Adsorption Studies of Malachite Green Dye on Mesoporous Silica Synthesized in 1-Octyl-3-Methylimidazolium Chloride Ionic Liquid

A Dissertation
Submitted in partial fulfilment

FOR THE DEGREE
OF
MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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*This is to certify that the dissertation entitled****“Adsorption Studies of Malachite Green Dye on Mesoporous Silica Synthesized in 1-Octyl-3-Methylimidazolium Chloride Ionic Liquid”*** *being submitted by* ***JhumaMondal****to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science in Chemistry is a record of bonafide research work carried out by her under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.*

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ACKNOWLEDGEMENTS

At the very first, I take this great opportunity to express my best regards, sincere thanks from the deepest chore of my heart profound to my guide Dr. Priyabrat Dash for not only providing me the facilities but also a higher learning environment where the creative, curious minds always find their best destination. His brilliant suggestions and inspiration helped me to bring out this project report into light.

I am also thankful to all the PhD scholars of Department of Chemistry, NIT, Rourkela for their unending help in every steps and encouragement, proficient guidance, suggestions throughout the entire summer project duration. I would like to specially thank BasantiEkka, Lipeeka Rout and Aniket Kumar, not only for their endless help during lab work and valuable suggestions but also helping me in bringing out this report. It is my pleasure to thank my lab seniors and for their co-operation and continuous encouragement throughout the entire period of the project and special thanks for making a friendly atmosphere in the lab. Finally, I am honestly grateful to my family members for their endless love, unending support and blessing, specially my parent and my elder brother who are all in my life. Last but not the least thanks to almighty God who helped me to bring out my project.

Jhuma Mondal

ABSTRACT

In this work, one long-chain ionic liquid (IL), 1-octyl-3-methylimidazolium chloride, was used as a template for the preparation of mesoporous silica via a modified sol-gel route. The morphology of the obtained material was characterized by scanning electron microscopy (SEM). The various vibrational modes of different functional groups in the mesoporous silica materials were revealed by Fourier transform infrared (FTIR) spectroscopy. N_2 adsorption-desorption isotherms measurement was used to characterize the pore diameter and BET surface area. The adsorption capacity of malachite green dye from aqueous solution has been performed using the mesoporous silica synthesized in ionic liquid. The adsorption equilibrium of dye on mesoporous silica was found to be at 150 min. The maximum malachite green dye adsorption was found to be 97 %.

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INTRODUCTION

1.1 General introduction

A porous material is simply some kind of solid material that has holes in it. The holes are called as pores. The pores are typically filled with a fluid(liquid or gas).Pores are classified into two types: open pores which connect to the surface of the materials, and closed pores which are isolated from the outside. Pores have various shapes and morphology such as cylindrical, spherical and slit types. There are also pores taking more complex shapes such as hexagonal shape. Typical porous materials include some kind of silica and alumina that have similarly sized fine pores. Porous solids are of scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but throughout the bulk of the material.

A porous medium is most often characterized by its porosity. Other properties of the porous materials (e.g. permeability, tensile, strength, electrical conductivity) can sometimes be derived from the respective properties of its constituents (solid matrix and fluid). Porous materials possess unique properties that the bulk correspondent materials do not have such as high specific area, fluid permeability and shape-selective effects. Different porous materials with varying pore size, porosity, pore size distribution and surface properties that will eventually determine their potential applications. These materials also show high adsorption capacity, excellent mechanical properties, good stability and durability. Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. The size of the pores is generally 100 nm or smaller. Most of the nanoporous materials can be classified as bulk materials or membranes. Activated carbon and zeolites are two examples of bulk nanoporous materials, while cell membranes can be thought of as nanoporous membranes.

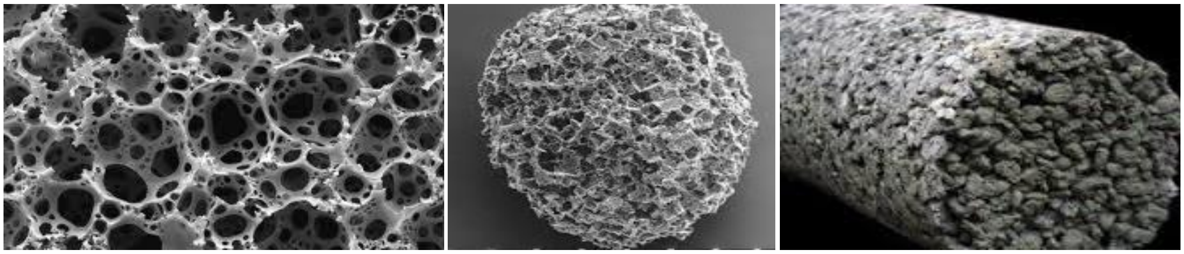


Fig.1 Examples of Porous Materials.

