent metals ($CeO_2.nH_2O$, $ZrO_2.nH_2O$, and $HfO_2.nH_2O$) or pentavalent metals ($Ta_2O_5.nH_2O$) showed good adsorption property for boron. The boron sorption study was also performed by glucamine type resin (Diaion CRB 02) using the residual brine after salt production from seawater (Ooi et al. 1996).

Due to high boron content of its wastewater, Denizli-Kizildere geothermal field in Turkey has been the subject of some boron removal studies. The water disposed away from the power plant has a capacity of 1500 tons/hour and contains boron at an approximate concentration of 30 mg/L. When the average level of boron in irrigation waters (generally given as 1 mg/L) is considered, the very high level of boron in the disposed water of Kizildere makes the use of this water for irrigation purposes impossible. In one of the studies on the investigation of boron removal from Kizildere geothermal wastewater, Recepoglu and Peker (1991) used Amberlite IRA 743. For the same purpose, Kabay et al. (2004) employed three different chelating resins, namely Diaion CRB 01, Diaion CRB 02, and Purolite S 108. The chemical structures of these resins are given in Figure 1.2. Diaion CRB 01 and CRB 02 have the same chemical structure but different physical characteristics. These resins have common in N-methylglucamine functional group and they just differ in the polymer chain.



(a) **(b)**

(c)

Figure 1.2. Chemical structures of (a) Amberlite IRA 743, (b) Diaion CRB 02, and (c) Purolite S 108.

It has been suggested by various researchers that boron is retained by Amberlite IRA 743, a very well known boron selective resin, according to the following reaction scheme: a borate ion is complexed by sorbitol groups, and a proton is retained by a tertiary amine site that behaves as a weakly basic anion exchanger [Simonnot et.al, 2000 and the references therein]. The reactions can be expressed as follows:

$H_3BO_3 + H_2O === B(OH)_4^- + H^+$ (Boric acid dissociation) (1)

$B(OH)_4^- + 2\text{-CHOH-CHOH-} == 4H_2O + B^-(OCH)^-$ (Boron complexation) (2)

$-CH_2-N(CH_3)-CH_2- + H^+ === -CH_2-N^+H(CH_2)-CH_2-$ (Amine protonation) (3)

Figure 1.3. shows the structure of Amberlite IRA 743 before and after sorption of boron as borate $[B(OH)_4]^-$.

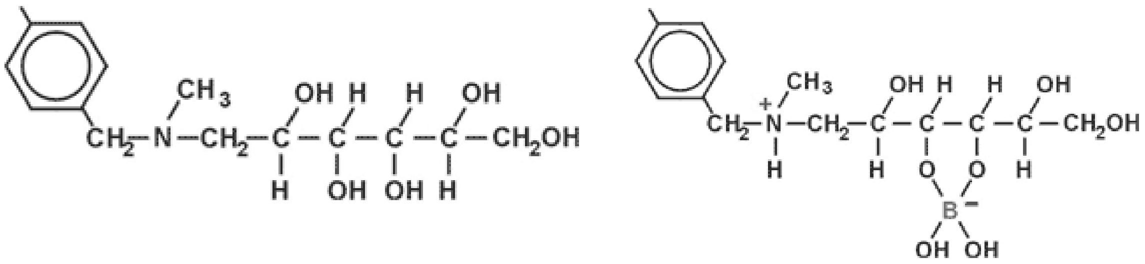


Figure 1.3. The boron selective resin Amberlite IRA 743 before and after boron sorption. (Rohm and Haas, 1997)

1.5. Aim of the Study

One of the goals of this study was to investigate the analytical methods for boron determination. The spectrophotometric methods (using carmine and azomethine-H as complexing agent) were tried, and roughly compared. Among the boron determination methods the more convenient ICP-OES was tried to be optimized.

The other goal was to develop a novel sorbent material for pre-concentration and removal applications of boron-containing water samples. For this purpose an inorganic support material, like silicious MCM-41 and amorphous silica, was functionalized with N-methylglucamine. The newly synthesized material was characterized by XRD, DRIFTS, BET (Brunauer-Emmett-Teller) isotherm techniques, and elemental analysis. Also, the boron sorption capability of the sorbent was examined for environmental water samples.

1.6. Synthesis of New Sorbent Material for Boron

Various synthesis procedures can be found in literature for developing new resins for boron removal. For instance, Biçak et al. (2000) synthesized a boron-specific resin by modification of crosslinked glycidyl methacrylate-based polymers. Inukai et al. (2004) synthesized resins for boron sorption, with natural organic polymer support cellulose. These studies include the functionalization of the polymer chain with the boron-binding group N-methylglucamine. In addition to the use organic polymers, the functionalization can be done by using an inorganic support material. Silica gel is one of the most widely used for this purpose as being an amorphous inorganic polymer with composed silioxane groups (Si-O-Si) in the invard region and silanol groups (Si-OH) distributed on the surface. In recent years modification of silica by inorganic or organic functional groups has been the subject of considerable interest due to many possibilities of application. Surface modifications are usually achieved with silanation using an appropriate organosilane reagent (Cestari et al., 2000; Vieira et al., 1999; Flounders et al., 1995; Park et al., 2002). Also, micelle-templated silica (MTS) materials (recently disclosed by Mobil's researchers as MCM-41; Beck et al., 1992) have been extensively used for modification. Due to their high surface area and their regular mesoporous system of pore-monodispersed size, MTS constitute excellent mineral supports for the preparation of inorganic-organic hybrid materials by grafting organic chains onto their surface through silanation (Brunel et al.,1995).

1.6.1. Functionalization of Silica Surface

Various methods of functionalizing the surface of periodic mesoporous materials with organic groups have been investigated in recent years because surface modification permits tailoring of the surface properties for numerous potential applications including catalysis, ion exchange, encapsulation of transition-metal complexes or semiconductor clusters, chemical sensing, and nano material fabrication (Kresge et al., 1992; Diaz et al.,1996). As a support for organic functional groups, hexagonally ordered MCM-41 (Beck et al., 1992; Rao et al., 1997) is particularly interesting due to its high surface area and uniform pore size distribution in the mesopore size range. Hybrid mesoporous sieves take advantage of the inorganic support, as well as of the organic surface groups. The polymeric silica framework of MCM-41 provides structural order, as well as thermal and mechanical stability, whereas organic species incorporated into inorganic phases permit versatile control of interfacial and bulk materials characteristics, such as porosity, hydrophobicity, and optical, electrical, or magnetic properties.

Organic functionalization of the internal surface of a MCM-41 host can be achieved either by covalently grafting various organic species onto the channel walls (Beck et al., 1992) or by incorporating functionalities directly during the preparation. The first approach, a postsynthesis grafting (PSG) process, has been widely employed to anchor specific organic groups onto surface silanols of diverse silica supports.

Typically, organochlorosilanes or organoalkoxysilanes are used as precursors for the surface modification. In this method, the host materials should be dried carefully prior to adding precursors to avoid self-condensation of precursors in the presence of H_2O.

1.6.1.2 Why MCM-41?

Due to their highly ordered three-dimensional mesoporous structures with a pore size from 10 to 100 Å, a new family of mesoporous molecular sieves named M41S has been technologically important in a variety of applications utilizing catalysts, molecular sieves and adsorbents. The M41S family is classified into several members: MCM-41 (hexagonal), MCM-48 (cubic) and other species (Beck et al., 1992; Tanev et al., 1994; Beck et al., 1996). MCM-41 exhibits extremely high surface area and well defined pore size as well as high thermal stability and flexible framework composition. The syntheses of which were first reported by researchers of the Mobil Oil Corporation (Beck et al., 1992; Kresge et al., 1992).

The originally proposed mechanistic pathways of the formation of the MCM-41 structure are illustrated in Figure 1.4. In the first, the presence of the liquid-crystal mesophase prior to the addition of the reagents, i.e., preexistence of surfactant aggregates (rod-like micelles), followed by the migration and polymerization of silicate anions, results in the formation of the MCM-41 structure.

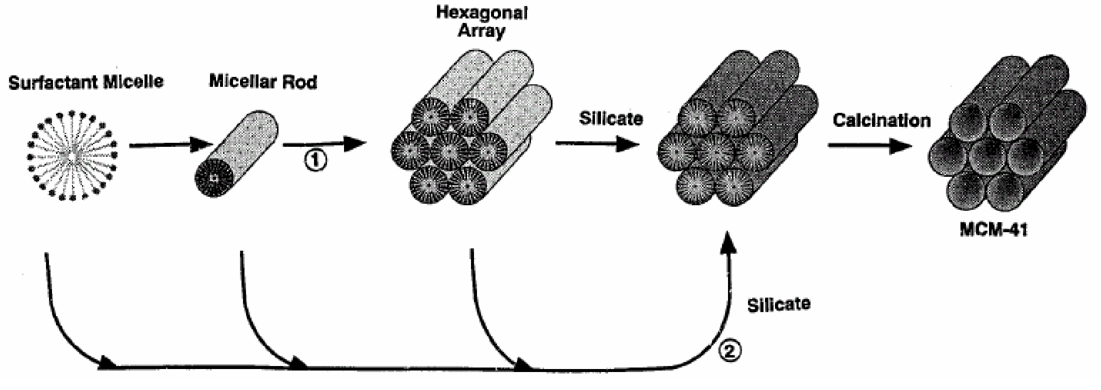


Figure 1.4. Possible mechanistic pathways for the formation of MCM-41. (1) liquid-crystal-phase-initiated and (2) silicate-anion-initiated (Vartuli et al.,1998).

The advantages of the ordered silicate mesoporous materials for separation applications include a regular array of uniform pores, controllable pore size, and the ability to functionalize the surface for particular separations. Furthermore, MCM-41 has a rigid structure and so avoids the swelling problems encountered with some other adsorbents. Potential separation applications for MCM-41 include protein separation (Kisler et al., 2001; Han et al., 1999) and mercury removal from waste streams (Feng et al., 1997). However, the stability of these materials in aqueous solutions is of concern. Although the properties of M41S materials have been widely investigated, only limited studies have been performed after their exposure to aqueous solutions. Most of these studies have focused on the hydrothermal stability of the materials by assessing their structure before and after treatment in boiling water for up to 48 hours (Lim et al., 1999; Yamamoto and Tatsumi, 2001). However, it is important that the pore structure integrity must retain throughout repeated adsorption and regeneration cycles which are generally performed around room temperature, if these materials are to be economically employed in separation processes involving aqueous solutions. A recent work has shown that the M41S materials are modified by prolonged exposure to water and water vapour, leading to decreased structural regularity, pore shape uniformity, pore size, and pore volume (Yamamoto and Tatsumi, 2001).

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals and Reagents

All reagents were of analytical grade. Ultra pure water (18 MO) was used throughout the study. All reagents were stored in polyethylene/polypropylene containers. Plasticware were cleaned by soaking them in dilute nitric acid (10% v/v) and rinsed with deionized water prior to use.

a) Standard boron stock solution (1000 mg/L) : Prepared by dissolving 5.716 g anhydrous H_3BO_3 in ultra pure water and diluted to 1000 mL

b) Carmine reagent: Prepared by dissolving 920.0 mg carmine in 1.0 L of concentrated H_2SO_4.

c) Azomethine-H solution: Prepared by dissolving 1.0 g of azomethine-H and 2.0 g of ascorbic acid in about 70 mL of deionised water. The mixture is warmed for complete dissolution and diluted to 100 mL. This solution can be stored for 1-2 days only in a boron-free bottle.

d) Buffer solution (for Azomethine-H method): Prepared by dissolving 3.0 g Na_2EDTA in a mixture of 150 mL deionized water and 125 mL glacial acetic acid and addition of 250.0 g ammonium acetate. The mixture is warmed and stirred for complete dissolution. The solution is stored in a plastic bottle.

e) Mannitol solution: Prepared by dissolving 5.0 g of mannitol in ultrapure water and diluting to 50.0 mL

f) Calibration standards: Lower concentration standards were prepared daily from their stock solutions.

g) pH adjustment: Various concentrations of $HCl_{(aq)}$, $NaOH_{(aq)}$ and $NH_{3(aq)}$ solutions were used.

h) Sodium silicate (27% SiO_2, 14% NaOH) was used as the silica source for the synthesis of support material MCM-41.

i) Cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$) as quaternary ammonium surfactant for the synthesis of support material MCM-41.

2.2. Instrumentation and Apparatus

2.2.1. Apparatus

In sorption studies with batch method, Yellowline RS 10 orbital shaker was used to provide efficient mixing. The pH measurements were performed by using InoLab Level 1 pHmeter. Honeywell UDC 3000 “U” type oven was used for calcination of MCM-41.

2.2.2. UV-VIS Spectrophotometry

Spectrophotometric determinations of boron with carmine and azomethine-H complexing agents were performed by using Varian Carry 50 Scan Spectrophotometer with 1.0 cm quartz cuvettes as sample holder.

2.2.3. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

A Varian Liberty Series II Axial view ICP-OES was used in boron determinations throughout the study. The instrumentation and operating conditions are listed in Table 2.1.

Table 2.1. Instrumentation and operating conditions for ICP-OES.

Spectrometer	
Varian Liberty Series II ICP Atomic emission spectrometer	
Axial view	
Monochromator	
Czerny-Turner	0.75 meter
Grating	90x100 mm holographic
Grating density	1800 grooves/mm
Detection	
R199UH UV enhanced solar blind 175-300 nm with Cs-Te photocathode for UV region	
R446 300-940 nm wide range with multi-alkali photocathode for visible region	
Plasma conditions	
40 MHz, axial view	
Incident power (kW)	1.2
Argon flow rates (l min^{-1})	
Plasma	15
Auxiliary	1.5
Argon pressure of nebulizer	200 bar
Nebulizers	
Concentric Glass Nebulizer	
Concentric (Sturman-Masters double pass type) with cyclonic chamber	
Sample injection modes	
Continuous nebulization	
Signal processing	
Line measurement	Peak height
Background correction	Polynomial plotted background correction

2.3. Synthesis and Characterization of the New Sorbent for Boron Sorption

2.3.1. Synthesis of Support Material

2.3.1.1. Synthesis of MCM-41

The synthesis of pure-silica MCM-41 was carried out by the following procedures by Lin et al. (1997) in which the surfactant cetyltrimethylammonium bromide (CTMAB) was used as the template. In the preparation of as-synthesized mesoporous pure silica MCM-41 materials, the delayed neutralization process that was reported by Lin and Mou (2002) was used. Briefly, the first step was the preparation of an aqueous surfactant solution by dissolving 49.2 g of cetyltrimethylammonium bromide in 243.0 mL of water at 50°C with stirring. After the addition of 45.0 mL sodium silicate, a clear gel mixture was formed. The resulting gel was continued to be stirred for a further 20 minutes. Subsequently, with vigorous stirring, an appropriate amount (35.0- 40.0 mL) of 1.10 M H_2SO_4 was added drop wise into the gel mixture at room temperature to adjust the pH of the composition to 10.0. The molar ratio of the resulting gel composition was: $1C_{16}TMAB:0.48SiO_2:0.39Na_2O:0.29H_2SO_4:60H_2O$. The gel was sealed in Teflon-lined stainless steel autoclave and heated to and kept at 100°C under static conditions for 48 hours. After the autoclave was cooled down to room temperature, the as-synthesized MCM-41 material was filtered, washed with a large amount of deionised water until the pH of the wash liquid was neutral. Then the synthesized MCM-41 was left drying in air at room temperature for overnight. To remove the occluded organic species the material was calcined by heating the samples at 550°C under a continuous flow of dry air for 6 hours. A heating rate of 1°C min^{-1} was applied to attain the final temperature. The synthesis procedure is outlined in Figure 2.1.

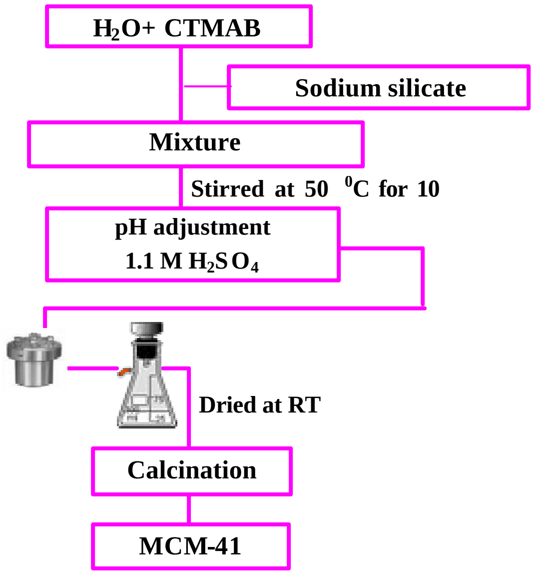


Figure 2.1. Flow chart of the synthesis of MCM-41

2.3.1.2. Synthesis of Amorphous Silica

In this study two types of amorphous silica were used. One of them is commercial silica that was purchased from Aldrich. The other one was synthesized by Balköse and her group (personal communication). During synthesis gelation was performed at pH 3.65. Commercial silica was purchased from Aldrich (Davisil silica gel, 635 grade) its particle size 150-250 µm (60-100 mesh). The surface area and pore volume of the silica is 480m^2/g and 0.75cm^3/g, respectively.