The pores of solids are classified according to size: (Fig. 2) pore sizes in the range of 2 nm and below are called micropores, those in the range of 2 nm to 50 nm are denoted mesopores, and those above 50 nm are macropores.

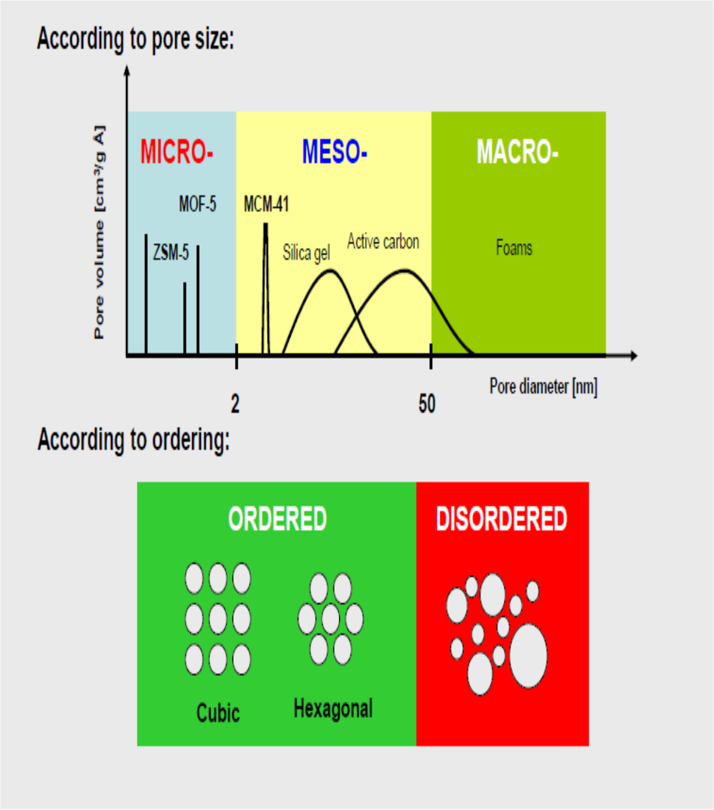


Fig.2 Types of porous materials.

1.2 Mesoporous materials

Porous materials have become more and more important in either science or technology. They can be grouped into three classes based on their pore diameter (d): microporous, $d < 2.0$ nm; mesoporous, $2.0 < d < 50$ nm; macroporous, $d > 50$ nm. Among them, mesoporous materials have attracted more attention due to tailoring ability of the pore structure over a wide range, and the potential applications in catalysis, separation, sensor etc. Mesoporous silica is a form of silica and a recent development in mesoporous materials with well-defined pore geometry which has attracted considerable attention due to their high surface area, pore volume, and uniform pore channel for use in a wide range of application areas such as catalysts, molecular recognition as in a chemical sensor, and separation processes. Among the wide variety of potential application areas, in particular, the development of functionalized mesoporous silica for liquid-phase separation application has attracted a great deal of interest, due to easy-tunable surface functionality and uniform pore structure. Silica is well known for its use in the preparation of low refractive index materials, because it is chemically inert, thermally stable and inexpensive [1].

The design, synthesis and modification of porous materials are in some aspects more challenging than the synthesis of dense materials. Mesoporous materials based on MCM-41(mobile crystalline materials) are silicates obtained by hydrothermal synthesis and a liquid templating mechanism. Mesoporous materials based on MCM-41 show excellent thermal, hydrothermal and hydrolytic stabilities [2-5].

1.3 Ionic liquid as a novel media for the synthesis of porous silica

Ionic liquids are liquids that consist exclusively or almost exclusively of ions[6].This definition includes liquids that are traditionally known as molten salts, or fused salts, which have high melting point. The use of the term ionic liquids has generally been limited to those liquids, as defined above, that have melting points or glass-transition temperatures below 100º C. Aqueous solutions of salts are not classified as" ionic liquids" as they do not consist of ions. Ionic liquids that are liquid at or around room temperature are often called "room temperature ionic liquid" [7]. Ionic liquid (ILs) typically contains bulky organic cations with a low degree of symmetry such as imidazolium, pyrrolidinium, tetraalkylphosphonium, trialkylsulfonium or quaternary ammonium. ILshas been accepted as a new green chemical revolution which excited both the academia and the chemical industries. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses[8]. ILs has been known for a long time, but their extensive use as solvents in chemical processes for synthesis and catalysis has recently become significant. Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications such as replacing them with volatile organic solvents[9-11]. ILs have been extensively used in making new materials, conducting heat effectively, supporting enzyme-catalyzed reactions, hosting of catalysts, purification of gases, homogenous and heterogeneous catalysis, biological reactions media and removal of metal ions [12-16]. The mesoporous materials have attract much attention of chemists and scientists for a long time due to their potential application in catalysis, adsorption, separation, drug delivery and due to scientific interest in the challenges posed by their synthesis, processing, and characterization[17]. The mesoporous materials of M41S family are generally obtained using surfactants such as primary amines and quaternary ammonium ions [18, 19]. The synthesis of mesoporous silica depends on a super molecular templating mechanism with an amphiphilic molecule, which is using surfactants as a structure directing template. Recently, the scientists of research groups focus on using a new class of cationic amphiphiles based on ionic liquid to prepare shape-selective mesostructured materials. Ionic liquids (ILs) have attracted much attention due to the unusual properties, especially their low vapour pressure, high thermal and chemical stability, and excellent solvating power for organic and inorganic compounds. Seddon group first reported MCM-41 synthesised by hydrothermal method using 1-alkyl-3-methylimidazolium halides (CnMIM) X salts as templates [20]. Zhou and Antonietti used (CnMIM) X (n= 10, 14, 16, 18) templates to synthesise mechanically stable silica with ordered lamellar super-micropores via the nanocasting approach [21]. In addition to this, they used (C_4MIM) BF_4 a room temperature ionic liquid as template for synthesizing mesoporous silica with wormhole framework via a convenient nanocasting technique. The nanocasting technique is an efficiently high concentration way to prepare monolithic porous materials. Its principle is that hydrolysis and condensation of inorganic precursors are strictly limited to take place in an aqueous domain of the microphages-separated medium, derived from the self-assembly phase of the template used. As a result, the solidification inorganic compound is thought to be a replication of the original phase structure, predetermined by selection of the template phase. Due to the solidification of the inorganic precursor in a homogeneous bulk liquid crystal, this nanocasting method allows the preparation of large monoliths of porous materials.

Li and co-workers used a series of 1-alkyl-3-methylimidazolium bromide (CnMIM) Br (n=12, 14, 16) a kind of amphiphilic room temperature ionic liquids as a template via a sol-gel nanocasting technique and the result indicate that with increasing alkyl chain of room temperature ionic liquids used as templates, the pore diameter of the mesoporous materials became bigger [22]. ILs is emerging as a green reaction media.The use of ionic liquids as reaction medium may offer a convenient solution to both the solvent emission and catalytic recycling problem [23].Currently reports are available in the open literature on synthesis of silica using acidic ionic liquids. Acidic ionic liquids are the ionic liquids which are functionalised by some acidic group like H_2SO_4, Na_2HSO_4 etc. Acidic ILs are soluble in water and non-corrosive. These ILs are used as acid catalysts in many reactions like esterification, oxidation, alkylation, Beckmann Rearrangement, Cyclotrimerisation and so on. Much effort has been focused on developing ordered periodic mesoporous silica with well-defined, controlled pore channels by sol–gel templating using amphiphilic surfactants as templates [24]. Since most long-chain ILs possesses both a hydrophilic ionic head group and a hydrophobic organic chain, they represent a category of surfactant, so they can be used as templates to prepare microporous and mesoporous materials [25]. For synthesis of mesoporous silica a template and an acid catalyst is needed so use of an acidic ionic liquids in which the cation acts as a template and the anion as the acid source can give a mesostructured silica materials. Pujari and groups used acidic ionic liquids like 1-alkyl-3-methylimidazolium hydrogen sulfate [CnMIM] HSO_4 (n = 8, 10, 12, 16) to synthesize high surface area ordered mesoporous silica using a one-step synthetic route [26].Here they describe the one-pot microwave synthesis of the acidic ionic liquids 1-alkyl-3-methylimidazolium hydrogensulfate (where alkyl = octyl, decyl, dodecyl, hexadecyl) andtheir subsequent application as both templates and acid source for the synthesis of ordered, high-surface-area mesoporous silicas.