2.3.1.2.1. Acid Treatment of Amorphous Silica

To increase the free silanol (Si-OH) groups on the surface of amorphous silica, acetic acid treatment was made. Amorphous silica (3.0 g) was mixed with 50.0 mL of 0.01 M CH_3COOH and the suspension was shaken under vacuum in ultrasonic bath for 1 hour. The resulting suspension was filtered and washed with ultra pure water until filtrate reached the neutral pH. After the acid treatment, silica was evacuated overnight at 120°C prior to silanation.

2.4. Synthesis of the Sorbent for Boron Sorption

The novel sorbent material for B was synthesized in two steps. In the first step the support material (MCM-41/amorphous silica) was grafted by using an alkoxysilane (3-bromopropyl-trimethoxysilane). In the second step the grafted MCM-41/silica was reacted with N-methylglucamine, a boron-binding functional group, in a substitution reaction. In this study, the synthesis procedure of MCM-41 functionalized with N-methylglucamine was similar to the suggested by Brunel (1998) with several modifications.

2.4.1. Preparation of Grafted MCM-41/Silica (Br-propylsilyl-MCM-41/Silica)

The grafted MCM-41/silica (3-bromopropylsilyl-MCM-41/silica) was prepared by addition of (3-bromopropyl)trimethoxysilane at varying amounts from 0.5 to 10 mmol to suspensions of freshly evacuated (120^{o}C, 2 bar, 16 h) 3.0 g of MCM-41/silica in dried trichloromethane (50 mL). The reaction mixture was left refluxing under argon atmosphere for overnight. After filtration, the modified material was washed with a diethyl ether-dichloromethane mixture (1:1) for 12 hours in a soxhlet apparatus. The schematic illustration of grafting of the support material is given in Figure 2.2.

2.4.2. Preparation of MCM-41/Silica Functionalized with N-Methylglucamine

MCM-41/silica functionalized with N-methylglucamine was prepared by addition of N-methylglucamine at varying amounts from 1.5 to 30 mmol (depends on silanation ratio) to suspensions of Br-propylsilyl-MCM-41 (3.0 g) in refluxing water (30 mL). After stirring overnight, the modified material was separated by filtration, washed, and then treated with the water in a soxhlet apparatus for 16 hours. The proposed functionalization reaction way is illustrated in Figure 2.3.

In this study two types of solvents, ethanol and water, were tried for functionalization reaction. Due to the higher solubility of N-methylglucamine in water, it was used for functionalization reaction throughout the study.

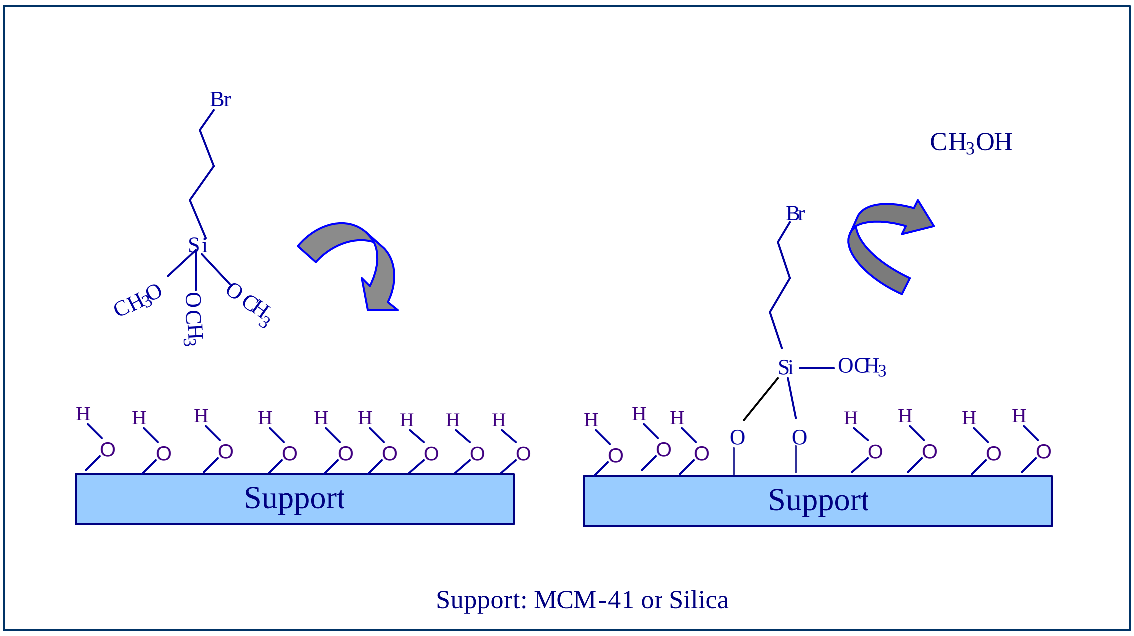


Figure 2.2. Schematic illustration of grafting of MCM-41/silica with (3-bromopropyl)trimethoxy silane.

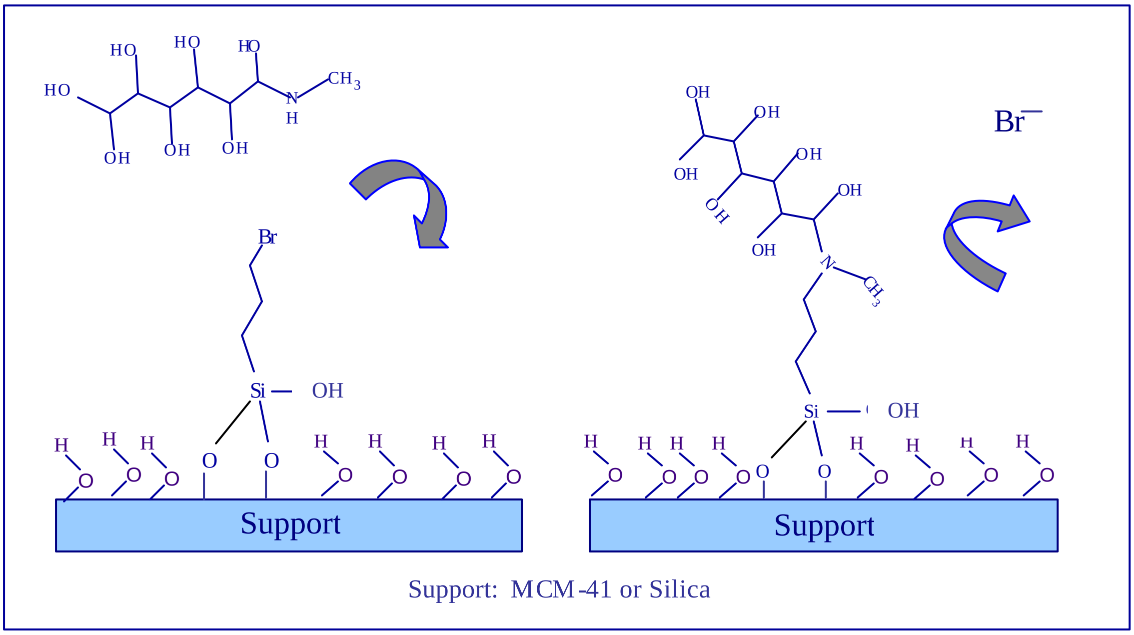


Figure 2.3. Schematic illustration of preparation of MCM-41/silica functionalized with N-methylglucamine.

2.5. Characterization of the Synthesized Sorbent

Firstly, a number of characterization experiments were performed to understand whether the framework of MCM-41 support collapsed during the functionalization reactions and secondly, whether the functional groups were attached to the support material. Characterization of the sorbents was carried out by using X-Ray Diffraction (for the MCM-41 support), Diffuse Reflectance Infrared Fourier Transform Spectrometry (DRIFTS), BET analysis and elemental analysis.

In addition to the characterization experiments mentioned above, the sorption behaviour of the novel sorbents gave valuable information about the modification of the support upon the addition of N-methylglucamine. If the functional groups had not been attached to the support, it would not have shown any sorption. (As will be shown later, the starting material had minor boron (as borate) sorption capability whereas it was significantly adsorbed boron after modification with N-methylglucamine.)

2.5.1. X-Ray Diffraction Measurements

X-Ray powder diffraction (XRD) data were collected on a Philips X’Pert Pro diffractometer using Cu Ka radiation (?=0.154 nm). Samples were prepared by compressing in the cassette sample holder without any adhesive substance.

2.5.2. DRIFTS Measurements of the N-MGCMN-modified MCM-41

DRIFTS measurements were carried out using Nicolet Magna 550 FTIR spectrometer equipped with Spectra-Tech Collector II model 0030-0XX diffuse reflectance accessory. The spectra were collected at a resolution of 8 cm^{-1} and averaged over 32 scans. In a typical measurement, 1 mg of sample was mixed with and completely dispersed in 10 mg KBr.

2.5.3. Elemental Analysis

Samples were placed in narrow tubes sealed at one end and dried in a 100^{o}C oil bath under vacuum for 2 days. The open end was also sealed under vacuum, and the samples prepared so were sent to TUBITAK Ankara Test and Analysis Laboratories (ATAL). The elemental analyzer used was LECO CHNS 932.

2.5.4. BET Analysis

Specific surface areas of the synthesized sorbent and the pure support materials were measured using a static process by means of a Micromeritics ASAP 2010 instrument using nitrogen at 77 K. The specific surface area was calculated by the BET method and average pore diameters and pore size distributions were calculated from the adsorption branch of the isotherm using the Barrett, Joyner and Helenda (BJH) method. All samples were degassed for 3 hours at 423 K.

2.6. Determination of Boron

Although the plasma-source methods are known as more efficient methods for determination of boron in various matrices, UV-Vis spectrophotometric methods were also tried and optimized.

2.6.1. UV-Vis Spectrophotometry

2.6.1.1. Carmine Method

The carminic acid gives a blue-red complex with boron. The colour intensity of the complex is related to boron concentration of the solution and the absorbance of the complex is measured by using a UV-Vis spectrophotometer. The method is useful for boron concentrations between 1.0 to 10.0 mg/L. The samples that are out of this concentration range should be diluted or preconcentrated accordingly.

Color Development: A series of boron standard solutions (between 1.0 to 10.0 mg/L) were prepared in such a way that, the necessary amount of stock boron standard (1000 mg/L) is taken into 10 mL volumetric flask and diluted to 10 mL. A portion (1.0 mL) of standard solutions and samples were transferred to a test tube, two drops of concentrated $HCl_{(aq)}$ were added and followed by a careful addition of 5.0 mL of concentrated $H_2SO_{4(aq)}$. The mixture heated due to exothermicity of solvation of acid was allowed to cool room temperature. Then freshly prepared carmine reagent (5.0 mL) was added to all solutions and mixed well. After 45-60 minutes, the absorbance of the blue-red boron-carmine complex was measured at 604 nm. The concentration of boron in sample solutions was determined from the calibration graph.

2.6.1.2. Azomethine-H Method

Boron reacts with azomethine-H to form a yellow complex, which can be then measured by a UV-Vis spectrophotometer. The intensity of the absorbance is related to the boron concentration of the solution. The method works in acetic acid-ammonium acetate buffer with a pH of 4.6 and interfering species are masked by the use of EDTA. The method is useful for boron concentrations of 0.1 to 1.0 mg/L range.

Color Development: A series of standard solutions (between 0.1 to 1.0 mg/L) were prepared by diluting the required volumes of stock boron standard solution. Two millilitres of standard or sample solutions were transferred into a 10 mL plastic test tube. A 0.80 mL portion of the buffer solution and 1.0 mL of freshly prepared azomethine-H solution were added to each of standard and sample solutions. Deionised water (1.2 mL) was added to make up the solutions to 5.0 mL. The solutions were mixed and stored at <20^{o}C for 20 minutes. (The colored solutions should be kept below 20^{o}C, otherwise the color fades).The absorbance was measured at 420 nm using 1.0 cm cuvette with a UV-Vis spectrophotometer. In this study Varian Carry 50 Scan Spectrometer was used. The concentration of boron in sample solutions was determined from the calibration graph.

2.6.2. ICP-OES Method

2.6.2.1. Optimization of ICP-OES for Boron Determination

The usual practice in any measurement is to use the optimum conditions obtained in order to secure satisfactory results. For the most of the cases the conditions leading the most sensitive results were usually the optimum conditions. To achieve sensitive measurement, the most sensitive and interference free boron emission lines should have been chosen. For this purpose the most sensitive emission lines of boron, 249.773 nm and 249.678 nm, were chosen. Boron emission line of 208.959 nm was also chosen in case Fe interferes.

An experiment was performed to investigate the possible iron interference at these three wavelengths. A series of iron standard solutions were prepared between 0.5 to 100.0 mg/L and these solutions were measured at the given boron emission lines. The related figures are given in Appendix C. As can be seen from the figures high concentrations of Fe may cause interference at 249.773 and 249.678 nm but not at 208.959 nm.

The most important drawback of boron determination with ICP methods is the memory effect of boron. To obtain reliable measurements the memory effect of boron was tried to be minimized.

2.6.2.1.1. Reduction of Memory Effect

As mentioned before the memory effect of the boric acid is the most important drawback of boron determinations with ICP methods. Different mechanisms for its memory effect in ICP methods and also some measures to reduce its extent have been proposed. In this study several solutions were investigated to reduce the memory effect; namely HCl, HNO_3, NH_3, mannitol and a mixture of mannitol-ammonia as diluent and flush solution as suggested by Da-Hai Sun and et.al (2000).

2.6.2.2. Calibration Strategies for Boron with ICP-OES

2.6.2.2.1. Aqueous Calibration Plot

Standard solutions from 0.1 mg/L to 20.0 mg/L were prepared from 1000 mg/L boron standard with simple dilution. All standards contained 0.1 M NH_3 and 0.25 % (w/v) mannitol.

2.6.2.2.2. Matrix-Matched Calibration Plot

In order to plot matrix-matched calibration curves of boron, standard solutions from 1.0 mg/L to 20.0 mg/L were mixed with 0.1 g of MCM-41 functionalized with N-methylglucamine. The solutions were shaken manually for 1-2 minutes and then placed on the shaker for 30 minutes at room temperature. The contents were collected on filter papers and then were eluted using 1M HNO_3 solution. The resultant solutions were analyzed by ICP-OES.

2.7. Boron Sorption Studies

To provide a reliable boron determination, matrix isolation or a preconcentration step can be necessary especially for difficult matrices. In order to find the appropriate sorbent for matrix removal and also preconcentration of boron, various adsorbents such as ion exchangers, chelating resins, natural and synthetic zeolites were tried. As an initial experiment, 10 mg/L boron solution was prepared from the stock solution. First sorption experiments were performed in pure water. The pH of the pure water was approximately 6.4 and about 0.1 g sorbent was added to the solutions. The mixture was shaken manually for 1-2 minutes and then placed on the shaker for 50 minutes. The contents were filtered through filter paper and the filtrate, after addition of ammonia and mannitol, was measured by ICP-OES using the optimum conditions.

The investigated adsorbents for B sorption are given in Table 2.2. These adsorbents were chosen by educated guess from the adsorbents that exist in our laboratory

Table 2.2. Types of adsorbents investigated for B sorption and/or matrix removal.

Anion Exchangers	**Cation Exchangers**	**Adsorbents**	**Chelating Resins**	**Zeolites**
Amberlite IRA400	Amberlite IRC718	Florisil	DuoliteGT73	Mordenite
Amberlite IRA938	Amberlite IRC 50	Amberlite XAD-7HP	Chelex 100	Y Type
Amberlite CG400	Amberlite SK116	Silica-Gel		ZSM-5
Amberlite IRA 401S	Dowex 50Wx4	Alumina		Clinoptilolite
Amberite IRA67		Zirconium oxide		
DiaionSA20A				

2.7.1. Studies with Synthesized Sorbent Material (MCM-41 modified with N-MGCMN)

The boron sorption studies with synthesized sorbent (MCM-41 modified with N-MGCMN) were performed with the same procedure as described above. To understand the boron sorption behaviour of the synthesized sorbent, support material (MCM-41), grafted MCM-41 (Br-propyl-MCM-41), and N-MGCMN modified MCM-41 were investigated.