1.4 Malachite green dyes

Malachite green (MG) dye in an organic compound that is used as dyestuff and has emerged as controversial agent in aquaculture[27].Dyes are important pollutants, cause in environmental and health problems to human being and aquatic animals. MG is most commonly used for the dying of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. It is a toxic chemical and largely used to treat parasites, fungal infections, and bacterial infections in fish and fish eggs[28].Despite its extensive use, MG is a highly controversial compound due to its reported toxic properties which are known to cause carcinogenesis, mutagenesis, and respiratory toxicity. Adsorption methods employing solid adsorbents are widely used to remove certain classes of chemical pollutants from waste water. Some adsorbents, such as chitosan, activated carbon, soil, ground shrimp skeleton, ground oyster Shell, ground charcoal, TriSylsilicas, de-oiled soyaand microalgae were used to remove MG from industrial wastewater[29].

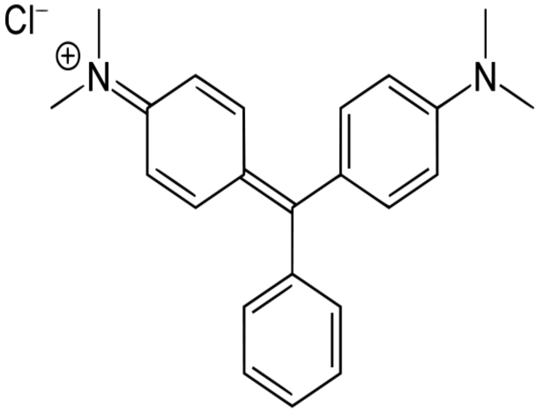


Fig.3 Structure of malachite green dye.

In adsorption methods, MG adsorption studies were already reported in rice husk-based carbon, activated carbon, hen feather etc. The activation of low cost adsorbents needs some chemical treatments that can cause environmental pollution. Moreover, the conventional adsorbents are environmentally unstable and they liberate dye again to the environment after the adsorption. Hence, we attempted to study the possibility of using mesoporous silica as an adsorbent for removal of MG from aqueous solution.

1.5Objectives of the study

Removal study of malachite green from aqueous solution as well as contaminated water has been carried out by several research groups [30, 31]. However, the use of mesoporous silica synthesised from ionic liquid to remove dye has not been studied much. Therefore, a knowledge gap exists in this area. In this work we focused on the use of ionic liquid mediated silica for removal of malachite green (cationic dye) from aqueous solutions. Therefore the main objectives of the present study are:

- To synthesize, purify and characterize 1-octyl3-methylimidazolium chloride (OMIMCl) ionic liquid.
- Synthesis of mesoporous silica using OMIMCl.
- To characterize the mesoporous silica by FTIR and SEM.
- Study of adsorption capacity of malachite green using mesoporous silica.

Chapter-2

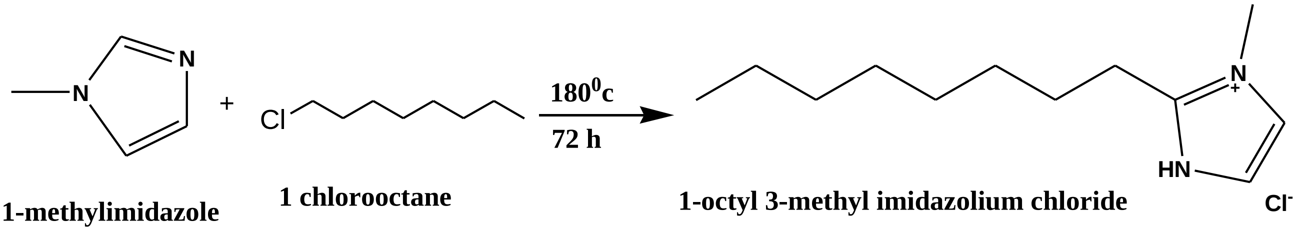
MATERIALS AND METHODS

2.1 Materials

1-methylimidazole (99%) and 1-chlorooctane (99%) and were purchased from Sigma-Aldrich and were distilled over KOH and P_2O_5, respectively. Sodium hydroxide, ethanol and methanol were purchased from Himedia and were used without any further purification.

2.2 Synthesis of Ionic Liquid

2.2.1 Synthesis of 1-octyl-3-methylimidazolium chloride (OMIMCl)



1-methylimidazole **1 chlorooctane** **1-octyl 3-methyl imidazolium chloride**

1-octyl-3-methylimidazolium chloride was synthesized according to reported procedures [32]. To a 100 ml round bottom flask equipped with reflux condenser, magnetic stirring bar connected with a nitrogen cylinder, 1-methyl imidazole 10 ml (125 mmol) and toluene 12.6 ml (mole) was added in ice bath. After 5 min. of stirring 1-chlorooctane 23.44 ml (138 mmol) was added. The solution was heated to reflux at 125 °C for 72 h, yielding a two phase mixture of [OMIMCl] and toluene. Then the toluene was decanted and the product was recrystallized with acetone. The yield of the product was calculated to be 70 %.

2.2.2Synthesis of silica by formic acid (solvolytic method):

In a typical synthesis of silica ionogels, the ionic liquid(IL) and formic acid(FA) were stirred at room temperature for 10 min before adding the silica precursor(TEOS) in a molar ratio of 1 TEOS/0.5 IL/7.8 FA. The resulting solution was stirred at room temperature for 10 min. Gel times depended on the IL. The removal of IL was performed by means of Soxhlet extractor with refluxing acetonitrile.

2.3 Characterization of Adsorbent

The materials synthesized in above sections were characterized by N_2 adsorption-desorption isotherm, Infra-Red Spectroscopy (IR) and Scanning Electron Microscopy (SEM). To check purity of ionic liquid, NMR was taken.

N_2 adsorption-desorption isotherm

Surface area was calculated by using the BET (Brunauer–Emmet–Teller) equation. The pore size distribution and pore volume were obtained by applying the BJH (Barrett–Joyner–Halenda) method. The samples were degassed at 150 °C in vacuum. Helium was used as carrier gas and surface area was measured by N_2 adsorption-desorption method.

Infrared Spectroscopy (IR)

The IR spectra of mesoporous silica (as KBr pellets) were recorded using Perkin-Elmer infrared spectrometer with a resolution of 4 cm^{-1}, in the range of 400 cm^{-1} to 4000 cm^{-1}. Nearly 3-4 mg of the sample was mixed thoroughly with 30 mg of oven dried KBr and made into pallets.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was taken using JEOL JSM-6480 LV microscope (acceleration voltage 15 kV). The sample powders were deposited on a carbon tape before mounting on a sample holder for SEM analysis.

Nuclear magnetic resonance (NMR) spectroscopy

Since ionic liquids are predominantly used as solvents so it is necessary for the application of nuclear magnetic resonance spectroscopy to check the purity of the ionic liquids. NMR was taken on a 400 MH_ZBruker instrument.

2.4 Adsorption experiments

In order to know the dye removal ability of the mesoporous materials, a set of adsorption experiments were performed by shaking a fixed amount of mesoporous silica in 100 ml of 10 mg/L dye solution (MG) in polylab plastic bottles at 250 rpm using a temperature-controlled shaker. Initial pH of the solution to the desired value for these experiments was adjusted by the addition of required 0.1 M HCl or 0.1 M NaOH solution. After the predetermined period, the adsorbent solution mixtures were centrifuged off and final concentrations of the solution were measured by UV-Vis spectrophotometer at 617 nm. The amount of malachite green adsorbed on the mesoporous silica synthesised in ionic liquid medium was obtained from the following equation:

$$Qe = \frac{(Co-Ce)V}{W} \tag{1}$$

where Qe is the amount of malachite green dye adsorbed (mg/L), Co and Ce are the initial and equilibrium liquid-phase concentrations of MG (mg/L), respectively, V is the volume of the solution and W is the amount of the mesoporous silica adsorbent (g).