2.7.1.1. Effect of Sorbent Amount

The amount of sorbent is an important factor for quantitative sorption of the analytes from a given solution. For this purpose, 20.0 mL of 10.0 mg/L boron solutions were shaken with varying amounts of N-MGCMN-modified MCM-41 (0.01g to 0.40g) for 30 minutes. After filtration the resultant solutions were analyzed by ICP-OES as stated before.

2.7.1.2. Kinetic Study

Kinetic behaviour of the new sorbent N-MGCMN modified MCM-41 was examined in order to get a measure of the performance of the sorbent. For this purpose, boron removal was monitored with time. The experiment was performed in batch mode, 20.0 mL of 10.0 mg/L boron (as H_3BO_3) solutions containing 0.1 g of N-MGCMN modified MCM-41 were shaken from 1 min to 48 hours. After filtration, $NH_{3(aq)}$ and mannitol reagent were added at concentration 0.1 M and 0.25 % w/v, respectively, to the resultant solutions and were analyzed by ICP-OES using the optimum conditions.

The Lagergen's kinetic model was applied to obtained data and apparent rate constant was determined for the sorption process. The related equations for kinetic study is given in Appendix E

2.7.1.3 Sorption Isotherms

The equilibrium sorption isotherms were conducted in batch mode at natural pH (6-8). The range of concentration of boron solutions varied from 0.5 to 200.0 mg/L. Twenty milliliters of these solutions were shaken with 0.1 g N-MGCMN-modified MCM-41 sorbent for 30 minutes and resultant solutions were analyzed by ICP-OES. The adsorbed boron amount per unit mass of solid was calculated from the mass balance. Two sorption isotherm models Freundlich and Dubinin-Radushkevich (D-R) were applied for the sorption equilibrium of N-MGCMN-modified MCM-41. The related expressions of sorption isotherms are given in Appendix F.

2.7.1.4. Effect of pH on Sorption

Due to the electron deficiency, boron is not found free in nature; instead, it is found as oxo compounds. In aqueous solutions, the form of boron is pH dependent, at low pH it is found as boric acid (H_3BO_3) and at high pH it is found as borate anion ($B(OH)_4^-$). Thus the sorption of the boron in aqueous solutions is expected to be pH dependent.

To understand the uptake behaviour of N-MGCMN modified MCM-41 sorbent in a large pH range, separate solutions of boron at 10.0 mg/L concentration were prepared in different buffer solutions from pH 3.0 to 11.5 .These pH range were chosen considering the different forms of boron in the aqueous solutions as shown Figure 1.1. The sorbent (0.1g) was added immediately to these solutions. The mixtures were shaken manually for 1-2 minutes and then placed on the shaker for 30 minutes at room temperature. The contents were collected on filter papers. The resultant solutions were analyzed by ICP-OES using the optimum conditions.

2.8. Desorption from N-MGCMN-modified MCM-41

After collection of boron by sorbent, their release was investigated using several eluents (HNO_3, H_2SO_4 and HCl). For this purpose, 20.0 mL of 10.0 mg/L boron was prepared and 0.1 g of sorbent was added to it. After shaking for 30 minutes, the mixture was filtered and the sorbent was taken into the desorbing solution (20.0 mL). The new mixture was shaken once again for 30 minutes. At the end of this period, the solution was filtered and the filtrate was analyzed for its boron content.

2.9. Spike Recovery Tests

The performance of the proposed methodology with the use of N-MGCMN-modified MCM-41 in preconcentration from ultra pure water was investigated through spike recovery tests at various initial concentration levels changing between 0.8 mg/L and 10.0 mg/L which correspond to different initial volumes of 250 mL and 20.0 mL, respectively. In all spike recovery tests, the final volume was 20.0 mL.

2.10. Comparison of the Sorption Efficiency of N-MGCMN-modified MCM-41 with Amberlite IRA 743

To understand the efficiency of the synthesized sorbent material in terms of sorption capacity and applicability of the water samples with different matrices it was compared with the commercial resin Amberlite IRA 743. For this purpose, their reusability and preconcentration efficiencies were compared.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterization of the Synthesized Sorbent (N-MGCMN-modified MCM-41)

3.1.1. X-Ray Diffraction Measurements

The XRD pattern shows an intense peak at around 2^o and low intensity peaks at $3-6^o$, which are characteristic of the hexagonal structure of MCM-41. As can be seen from Figure 3.1, bromopropylsilyl-MCM-41 and N-methylglucamine-MCM-41 give the peaks at the same 2T values as the pure MCM-41. Thus it can be conculuded that hexagonal mesoporous crystal structure of MCM-41 did not been collapse during the functionalization reactions although the pH of boiling solution during N-methylglucamine functionalization was 11.

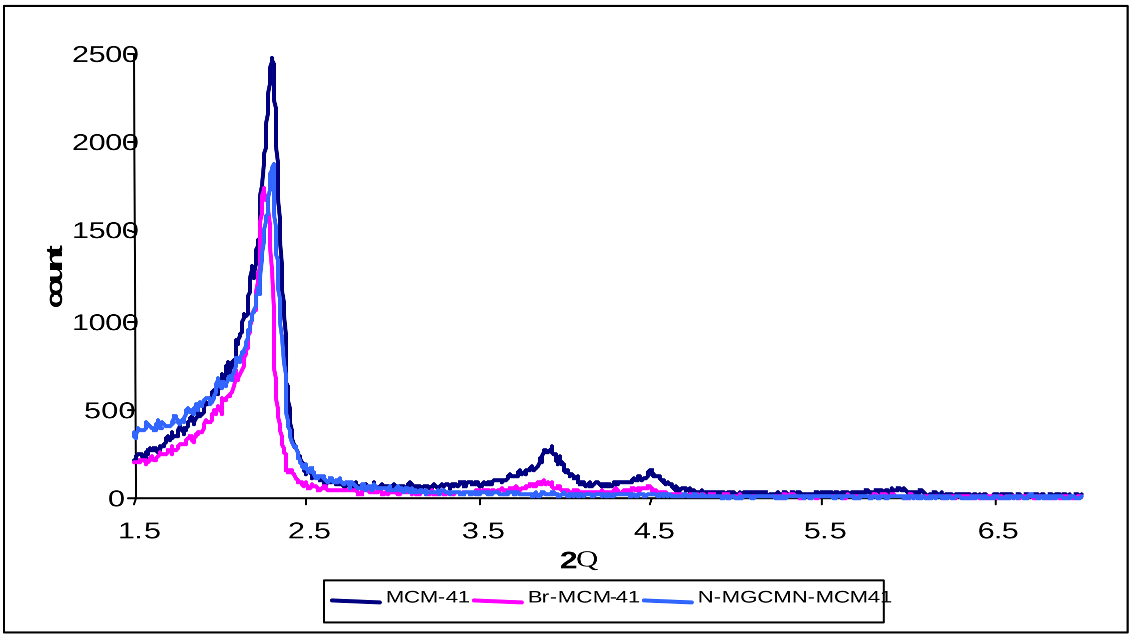


Figure 3.1. The X-Ray Diffraction Patterns of MCM-41, bromopropylsilyl-MCM-41 (Br-MCM-41) and N-methylglucamine-modified MCM-41 (N-MGCMN-MCM-41).

3.1.2. DRIFTS Measurement of the N-MGCMN-modified MCM-41

In order to understand whether the grafting procedures (3-bromopropyl)trimethoxysilane / N-methylglucamine had been established succesfully, DRIFTS spectra of compounds of pure MCM-41, N-methylglucamine (N-MGCMN) and resulting materials were taken (Figure 3.2). As can be seen from the figure functionalized MCM-41 spectra (bromopropylsilyl-MCM-41 and N-MGCMN-MCM-41) resemble the pure MCM-41 spectrum with the small additional peaks at about 2950 and 1450 cm^{-1}. These peaks are likely to correspond to a C-H stretching and C=O asymetric stretching band and might be an indication of the functional groups bonded to MCM-41.

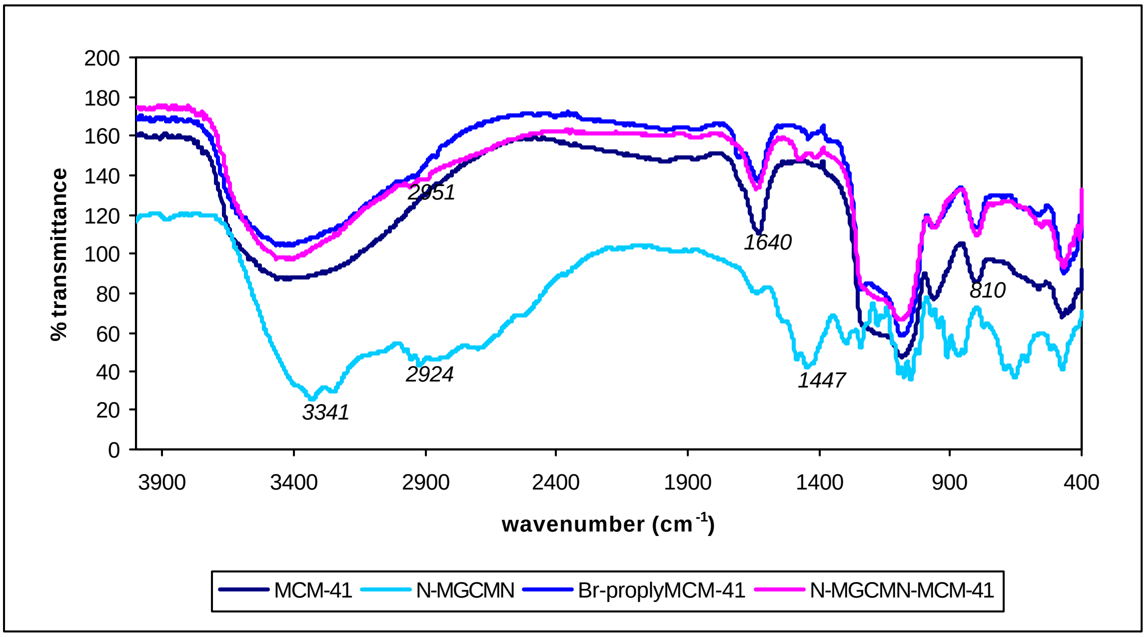


Figure 3.2. DRIFTS spectra of pure MCM-41, pure N-methylglucamine (N-MGCMN), synthesized bromopropylsilyl-MCM-41 and N-methylglucamine-modified MCM-41 (N-MGCMN-MCM-41).

3.1.3. Elemental Analysis

Both functionalized support materials (MCM-41 and silica) were investigated in terms of functionalization capacity. The molar content of the attached N-methylglucamine was calculated from N content of samples and is given in the Table 3.1. The detailed calculations are given in Appendix A

Table 3.1. Elemental analysis results of synthesized sorbent materials.

Materials		Silanation (mmol/g)	% C (w/w)	% N (w/w)	Calculated mmol of attached N-MGCMN
N-MGCMN-modified MCM-41		0.5	4.80	0.55	0.39
		1.0	6.85	0.69	0.49
		1.5	9.97	1.02	0.73
		10.0	13.62	1.42	1.01
N-MGCMN modified silica (synthesized)	pure	1.5	4.73	0.47	0.34
	acid treated	1.5	5.73	0.57	0.41
N-MGCMN modified silica (purchased) acid treated		1.5	7.19	0.72	0.51

As can be seen from the table, calculated amount of N-methylglucamine that is attached to MCM-41 and silica with varying amounts of silanation reagent is in agreement with the expected value.

There is a significance difference, in terms of functionalization ratio, between silica and MCM-41 support materials. It can be also said that the acid treatment of silica increased the functionalization yield and the purchased silica gave better functionalization than the synthesized. These differences can be accounted for by differences in accessible silanol groups of silica materials.

3.1.4. BET Analysis

N_2 sorption isotherm is an efficient way for providing information about the pore system of materials. As the organic fragments enter the channels, the isotherms are expected to have gradual changes at each stage of modification. As can be seen from Table 3.2, the pore volume and size were reduced apparently after modification. The table demonstrates also that the decrease of the pore volume from 1.42 to 0.46 cm^3/g is likely to be an indication of the organic groups having been successfully introduced into the inner channels. The pore distribution of modified MCM-41 was around 40 Å.

Table 3.2. BET analysis results of the MCM-41 and synthesized materials Br-propylsilyl-modified MCM-41 and N-MGCMN-modified MCM-41

Sample	Surface area[a] (m^2/g)	Average pore diameter[b] (Å)	Pore volume[c] (cm^3/g)
MCM-41	1652	26.3	1.42
Br-propyl MCM-41	1038	23.0	0.60
N-MGCMN-modified MCM-41*	603	40.6	0.46

[a] BET surface area
[b] Pore diameter according to the maximum of the BJH pore size distribution
[c] Single point total pore volume
[*] 0.73 mmol of N-methylglucamine bonded MCM-41.

N_2 sorption isotherm was also used for the silica-based sorbents to obtain information about their pore systems. As in the case of MCM-41-based materials, the pore was reduced apparently after modification (Table 3.3). The decrease of the pore volume from 0.82 to 0.59 cm^3/g for purchased and 0.70 to 0.54 cm^3/g for synthesized silica demonstrate also the introduction of organic functional groups into the inner channels. The pore distributions of modified silicas were around 55 Å and 60 Å for purchased and synthesized materials, respectively.

Table 3.3. BET analysis results of the silica and synthesized materials Br-propylsilyl-modified silica and N-MGCMN-modified silica

Sample*		Surface area[a] (m^2/g)	Average PoreDiameter[b] (Å)	Pore volume[c] (cm^3/g)
Purchased	Silica	520	54.5	0.82
	Br-propylsilyl silica	496	45.8	0.64
	N-MGCMN modified silica	350	55.8	0.59
Synthesized	Silica	326	70.0	0.70
	Br-propylsilyl silica	297	56.4	0.53
	N-MGCMN modified silica	283	59.5	0.54

*Acid treated before functionalization reaction and initial silane amount was 1.5 mmol
[a] BETsurface area
[b] Pore diameter according to the maximum of the BJH pore size distribution
[c] Single point total pore volume

3.2. Optimization of the Amount of Silane Reagent in the Synthesis of Sorbent

MCM-41 immobilized with N-Methylglucamine was synthesized in two steps. First step is the silanation of the MCM-41 with (3-bromopropyl)trimethoxysilane. In the second step a substitution reaction occurs between Br and N-Methylglucamine groups. For this reason the silanation ratio affects the amount of the B-binding functional group of N-methylglucamine that is attached on the surface of the support material, and also the boron sorption efficiency of the sorbent. To optimize the silanation ratio, 0.5, 1.0, 1.5 and 10.0 mmol of (3-bromopropyl)trimethoxysilane were used in silanation reactions. The amount of MCM-41 was 1.0 g in each case. After substitution (immobilization) of MCM-41 with N-methylglucamine, boron sorption efficiency was tested for each initial amount of silane reagent.

The percent sorption graphs are shown in Figure 3.3. As can be seen from the figure, the initial amount of 0.5 mmol silane did not show a good sorption relative to the others. MCM-41 modified with initial amount of 1 mmol silane can be used effectively if at least 200 mg of sorbent is added to 20.0 mL 10.0 mg/L boron solution. Initial amounts 1.5 and 10.0 mmol silane demonstrated very similar sorption behaviour especially after 100 mg of the final product is added to 20.0 mL 10.0 mg/L boron standard solution. But in terms of economy of the process, 1.5 mmol silane/per gram of MCM-41/silica was decided to be used in the preparation of N-methylglucamine-functionalized MCM-41/silica in subsequent preparations.

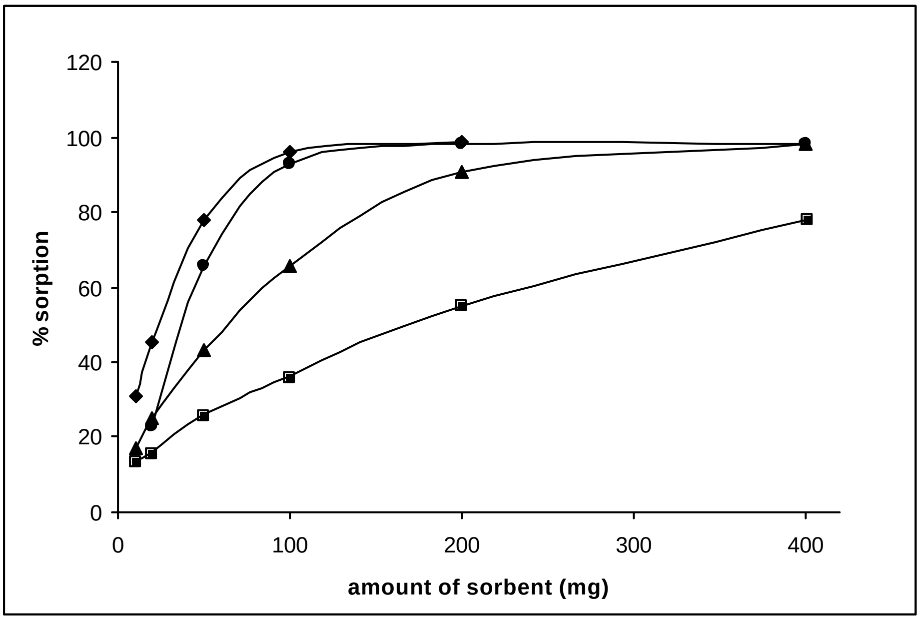


Figure 3.3. Percent sorption versus the amount of sorbent prepared with varying initial amount of silane reagent. (¦) 0.5 mmol silane for 1 g of MCM-41, (?) 1.5 mmol silane for 1 g of MCM-41, (?) 1 mmol silane for 1 g of MCM-41, (?) 10 mmol silane for 1 g of MCM-41. (Boron concentration = 10.0 mg/L, solution volume = 20.0 mL)

3.3. Reusability of the sorbent

Reusability is the one of the key parameters to assess the effectiveness of a sorbent. A series of sorption/desorption experiments were performed to understand the reusability of the synthesized N-methylglucamine-modified MCM-41.

In the first part of the assessment tests, the usual sorption/desorption process were realized to understand whether the hexagonal structure of the support (MCM-41) had been changed. X-Ray diffraction patterns, as given in Figure 3.4, demonstrated that no change in the structure of the material had occurred. Neither the pH during sorption (pH 3 and pH 11) nor the elution with 1.0 M HCl had a devastating effect on the sorbent. On the other hand, the support showed a decrease in its sorption capability when it was subjected to successive sorption/desorption steps (Table 3.4). Its sorption capacity decreased gradually

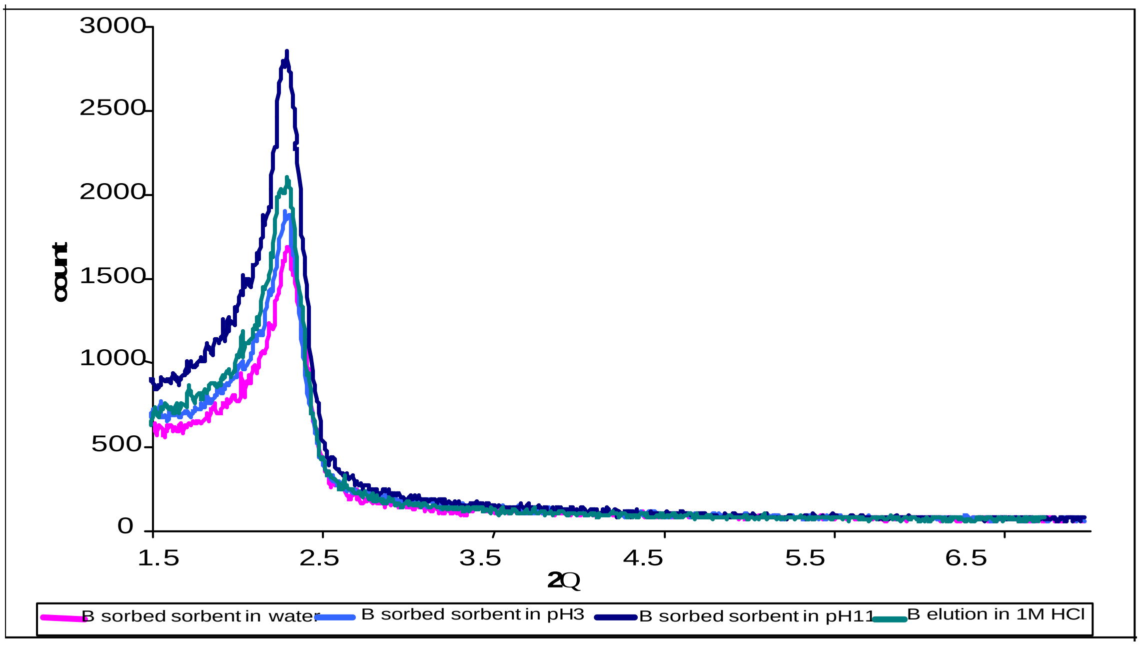


Figure 3.4. X-Ray Diffraction pattern for used sorbent.

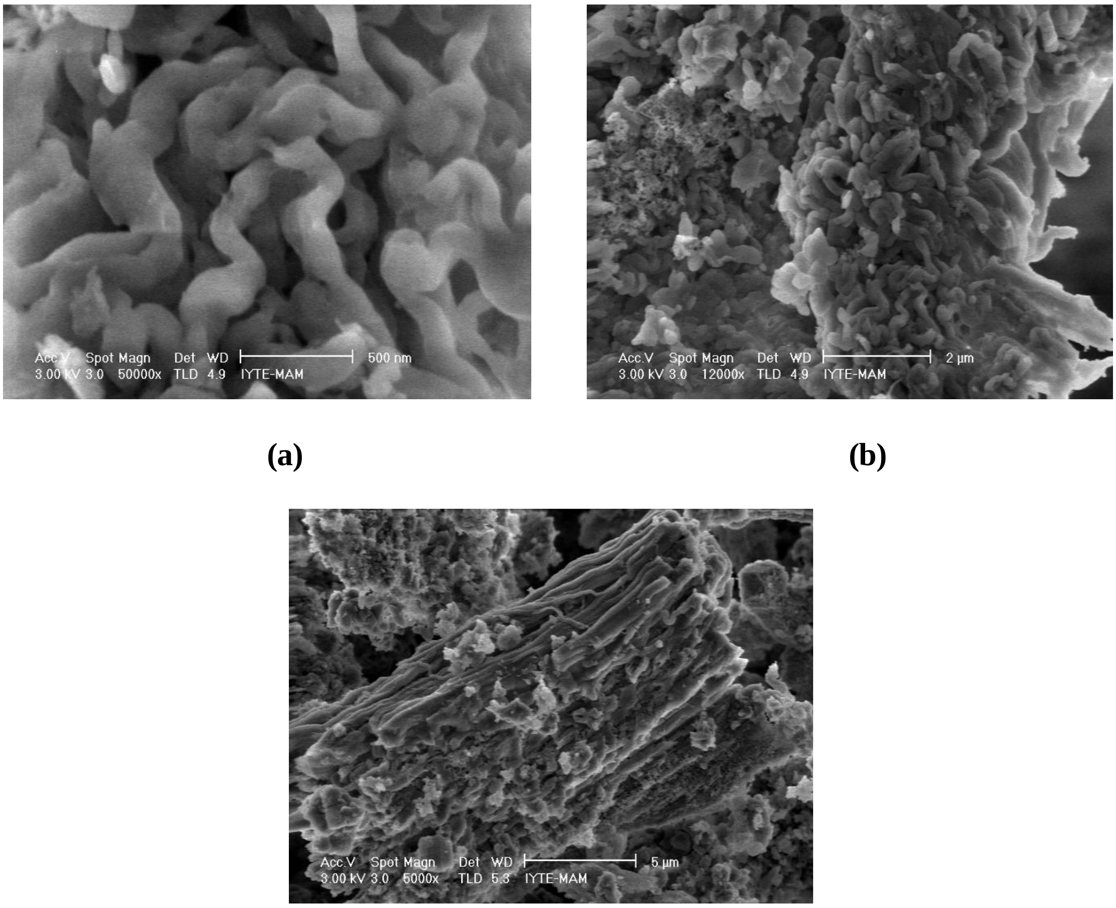
Table 3.4. Boron sorption (%) of successive sorption/desorption steps.

Usage	Boron Sorption (%)*
1st	91 (± 1)
2nd	82 (± 6)
3rd	67 (± 3)

* B concentration= 10.0 mg/L, 20mL

3.4. SEM Microimages of Sorbent

To understand the morphology of the sorbent, SEM microimages are investigated for pure MCM-41 and MCM-41 modified with N-methylglucamine; which are shown in Figure 3.5.



(a) **(b)**

(c)

Figure 3.5 SEM microimages of a) pure MCM-41 (50000X); b) pure MCM-41 (12000X); and c) MCM-41 modified with N-methylglucamine and used several times in successive sorption and elution processes (5000X).

As was stated previously (section 3.1.1 and 3.3) XRD indicated no change in the structure of MCM-41 upon modification with N-methylglucamine. The SEM microimages of pure and modified MCM-41 shown in the figure demonstrate the tubular morphology of MCM-41 before and after modification. The SEM findings supported the XRD results.

3.5. Determination of Boron

3.5.1. UV-Vis Spectrophotometry

3.5.1.1 Carmine method

Carmine forms a blue-red colored complex with boron. The absorption spectrum of boron-carmine complex was obtained by using a UV-Vis spectrophotometer and was shown in Figure B.1 (Appendix B). Although the standard method (APHA Standard Methods for the examination of water and wastewater 18th Ed.) suggests 585 nm for quantitative applications, any wavelength on the very broad spectrum could have been used in quantification and we used 604 nm for this purpose. The calibration graph is given in Figure 3.6.

It must be mentioned that this method is not very practical for our purpose since the colored complex can only be formed in concentrated sulphuric acid. Also it takes approximately 1.5 hours for the development of color. Another drawback of the method is its narrow linear dynamic range, 1-10 mg/L.

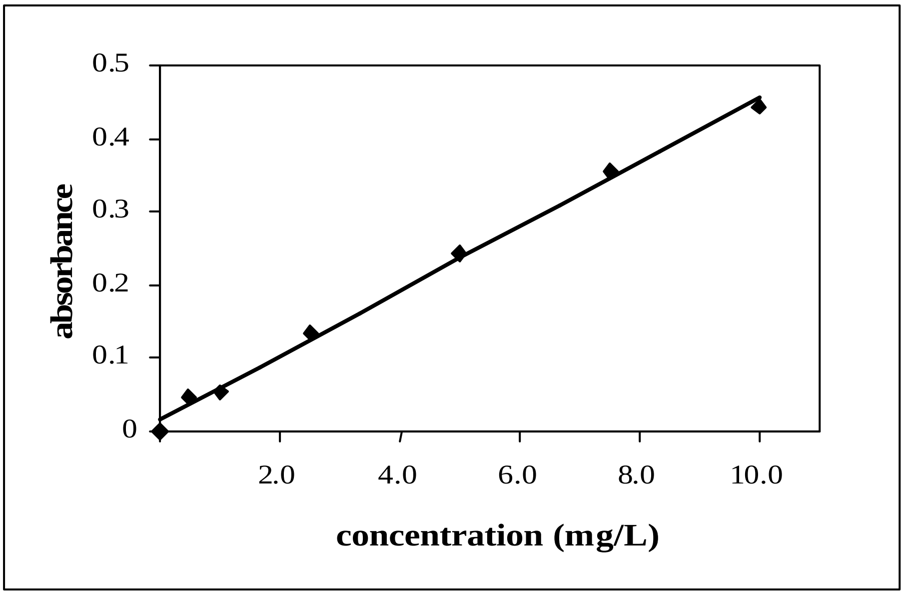


Figure 3.6. Calibration graph for carmine method. ($y= 0.044x + 0.0157$, $R^2= 0.9956$)

3.5.1.2. Azomethine-H method

Boron reacts with azomethine-H to form a yellow complex of which the absorption spectra for varying concentrations are given in Figure B2. (Appendix B). The absorbance peak maximum was observed at 420 nm and the quantitative measurements were done at this wavelength. The calibration graph is given in Figure 3.7.

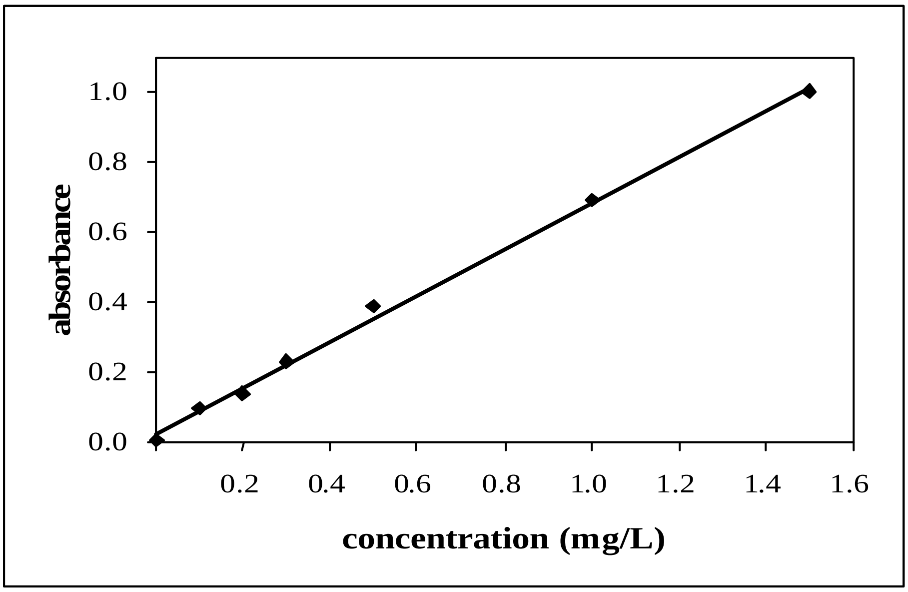


Figure 3.7. Calibration graph for azomethine-H method. ($y= 0.6603x + 0.0254$, $R^2= 0.9975$)

One of the drawbacks of this method is the dependence of the color on temperature (the color fades above 20°C). The method is also time consuming, taking about 30 minutes for color development. High amounts of chemicals are needed especially for buffer solution. Another drawback of the method, as in the case of carmine method is its narrow linear dynamic range (the method only works for 0.1 to 10.0 mg/L concentration range).

Considering the experimental difficulties in UV-Vis spectrophotometric methods faced with, it was decided to continue the subsequent experiments with ICP-OES since it is known to have a wider dynamic range (normally greater than 3 orders of magnitude or better).

3.5.2. Optimization of ICP-OES for Boron Determination

In recent years plasma-based techniques have been the methods of choice in boron determinations due to their high sensitivity. The availability of an ICP-OES instrument in the central laboratories (IYTE) gave us the opportunity to continue the later experiments with this technique. Initial studies were concentrated on the optimization of the ICP-OES measurements. Among the accessible wavelengths the three most intense B emission lines were chosen; namely, 249.773 nm, 249.678 nm, and 208.959 nm. As seen from Figure 3.8, the most sensitive B signal was obtained at 249.773 nm and all quantifications were conducted with the results obtained at this wavelength. But still, the measurements at the above-mentioned three wavelengths were obtained in case there occur interference.

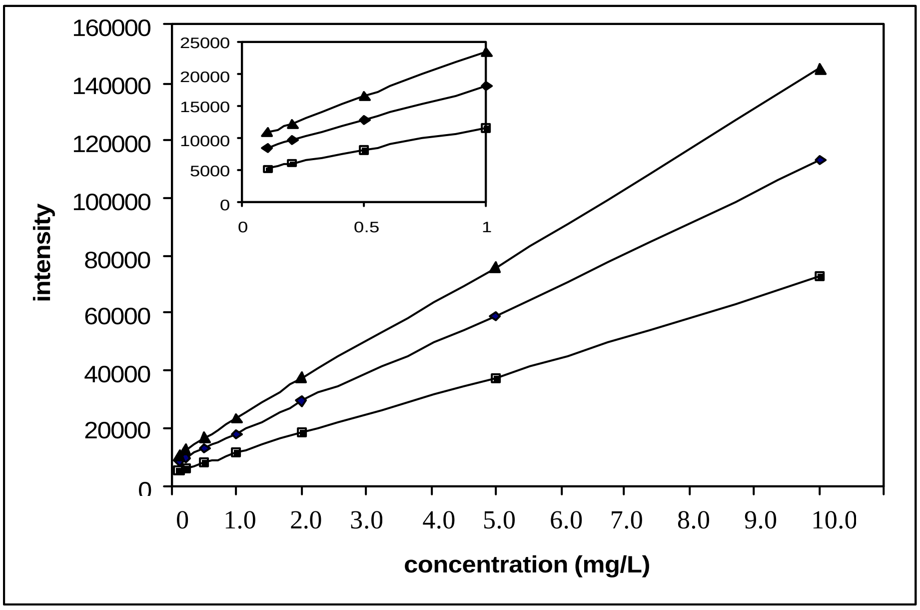


Figure 3.8. Calibration graphs of standard solutions of B at 3 of the most intense B emission lines. (?) at 208.959 nm (¦) at 249.678 nm(?) at 249.773 nm.

3.5.2.1. Reduction of Memory Effect

As mentioned before, memory effect caused by the adsorption of boron onto the walls of spray chamber, transport tubings etc. may complicate the ICP-OES measurements during boron determinations. Various mechanisms for the memory effect of boron in ICP spectrometry together with several measures have been proposed in literature to reduce its extent.

In one study, Sun et.al. (2000) suggested a mixture of mannitol (0.25 % w/v)-ammonia (0.1 M) to be used as diluent and flush solution in ICP-MS determination of boron. In our study, the effect of this mixture in reduction of memory effect caused by boron was investigated in a detailed manner. In the first of these studies, 10.0 mg/L boron standard solution was aspirated after which various flush solutions, namely 0.7 M HNO_3 , 1 M HCl, and 0.1 M NH_3/0.25 % (w/v) mannitol, were passed through the sample introduction system. The signal intensity was measured after each aspiration of flush solutions. As can be seen from Figure 3.9, the acidic solutions were not successful in decreasing the previous signal reading to the baseline level until 14th aspiration whereas the mannitol-ammonia mixture eliminated the memory effect immediately after aspiration. Therefore, in the subsequent experiments, this mixture was used as both the diluent and the flush solution.

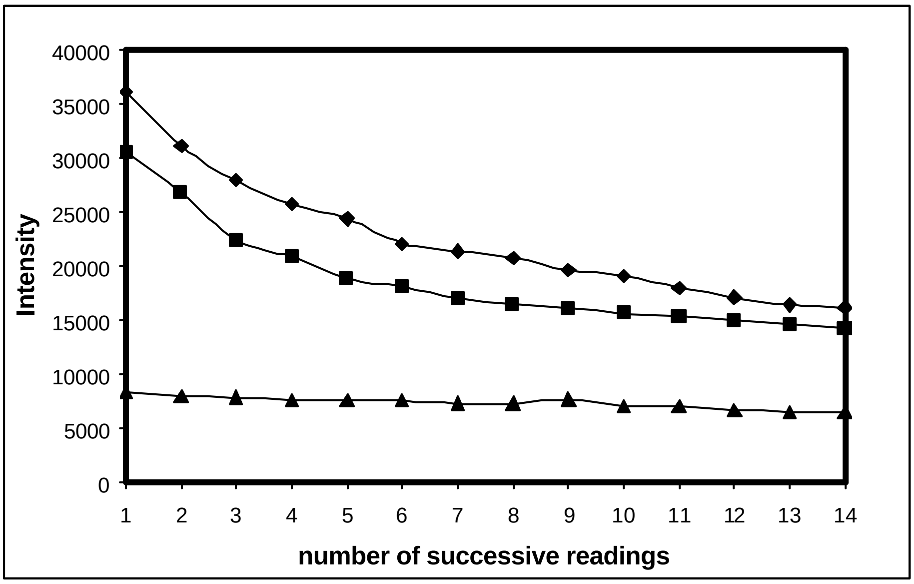


Figure 3.9. Successive readings (time elapsed between two measurements was 2 second) of various blank solutions aspirated after 10.0 mg/L boron standard solution. (?) %5 HNO_3, (¦) 1 M HCl, (?) 0.1 M NH_3- 0.25 % (w/v)mannitol. (Emission intensity was measured at 249.773 nm).

A slightly different experiment was performed to clarify the memory effect of boron, during measurement. The same boron concentration was prepared, this time, in the above-mentioned solutions and their emission intensities were measured at 249.773 nm. The results are shown in Figure 3.10. The same (number of counts) was obtained for four consecutive readings for boron standard prepared in ammonia-mannitol mixture, on the other hand, the emission intensity increased gradually for boron standard prepared in HNO_3 and HCl. These results demonstrate both the accumulate interference effect (memory) of boron on the succeeding solution, and also the appropriateness of ammonia-mannitol mixture for the reduction of memory effect in the measurements.

Another comparison among the diluent solutions was made through calibration graphs. Standard boron solutions (0.1-10.0 mg/L) were prepared in deionized water, in 0.7 M HNO_3, 1.0 M HCl, and in 0.1 M NH_3/0.25% (w/v) mannitol mixture. As shown in Figure 3.11, mannitol/ NH_3 mixture produced the most sensitive calibration plot. The linearity obtained with this mixture was also better than all the other plots. The better sensitivity and linearity obtained can be attributed without making too much speculation, to two effects; firstly, to the increased stability of borate in mannitol; and secondly, to the presence of NH_3 which is thought to prevent the adsorption of boron onto the walls of spray chamber and transport tubings.

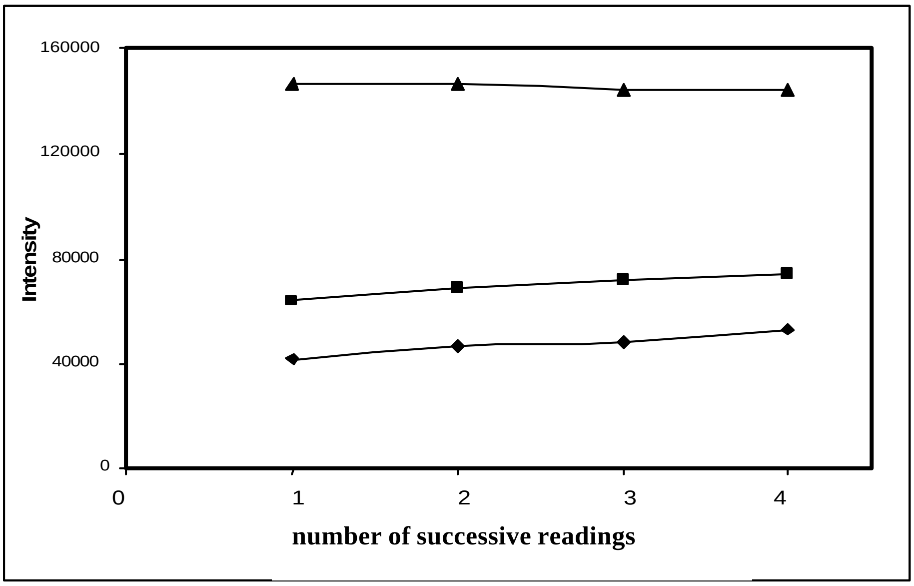


Figure 3.10. Successive readings (time elapsed between two measurements was 2 sec.) of 10.0 mg/L boron solutions that was prepared in various diluent solutions. (?) 10 mg/L in %5 HNO_3, (¦) 10 mg/L in HCl, (?) 10 mg/L in NH_3-Mannitol.

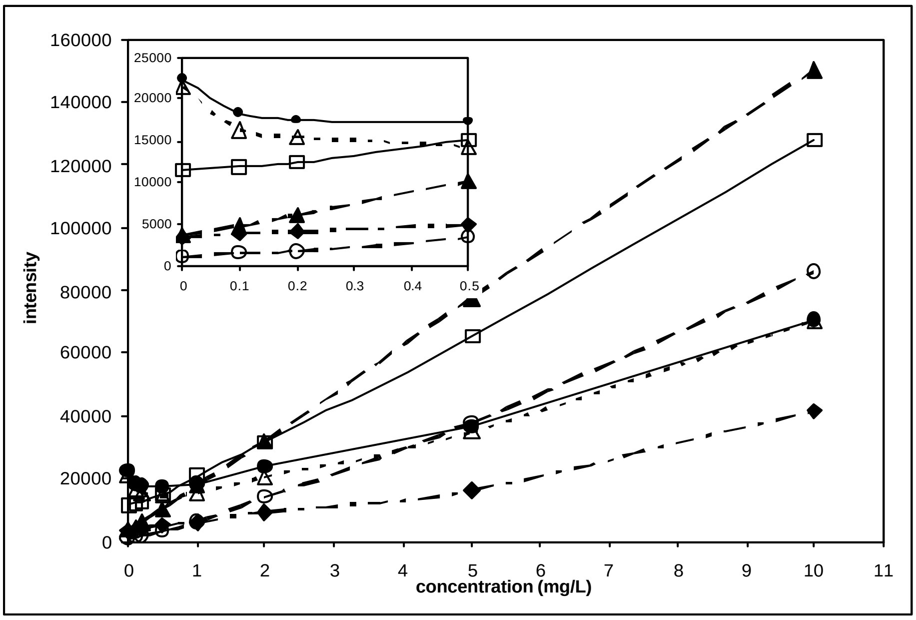


Figure 3.11. **C**alibration graphs of boron in various diluent solutions. (?) 0.1 M NH_3-0.25 % (w/v) mannitol mixture, (?) 0.25% (w/v) mannitol, (o) 0.1 M NH_3, (?) 0.7 M HNO_3, (?) 1.0 M HCl,. (?) ultrapure water.

Mannitol, with a chemical formula $C_6H_{14}O_6$, has a proper structure for borate ion to approach and to form a stable B-mannitol complex and so keeping boron in solution. Also seen in the figure, the calibration plots obtained with 0.1 M NH_3 alone and 0.25 % (w/v) mannitol alone. Both of these diluents produced calibration plots more sensitive and having better linearity than the acidic diluents; but neither NH_3 nor mannitol, as alone, was effective as their mixture. This result may demonstrate them working in a synergistic way.

3.5.3. Calibration Strategies with ICP-OES

As explained in Experimental, two calibration graphs were obtained; one plot with aqueous standards, and one plot with matrix-matched standards. The matrix-matched standard graph was obtained by employing the proposed sorption/desorption steps with the sorbents. This process includes the following steps; *i) bringing the pH of 10.0 mL standard to neutral pH, ii) addition of 0.1 g N-MGCMN-modified MCM-41, iii) shaking both manually (1 minute) and on a shaker for 30 minutes, iv) filtration, v) desorption of boron from sorbent on filter paper using 1.0 M* HNO_3*, vi) addition of ammonia and mannitol, and vii) analysis by ICP-OES.* These two graphs are shown in Figure 3.12. Both of the graphs were linear at least up to 10.0 mg/L. As seen, the calibration sensitivity (slope) is affected from sorption/desorption steps and the matrix-matched standards always give calibration sensitivities approximately 30 % lower than aqueous standards. (It should be stated that, this is an expected result when the percent recovery values obtained with various acids are considered. As will be shown in the subsequent sections, desorption was realized with 1.0 M HNO_3 in which the sorbent, N-MGCMN-modified MCM-41, was still taking up approximately 25% of boron. With the matrix-matched standard calibration, the limit of detection (LOD) values based on 3s (3 times the standard deviation above the blank value) was 0.07 mg/L for boron.

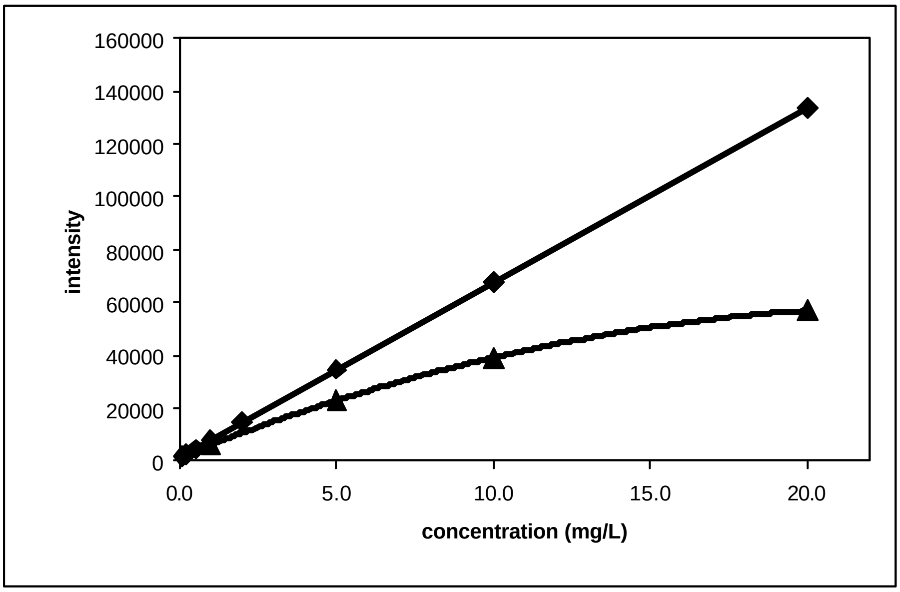


Figure 3.12. Calibration graphs for boron obtained with (?) aqueous standards ($y = 6482.5\,x + 3359.6$, $R^2 = 0.9998$) (?) matrix-matched standards ($y = -98.22\,x^2 + 4731.4\,x + 1711.6$, $R^2 = 1$)

3.6. Boron Sorption Studies

As a starting point in the search of an appropriate sorbent for matrix removal and/or preconcentration of boron, various materials such as ion exchangers, chelating resins, natural and synthetic zeolites (Table 2.2) were tried. To assess their sorption capacities, an aqueous boron standard (10.0 mg/L, 20.0 mL, pH = 6.4) was prepared and shaken with these sorbents. The contents were filtered through filter paper and the filtrate, after addition of ammonia/mannitol mixtures was measured by ICP-OES. None of the materials investigated has shown any sorption for boron under the given conditions. Therefore, it was decided to prepare a novel sorbent with the functional groups which are thought to be capable of forming a boron complex in the solution. After synthesis and characterization of the novel sorbent, the subsequent experiments were realized with this sorbent.

3.6.1. Studies with the Newly-Synthesized Sorbent (MCM-41 modified with N-Methylglucamine)

Boron sorption studies with the novel sorbent (N-MGCMN-modified MCM-41) were performed with the same procedure as described above. In addition to the synthesized material, sorption experiments were conducted with the starting materials (calcined MCM-41 or grafted Br-propyl-MCM-41) to understand whether they have also the capability of taking up boron from solution. The results are given in Table 3.5. As can be seen from the table, the inorganic support material (MCM-41) and the grafted MCM-41 (it can be thought as the intermediate of the synthesis procedure) exhibit minor sorption (around 10%) while N-MGCMN-functionalized MCM-41 shows an efficient sorption towards boron.

Table 3.5. Boron sorption efficiencies of support material, grafted support and functionalized support.

Material	Boron Sorption (%)*
Calcined MCM-41	9.2 (±0.2)
Br-propyl-MCM-41	11.1 (±0.3)
N-MGCMN-MCM-41	92.9 (±0.2)

*Boron concentration = 10.0 mg/L, solution volume = 20.0 mL

3.6.1.1. Effect of Sorbent Amount

As explained in section 2.7.1.1, the optimum amount of the sorbent for maximum take up was determined by increasing the amount of N-MGCMN-modified MCM-41 added into 20.0 mL of 10.0 mg/L boron standard. As can be seen from Figure 3.13, an efficient sorption was obtained with 0.1 g. of sorbent (the V/m ratio was kept at 200 in all experiment) . The percent sorption values did not change much with further increases in the amount. Therefore, all the following experiments were realized with 0.1 g of N-MGCMN-modified MCM-41.

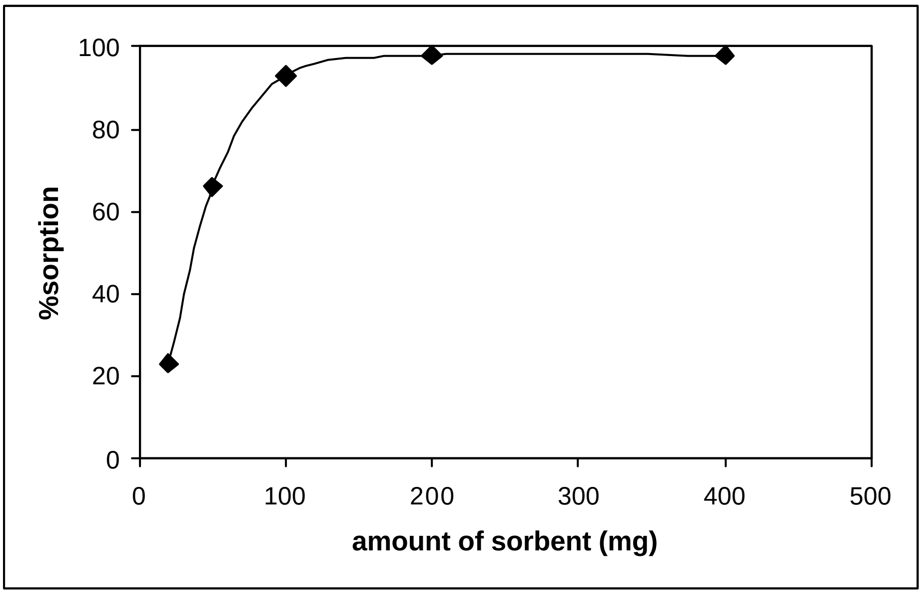


Figure 3.13. Boron sorption by N-MGCMN-modified MCM-41 vs. sorbent amount.

3.6.2. Studies with Silica modified with N-Methylglucamine

Some preliminary sorption studies were carried out also with purchased and synthesized silicas after functionalization with N-methylglucamine and effect of acid-treatment in their sorption capabilities were examined. As can be seen in Figure 3.14, the acid treatment with 0.01 M acetic acid enhances the sorption capability of both silicas. The reason for this enhancement could be attributed to the increased number of free silanol groups on the surface of the silicas which might have caused a more efficient silanation step with (3-bromopropyl)trimethoxy silane prior to functionalization with N-methylglucamine.

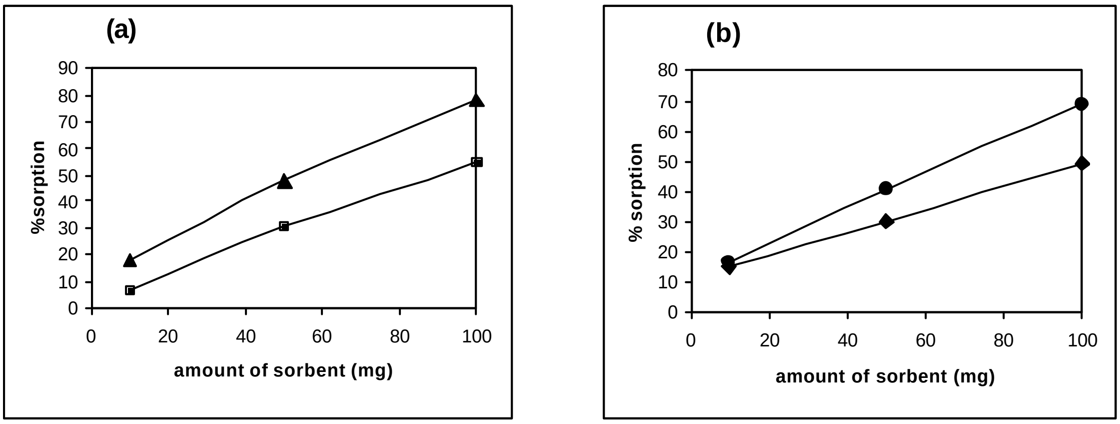


Figure 3.14. (a) Boron sorption of synthesized silica modified with N-methylglucamine before (¦) and after (?) acid treatment. (b) Boron sorption of purchased silica modified with N-methylglucamine before (?) and after (?) acid treatment.

3.6.3. Kinetic Study with N-MGCMN-modified MCM-41

Kinetic behaviour of the sorbent was examined by monitoring the percent sorption with time. For this purpose, 20 mL of 10.0 mg boron (as H_3BO_3) was shaken from 1 min to 48 hours, as explained in Experimental. After filtration, the usual ICP-OES measurement was performed. The results are shown in Figure 3.15. The sorption rate for boron was rapid; an interaction period of 1 minute supplied 75 % sorption whereas the equilibrium was reached after 30 minutes.

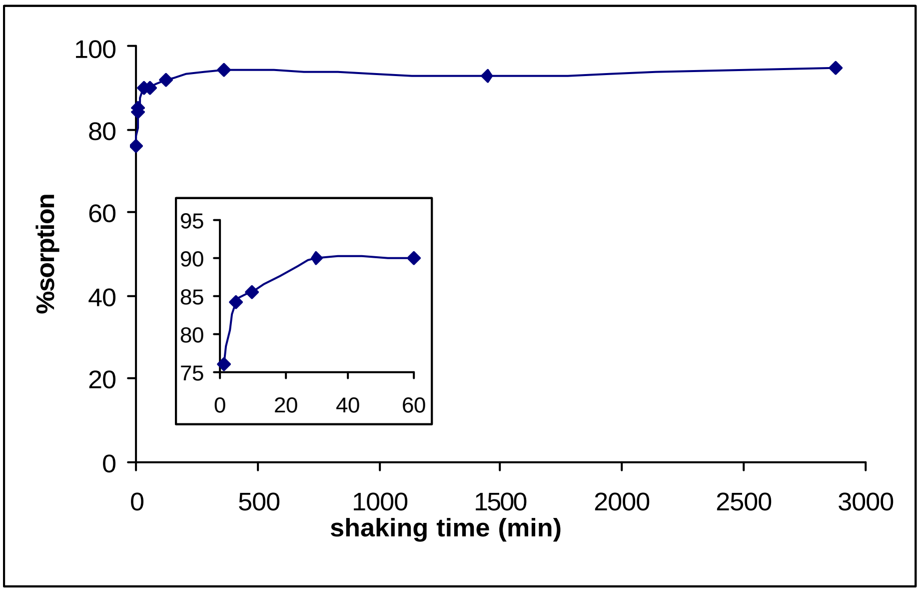


Figure 3.15. Kinetic study curve for boron removal by N-MGCMN-modified MCM-41.

The kinetic model Lagergen's equation (Lui et al., 1995) developed as pseudo first order kinetics was applied to fit the kinetic data of the N-MGCMN-modified MCM-41. The related equation is given in Appndix E. Figure 3.16 shows the function of this kinetic model versus time.

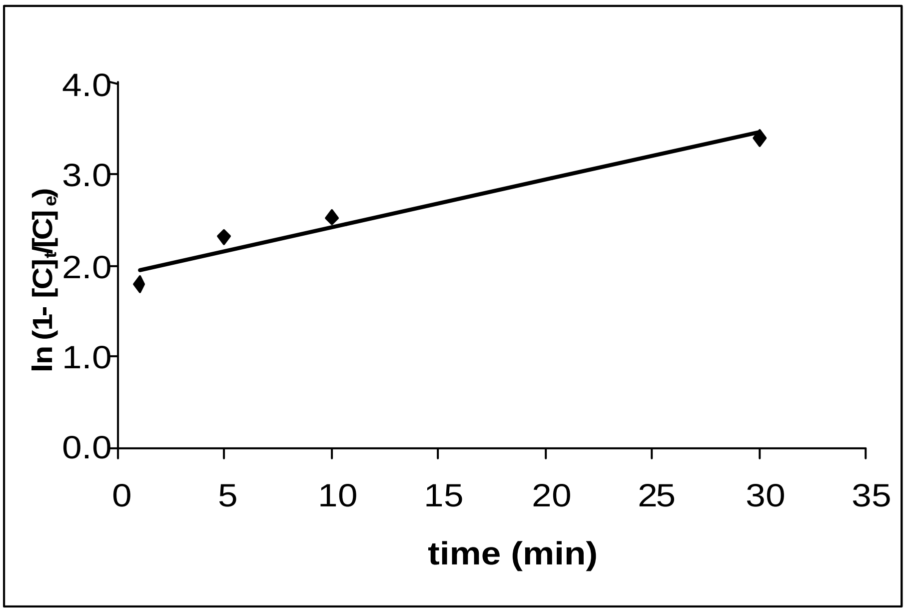


Figure 3.16. Kinetic behaviour of N-MGCMN-modified MCM-41 based on Lagergen's equation. ($y = 0.051x + 1.9182$, $R^2 = 0.9551$)

From the equation the rate constant was found as 0.051 min^{-1}, a value indicating that sorption proceeds with fast kinetic steps.

According to general pseudo first order equation the rate can be expressed:

Rate = 0.051 $[\text{sorbate}]^1$

And half coverage for first order kinetics:

$$t_{1/2}\frac{\ln 2}{k}=\frac{0.693}{k}$$

To quantitatively illustrate the fast sorption kinetics the $t_{1/2}$ (the time required 50% coverage) is ~ 14 min regadless of the initial concentration of the sorbate.

This relatively fast kinetics can be also a sign of the capability of the new sorbent to be used in column applications. Mini- or micro-columns can be prepared with the new sorbent if it has a proper particle size for column studies (micro-columns prepared with sorbents having particles smaller than 100 μm may suffer from high back-pressures during flow). The use of micro-columns is very advantageous in site-sampling and can allow high enrichment factors to be achieved since the elution can be realized with a few milliliters of the eluent.

3.6.4. Determination of Sorption Isotherms

The boron sorption experiments were performed in the batch mode. The equilibrium relationship between the amount of boron adsorbed per unit mass of N-MGCMN-modified MCM-41 ($[C]_s$) and the residual boron concentration ($[C]_l$) in solution phase were expressed by adsorption isotherms. The boron concentrations were changed from 0.5 to 200.0 mg/L while the amount of solid in each solution was held constant at 0.1 g. The applicability of the Freundlich and Dubinin-Radushkevich (D-R) sorption isotherms were tested under these specified conditions.

From the Freundlich isotherm model curves given in Figures 3.17 and 3.18 we can predict that heterogeneous sites exist for boron sorption. At low concentration level up to 5.0 mg/L, there are ‘high affinity, low capacity’ sorption sites. At high concentration level from 5.0 to 200.0 mg/L, there are ‘high capacity, low affinity’ sites and sorption take place on these sites.

The D-R sorption isotherm model is applicable at low concentration ranges and can be also used to describe sorption on both homogeneous and heterogeneous surfaces.

From Figure 3.19 and the equation (given in Appendix F, equation (5)) of the D-R isotherm model the maximum amount of boron as boric acid that can be sorbed by the sorbent was found as 0.8 mmol per gram of the sorbent and sorption energy was calculated as 11.5 kJ/mol.

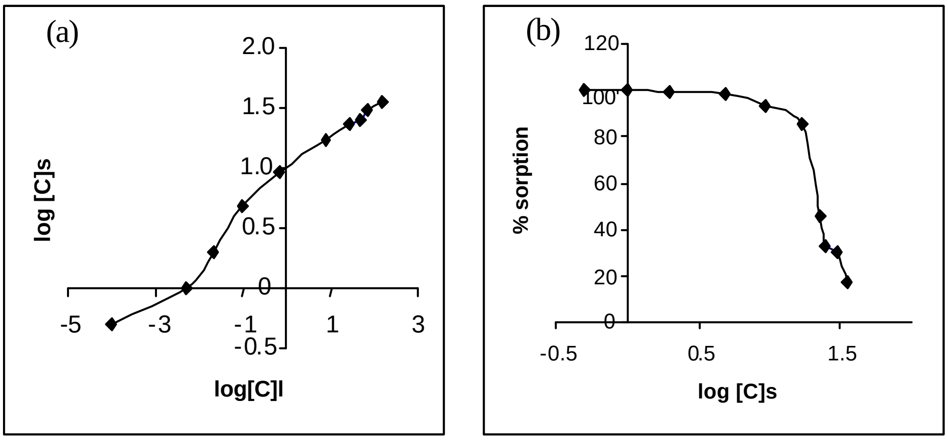


Figure 3.17. Freundlich sorption isotherm curves plotted for 0.5 mg/L to 200.0 mg/L concentration range; (a) when plotted according to equation (3) given in Appendix E, (b) when percent sorption plotted vs. $\log[C]_s$

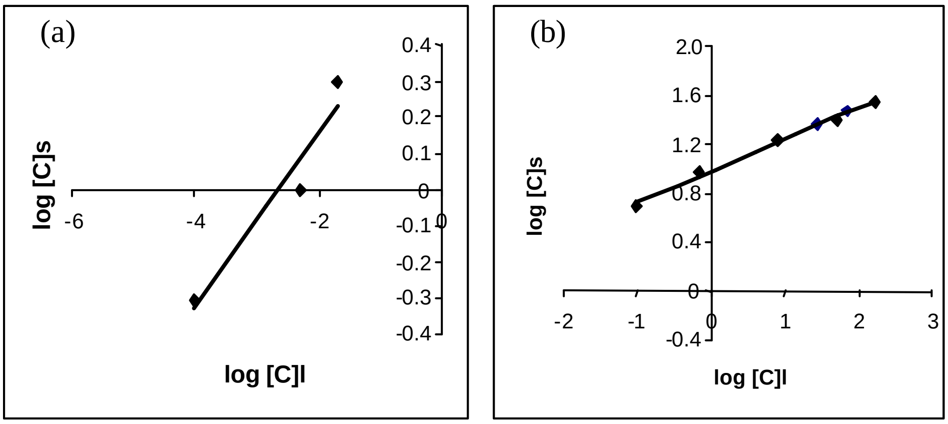


Figure 3.18. Freundlich isotherm model curves (a) when plotted for the initial boron concentrations of 0.5 to 2.0 mg/L ($y = 0.2415x + 0.6417$, $R^2 = 0.9296$), and (b) when plotted for the initial boron concentrations of 5.0 to 200.0 mg/L ($y = 0.2615x + 0.9793$, $R^2 = 0.9946$).

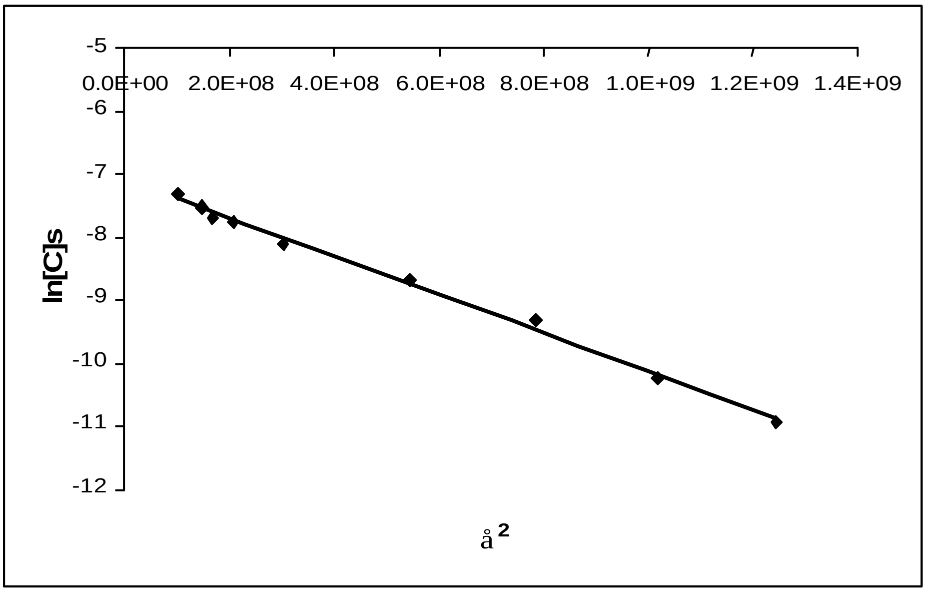


Figure 3.19. Dubinin-Radushkevich isotherm model plot. ($y = -3E\text{-}09x - 7.0765$, $R^2 = 0.9959$)

The adsorption energy can be used to investigate the sorption mechanism. In literature sorption which has the adsorption energy between 8-15 kj/mol shows the electrostatic forces and ion-exchange type mechanism. (Helfirrich, 1996) The sorption of boron by the N-methylglucamine (11.5 kj/mol) shows the ion-exchange mechanism.

3.6.5. Effect of pH on Sorption

The form of boron in solution depends strongly on the solution pH and takes the forms $B(OH)_3$ at acidic pH's or $B(OH)_4^-$ at basic pH's (Figure 1.1). According to the sorption mechanism proposed by Simonnot et al.(2000), and as outlined in Figure 1.3, basic pH's must provide a suitable environment for the sorption of boron by the functional groups like N-methylglucamine. As can be seen from Figure 3.20, any pH greater than 6 can be used for an efficient sorption. The interesting finding here, which can be considered as contradictory to the mechanism proposed in the above-mentioned study, is that the novel sorbent takes up boron from the solution even at a pH of 6. At this pH, the predicted form of boron is $B(OH)_3$ and its sorption by N-methylglucamine group is not expected if the same kind of interaction is valid. The efficient sorption of boron by the new sorbent at a pH of 6, might be explained by assuming either that there is another mechanism responsible for sorption, or that there might be some kind of conformational change when boron in its existing form approaches to the surface.

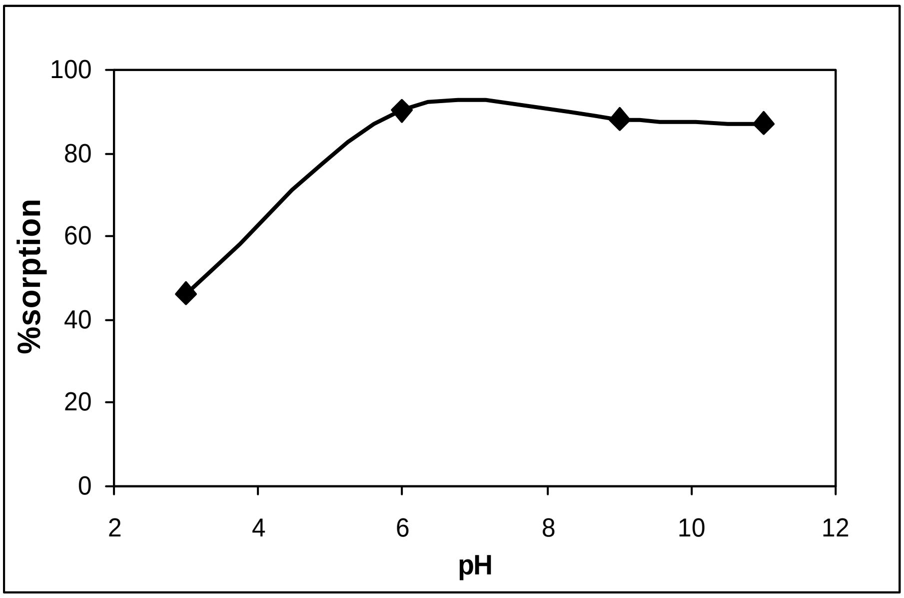


Figure 3.20. Boron sorption by N-MGCMN-modified MCM-41 as a function of pH. (Solution volume: 20.0 mL, sorbent amount: 0.1g)

The decrease in sorption in acidic pH's made us to think that the acidic solutions can be good candidates for desorption. This was proven in the following section and different acidic solutions were used for this purpose.

3.6.6. Desorption of Boron from N-MGCMN-modified MCM-41

As mentioned in the preceding paragraph, desorption studies were realized with acidic solvents, namely HNO_3, HCl and H_2SO_4, at different concentrations. After the usual sorption step (mixing and shaking 20.0 mL of 10.0 mg/L boron with 0.1 g of N-MGCMN-modified MCM-41), the mixture was filtered through filter paper and the sorbent was taken into the eluent. After having been shaken for another 30 minutes, the contents were filtered again and the filtrate was subjected to NH_3/mannitol treatment before ICP-OES measurements. Preliminary elution efficiencies are given in Table 3.6.

Although being preliminary, the table still indicated HCl as the most efficient eluent among the others and it was decided to carry out the desorption step with 1.0 M HCl.

In the following experiment during the aspiration of the solutions which were prepared through desorption with HCl we had a problem of obtaining a stable plasma and we realized that a white deposit was being formed (during aspiration) in the innermost tube (through which the sample aerosol is transported) of the ICP-OES torch (Appendix G, Figure G). To enlighten this situation giving rise to deposit formation in the torch, each parameter was changed in one-at-a-time manner and the deposit was thought to be NH_4Cl after desolvation of aerosols near the plasma. After this observation, HCl was replaced by HNO_3, the second most effective eluent in the table. As expected, no deposit was formed during transport when 1.0 M HNO_3 was used in the desorption step. Therefore, this solution was employed in the following experiments.

Table 3.6. Eluents used to desorb boron from N-MGCMN-modified MCM-41.

Eluent	% Recovery
1.0 M HNO_3	~ 75
2.0 M HNO_3	~ 70
1.0 M H_2SO_4	~ 65
2.0 M H_2SO_4	~ 50
1.0 M HCl	> 80
2.0 M HCl	> 80

3.7. Spike Recovery Tests

The performance of the proposed methodology with the use of N-MGCMN-modified MCM-41 in preconcentration from ultra pure water was investigated through spike recovery tests at various initial concentration levels between 0.8 mg/L and 10.0 mg/L which correspond to different initial volumes of 250 mL and 20.0 mL, respectively. The absolute amount of boron was 0.2 mg and the final volume was 20.0 mL in each case. The results are given in Table 3.7. As can be seen from the table, the method can be applied for the determination of boron in ultra pure water at all initial volumes examined, with a slight decrease for an initial volume of 250 mL (0.8 mg/L). The very simple matrix of ultra pure water enables high preconcentration factors to be attained. In addition to this experiment, the matrix removal capability of the method was also investigated through spike recovery tests for geothermal water. In contrast to ultra pure water, geothermal water had a heavy matrix which was expected to complicate the sorption/desorption steps. In these experiments, no preconcentration was applied; the initial and the final volumes were both 20.0 milliliters. The recovery values, as shown in Table 3.8, changed between 75 and 92 percent at different spike levels. These recoveries are not very efficient though, but still can be considered being sufficient for many studies containing similar matrices.

Table 3.7 Boron recovery results for ultra-pure water with N-methylglucamine-modified MCM-41 (n=3).

B spike (mg/L)	Initial Volume (mL)	Final Volume (mL)	Enrichment Factor	B found (mg/L)	Recovery (%)
10.0	20	20	1.0	9.5 (±0.6)	95 (±6)
4.0	50	20	2.5	9.0 (±0.3)	90 (±3)
2.0	100	20	5.0	8.9 (±0.6)	89 (±6)
0.8	250	20	12.5	8.3 (±1.0)	83 (±10)

Table 3.8. Boron recovery results for geothermal water with N-methylglucamine-modified MCM-41 (n=3).

Geothermal Water B concentration (mg/L)	Initial Volume (mL)	Final Volume (mL)	Boron spike (mg/L)	B must be found (mg/L)	B found (mg/L)	Recovery (%)
9.3	20	20	+ 0.0	9.3	7 (±0.2)	75 (±2)
9.3	20	20	+ 5.0	14.3	12 (±1.8)	86 (±13)
9.3	20	20	+ 10.0	19.3	19 (±2.1)	92 (±13)

3.8. Comparison of the Sorption Efficiency of N-MGCMN-modified MCM-41 with Amberlite IRA 743

To understand the efficiency of the synthesized sorbent material in terms of sorption capacity and applicability to the water samples with different matrices it was compared with the commercial resin Amberlite IRA 743. For this purpose, matrix-matched standard calibration graph was also plotted for the Amberlite IRA 743 to be used in quantification (section 2.6.2.2). Both aqueous and matrix-matched standard calibration graphs for Amberlite IRA 743 and N-methylglucamine modified MC-41 are shown in Figure 3.21. As can be seen from the figure, the sensitivities (slopes) are affected from sorption/desorption steps for both sorbent but the MCM-41 immobilizied with N-MGCMN gives lower calibration sensitivity than the Amberlite IRA743. It might be caused by the lower sorption capacity of the N-MGCMN-modified MCM-41

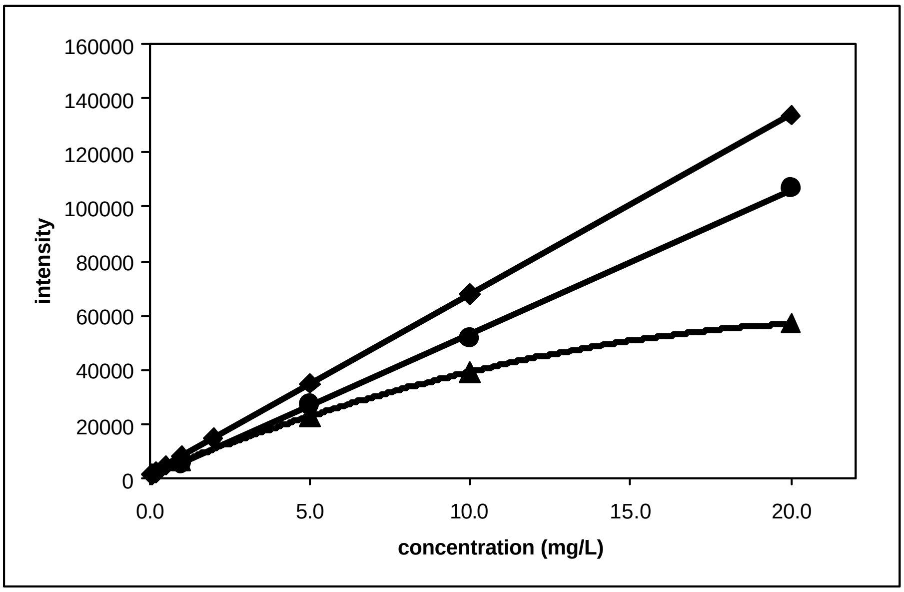


Figure 3.21. Calibration graphs for boron. (?) aqueous standard calibration graph $y = 6621.4x + 1436.3$ $R^2 = 0.9999$, (?) Amberlite IRA743 matrix-matched standard calibration graph $y = 5310.7x + 178.45$ $R^2 = 0.9994$. (?) N-methylglucamine-modified MCM-41 matrix-matched standard calibration graph $y = -98.22x^2 + 4731.4x + 1711.6$ $R^2 = 1$

3.8.1. Comparison of the amount of sorbent on sorption (Amberlite IRA 743)

The particle size of Amberlite IRA 743 beads used in this study was greater than 200 µm. It is used both in its original particle size and after it was ground down to size of 53-75 µm. The purpose of grounding was to make its physical size lose to our synthesized sorbent to obtain a better picture in comparing their performances. As can be seen in Figure 3.22, decrease in the particle size resulted in a better sorption performance for the same amount, possibly due to increased solid-liquid interaction with the smaller particles. When smaller size Amberlite IRA 743 and N-MGCMN-MCM-41 are compared, it can be said that the commercial resin has a better sorption performance for small amounts (<100 mg) whereas very similar sorption behaviour were observed with larger amounts than this value.

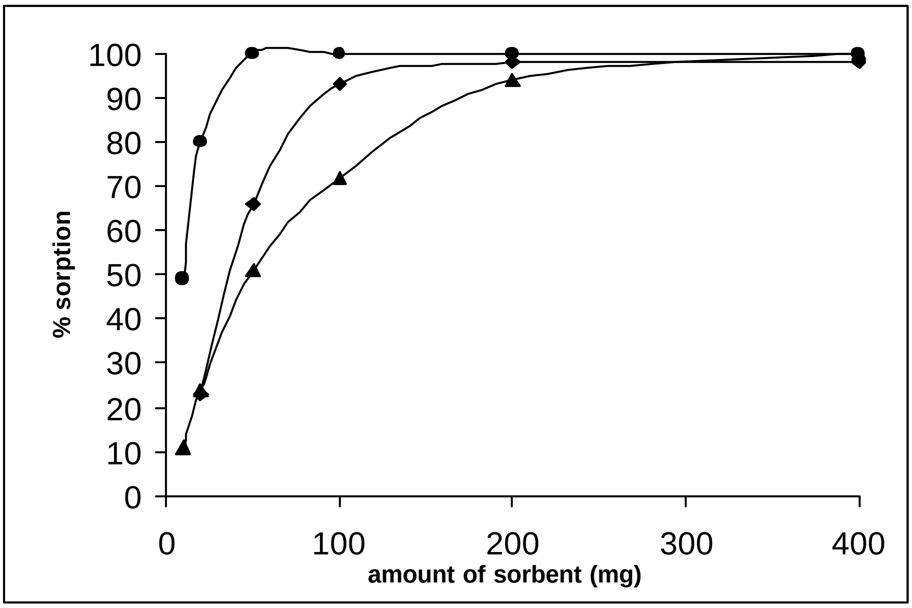


Figure 3.22. Comparison of the percent sorption vs. amount of sorbent **(?)** bead (as it was) IRA743, **(?)** 53-75 µm IRA743, **(?)** N-MGCMN-MCM-41

3.8.2. Reusability (Amberlite RA 743)

The reusability of amberlite IRA 743 was compared with that of N-MGCMN-MCM-41 in a way that, both original and ground Amberlite resins were subjected to usual sorptin/desorption steps succesviley. The results are given in Table 3.9. sorption data for N-MGCMN-MCM-41 were also given in the table for comparison. It can be said that after grinding (thus , after increasing its surface area) Amberlite IRA 743 shows very efficient sorption characteristics and can be used effectively even after third use.

Table 3.9. Comparison of the reusabilities of the sorbents

	% Sorption		
Usage	N-MGCMN modified MCM-41	Amberlite IRA 743	
		As it was	53-75 µm
1st	91 (± 1)	75 (± 2)	100 (± 0.1)
2nd	82 (± 6)	74 (± 3)	100 (± 0.2)
3rd	67 (± 3)	60 (± 2)	100 (± 0.1)

3.8.3. Spike Recovery Tests (Amberlite IRA 743)

A very similar set of experiments was repeated for the commercial resin as explained in section 3.7. The results are given in Table 3.10 and Table 3.11. As expected, the commercial resin worked very efficiently for ultrapure water and adsorbed boron at all concentrations studied. When the spike recovery results for geothermal water are considered, it can be said that sorption capability of commercial resin was also better than MCM-41 modified with N-methylglucamine.

Table 3.10. Boron recovery results for ultra-pure water with Amberlite IRA743 (n=3).

B spike (mg/L)	Initial Volume (mL)	Final Volume (mL)	Enrichment Factor	B found (mg/L)	Recovery (%)
10.0	20	20	1.0	9.8 (±0.1)	98 (±1)
4.0	50	20	2.5	9.3 (±0.5)	93 (±5)
2.0	100	20	5.0	8.9 (±0.2)	89 (±2)
0.8	250	20	12.5	8.7 (±0.3)	87 (±3)

Table 3.11. Boron recovery results for geothermal water with Amberlite IRA743 (n=3).

Geothermal Water B concentration (mg/L)	Initial Volume (mL)	Final Volume (mL)	Boron spike (mg/L)	B must be found	B found (mg/L)	Recovery (%)
9.3	20	20	+ 0.0	9.3	9 (±0.2)	96 (±2)
9.3	20	20	+ 5.0	14.3	14 (±0.2)	96 (±13)
9.3	20	20	+ 10.0	19.3	18 (±0.3)	93 (±13)

CONCLUSION

In this thesis, a novel sorbent that can be used for boron determination in various water samples has been synthesized. For this purpose, two different inorganic support materials, namely silica and MCM-41, were functionalized with N-methylglucamine, after several pretreatment procedures.

The support material MCM-41 was synthesized in our laboratory by hydrothermal synthesis method. Amorphous silica was synthesized by Prof. Balköse's group wheras the commercial silica was obtained from Aldrich. The silicas were treated with 0.01 M acetic acid to investigate the effect of acid treatment on functionalization yield. Before the functionalization reaction the surface of support materials were grafted by silanation with (3-bromopropyl)trimethoxy silane. To optimize the silanation ratio 0.5, 1.0, 1.5 and 10.0 mmol of initial amount of silane reagent were used per gram of support, and treatment with 1.5 mmol silane was found to be suitable for quantitative sorption at 0.1 mg sorbent amount. Functionalization of grafted MCM-41/silica was performed by reacting with N-methylglucamine in a substitution reaction. The characterization of new sorbent was performed with X-Ray Diffarction, DRIFTS, BET and elemental analyses.

After synthesis and characterization of the new sorbent, optimum application conditions were investigated. The optimum amount of sorbent for quantitative sorption was found as 0.1 g for 20.0 mL 10.0 mg/L boron solutions. The kinetic studies have shown that the sorbent can take up 85% of boron from solution in 5 minutes whereas 30 minutes was required for quantitative sorption. To investigate the sorption mechanism and maximum amount of boron that can be sorbed by the sorbent, Freundlich and Dubinin-Radushkevich sorption isotherms were applied. It was found that there exist heterogeneous sites for sorption for low and high concentration levels and 0.8 mmol of boron (as H_3BO_3) can be taken from the solution per gram of sorbent. Efficient sorption take place at a pH higher than 6 and desorption of the sorbed boron from the sorbent was realized with 1.0 M HNO_3.

It can be stated here that the new sorbent demonstrated very promising sorption characteristics for boron in waters. For the better assessment of its performance, several additional tests were repeated with the commercial resin Amberlite IRA 743, since it is used almost universally for boron removal in environmental waters. The sorption capacity of the synthesized sorbent was not found as efficient as the commercial resin; but, applicability to a real sample, at least to geothermal water, gave a promising result for proposed method.

Another potential advantage of the novel sorbent, although not been shown yet, can be the applicability to microcolumn works. Since an inorganic material was used as the support, we do not expect much swelling/contracting property with the new sorbent which can be considered as a big advantage in micro column studies since less back-pressure will be created.

In addition to the sorption studies mentioned above, some important results were also obtained during the initial optimization of the measurement parameters. A systematic study was carried out for the determination of boron with plasma techniques. Especially, valuable results were obtained in “memory reduction” studies with different diluent and flush solutions.

APPENDICES

Appendix A. Calculation of mmol of N-Methylglucamine Attached to the Support from Elemental Analysis Results

The boron binding functional group, N-methylglucamine consist of a secondary amine and a polyol site. It contains 1 mol of N for 1 mol N-methylglucamine. For tis reason the N content of sorbent material, N-Methylglucamine MCM-41/silica, can be used to calculate the functional group amount attached on the surface of MCM-41 or silica.

The calculations can be as follows:

$$\frac{\text{g of N}}{\text{100 g Sample}} \times \frac{\text{1000 mg N}}{\text{1g N}} \times \frac{\text{1 mmol N}}{\text{14 mg N}} \times \frac{\text{1mmol }\textbf{functional group}}{\text{1 mmol N}} = \frac{\text{mmol of N - methylglucamine}}{\text{1g MCM - 41/Silica}}$$

Appendix B Absorption Peaks with UV-Vis Spectrophotometry

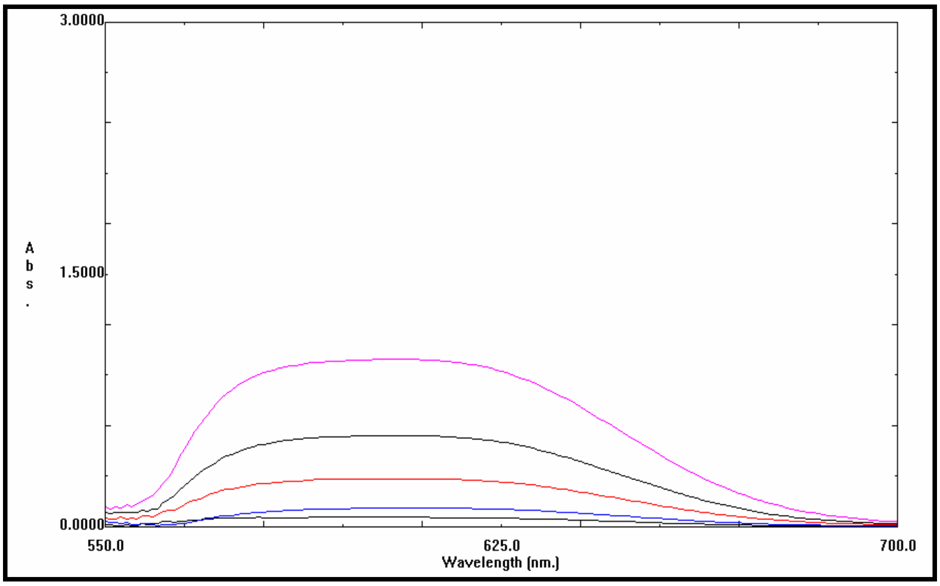


Figure B.1. Absorbance peaks of boron-carmine complex in standard solutions of boron with UV-Visible spectrophotometry.

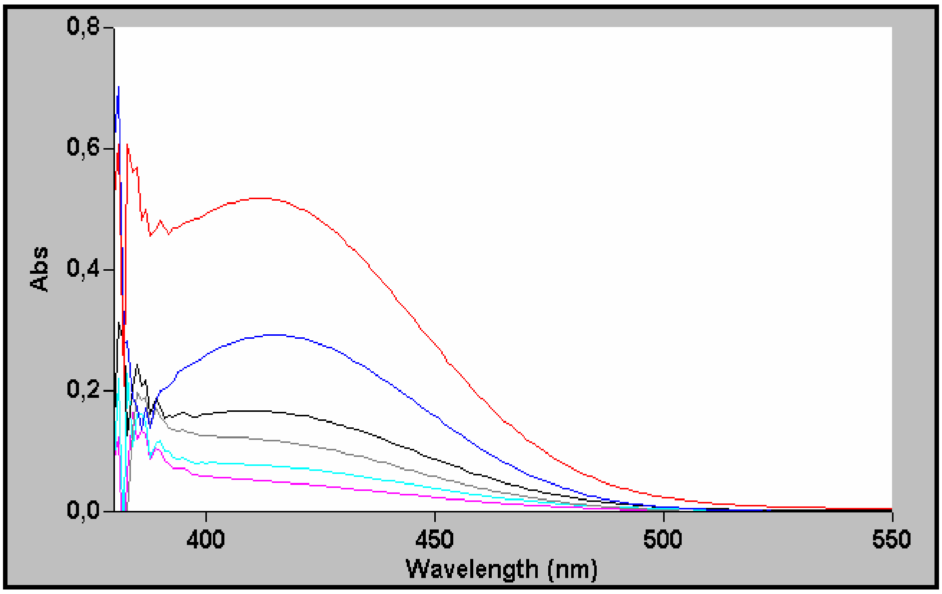


Figure B.2. Absorption peaks of boron-azomethine-H complex in standard solutions of boron with UV-Vis spectrophotometry.

C. Fe emission peaks measured at boron emission lines

Appendix D. Emission Peaks of Boron Standard Solutions with ICP-OES

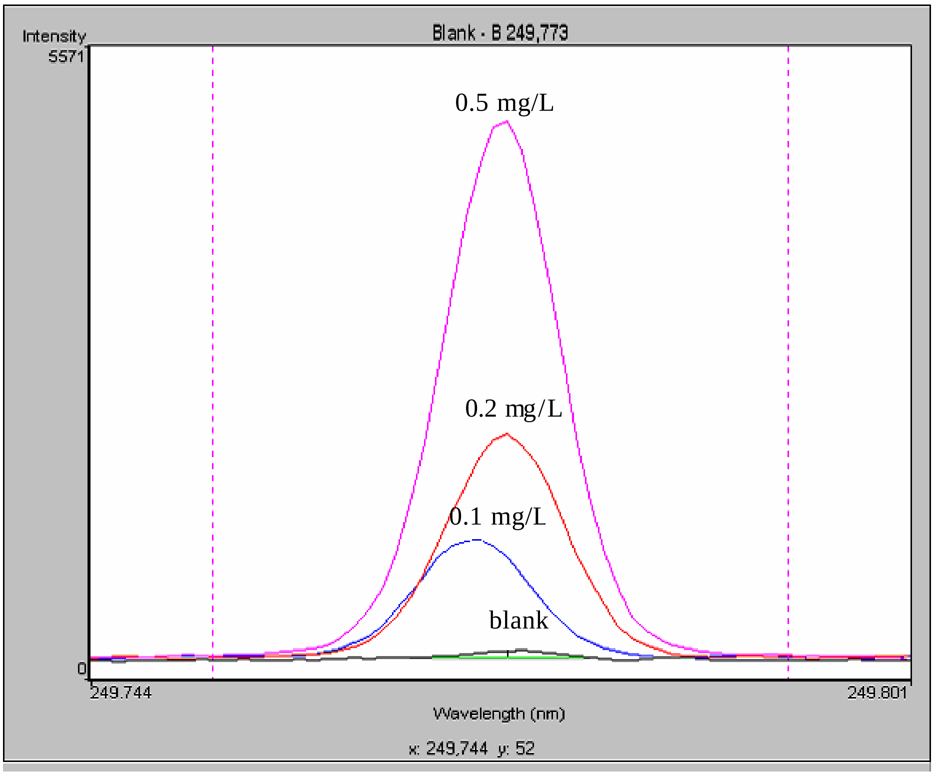


Figure D.1. B emission signals with ICP-OES at 249.773 nm. (Concentration between 0.1-0.5 mg/L)

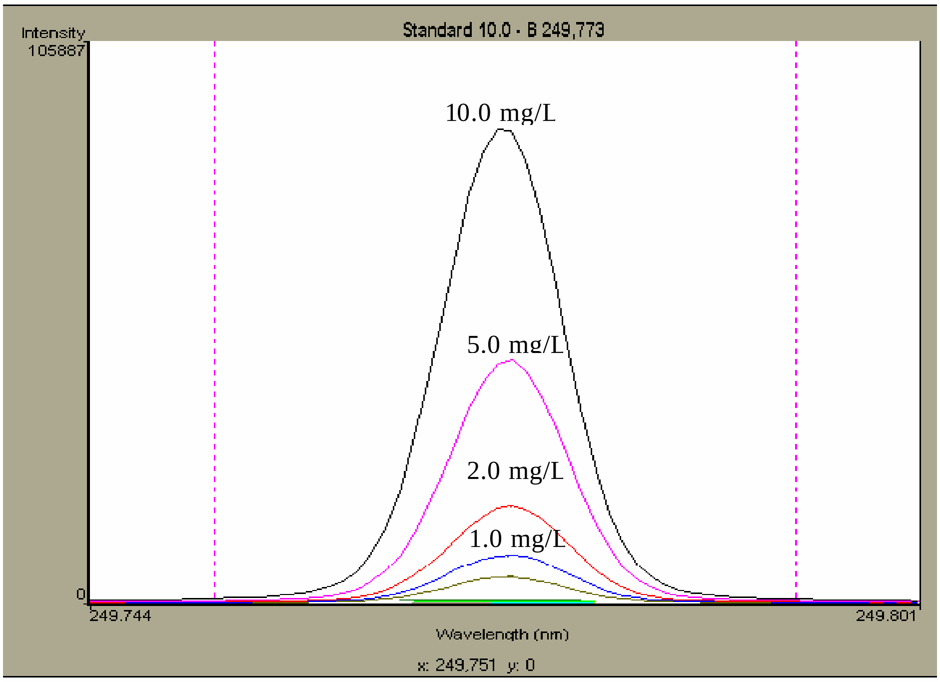


Figure D.2. B emission signals with ICP-OES at 249.773 nm. (Concentration between 1.0-10.0 mg/L)

Appendix E. Kinetic study

The Lagergen’s equation:

$$\mathrm{Ln}\ (1-[C]_t/[C]_e) = -\ ka.t \quad \text{..(1)}$$

where;

k_a: apparent rate constant

$[C]_t$: concentration on the solid phase at any time

$[C]_e$: concentration on the solid phase at equilibrium.

Appendix F. Sorption Isotherm Equations

Freundlich Isotherm Model

The general expression of Freundlich Isotherm is given as:

$$[C]_s = k.\ [C]_l^n \quad \text{…………………………..........................(2)}$$

where;

$[C]_s$: concentration on the solid phase

$[C]_l$: concentration at the liquid phase

k: a constant related to sorption affinity

n: a constant related to linearity of the sorption curve.

This expression can be linearized as:

$$\log [C]_s = \log k - n \log [C]_l \quad \text{……………..........................(3)}$$

The linear curves of log $[C]_s$ versus log $[C]_l$ show that sorption obeys the Freundlich isotherm model. In this curve slope gives the coefficient n and intercept gives the coefficient k.

Freundlich isotherm model allows for several kinds of adsorption sites on the solid, each kind having a different heat of adsorption. The Freundlich isotherm represents well the data at low and intermediate concentrations and is a good model for heterogenous surfaces. When the value of Freundlich constant n is equal to unity, Freundlich equation becomes linear and the Freundlich constant k becomes equvalent to the distribution ratio, R_d which is an empirical constant usually used in the quantificationof the sorption process. (Shahwan 2000)

Dubinin-Radushkevich (D-R) Isotherm Model

D-R Isotherm model is applicable at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces.
It can be represented by the general expression:

$$[C]_s = C_m \exp - (Ke^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots...(4)$$

When you take the logarithm of the D-R equation is:

$$\mathrm{Ln}\, [C]_s = \ln C_m - K e^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

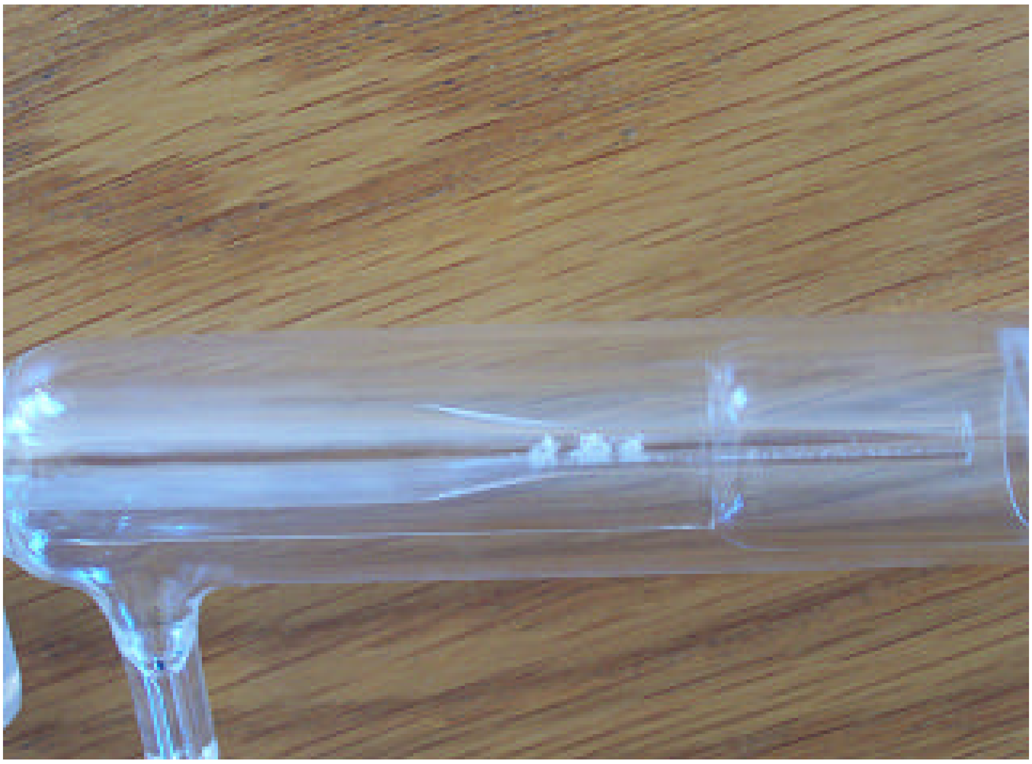
where:
$e = RT \ln (1 + 1/ [C]_l)$
$[C]_s$: concentration on the solid phase
$[C]_I$: concentration at the liquid phase
C_m : The maximum amount of B that can be sorbed by the sorbent.
K : a constant related to sorption energy.
$E = (2K)^{-1/2}$

The linear curves of ln [C]s versus e^2 show that sorption obeys D-R sorption isotherm model. The slope of this curve gives the logarithm of the C_m and the intercept of the curve gives the coeffient K hence the sorption energy.

The sortion energy can be defined as; the energy (kj/mol) required to transfer 1 mol of sorbate species to the surface of the sorbent from infinity in the bulk of the solution. (Shahwan 2000)

The entalpy changes for chemisorption are usually substantially greater in magnitude than those for physical adsorption. Typically ?H for chemisorption lies in the range -40 to – 800 kj/mol, whereas ?H for physical adsorption is usually from -4 to -40 kj/mol. (Levine 1988)

Appendix G. The Photograph of ICP-OES Torch and the White Deposit in Innermost Tube



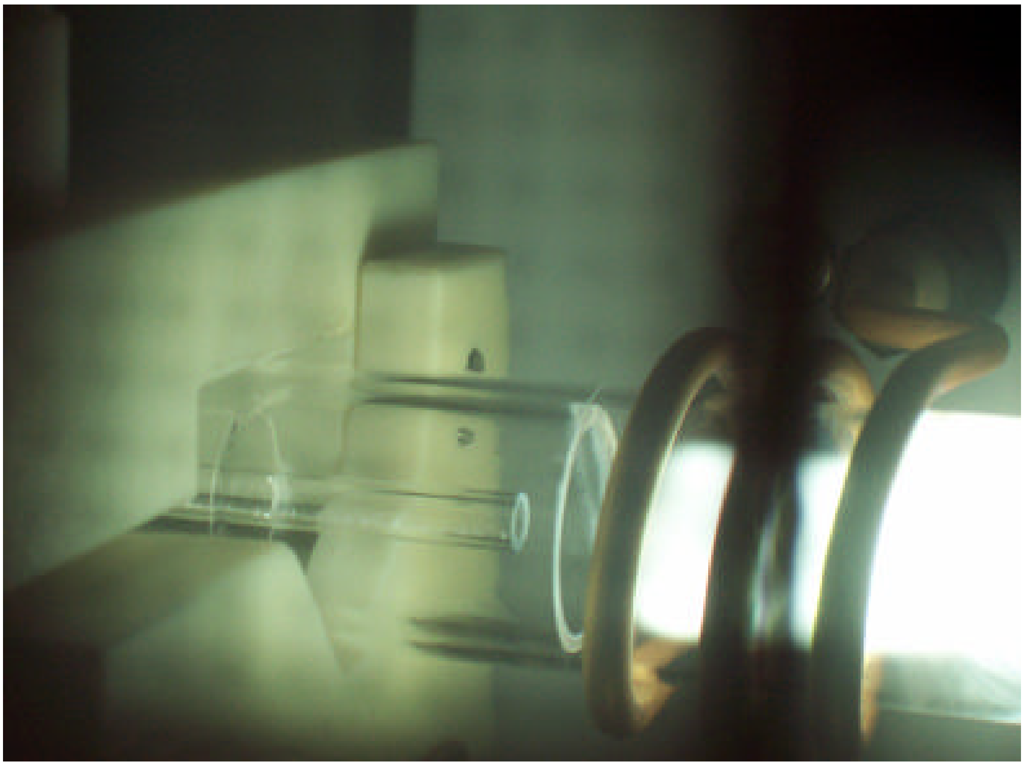


Figure G.. The photographs of ICP-OES torch and the deposit in the inner tube that was occurred while the samples, had been eluted with HCl, were measured.

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