Chapter-3

RESULTS AND DISCUSSION

3.1 NMR study

^{1}H, NMR spectra were recorded on Bruker Advance 400 spectrometer using $CDCl_3$ as solvent. Chemical shift values (δ) are expressed in parts per million units as internal standard. Coupling constant (J) are measured in Hz. Fig. 4 shows the ^{1}H NMR spectra of OMIMCl ionic liquid. From NMR data it is confirmed that the ionic liquid synthesised is pure and no other peak is there except product peak.

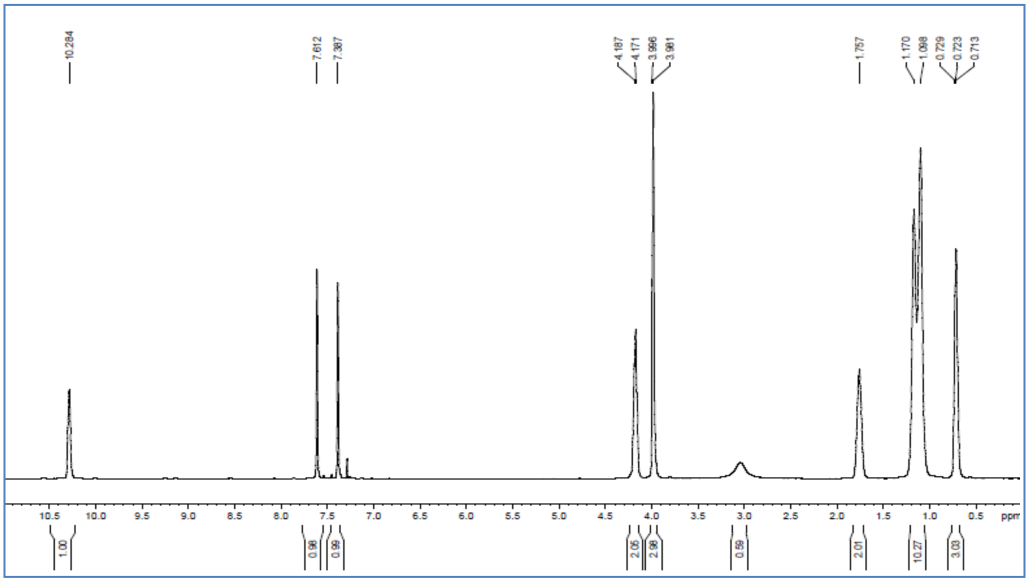


Fig.4^{1}H NMR spectra of OMIMCl ionic liquid.

^{1}H-NMR($CDCl_3$, 400MHz): δ(ppm) = 10.28 (s, 1H, NCHN), 7.61(t,1H,NCHCHN) 7.38(t,1H,NCHCHN), 4.17(t,2H,$NCH_2(CH_2)_6CH_3$), 3.98(s,3H,NCH_3), 0.71(t,3H,CH_3).

3.2N_2 adsorption-desorption isotherm

The pore characteristics of the mesoporous silica were characterized with N_2 adsorption-desorption isotherm. Textural properties obtained from the experimental isotherms are collected in Table 1. It can be seen that the material have a relatively large BET area, and the pores in the silica materials is in the size range of mesopore. The material has BET surface area of 898 $m^2\ g^{-1}$, pore volume of 0.84 cc g^{-1} and the pore diameter is 2.8 nm. It has been reported that the use 1-butyl-3-methylimidazolium chloride in synthesis of mesoporous silica leads to the BET surface area of 460 m^2 g^{-1}, pore diameter 2.5 nm and the pore volume of 0.27 cc g^{-1}. The higher BET surface area in case of 1-octyl-3-methylimdazolium chloride is due to long-chain ILs, which displayed significantly stronger tendency toward self-aggregation and supramolecular templating in the preparation of mesoporous silica [33].

Material	**Surface area (m^2/g)**	**Pore diameter (nm)**	**Pore Volume (cc/g)**
Silica	**898**	**2.8**	**0.84**

Table 1

3.3 FT-IR

The FTIR spectra of mesoporous silica synthesized in 1-octyl-3-methylimidazolium chloride showed several characteristic functional peaks that are related to silica matrix as shown in Fig.4. A broad absorption band at 3600 cm^{-1} is attributed to the stretching of the Si-OH group. The peak around 1649 cm^{-1} indicates the bending vibration of Si-OH group. The bands around 1422, 685 and 418 cm^{-1} are asymmetric stretching, symmetric stretching and bending of Si-O-Si vibration respectively.

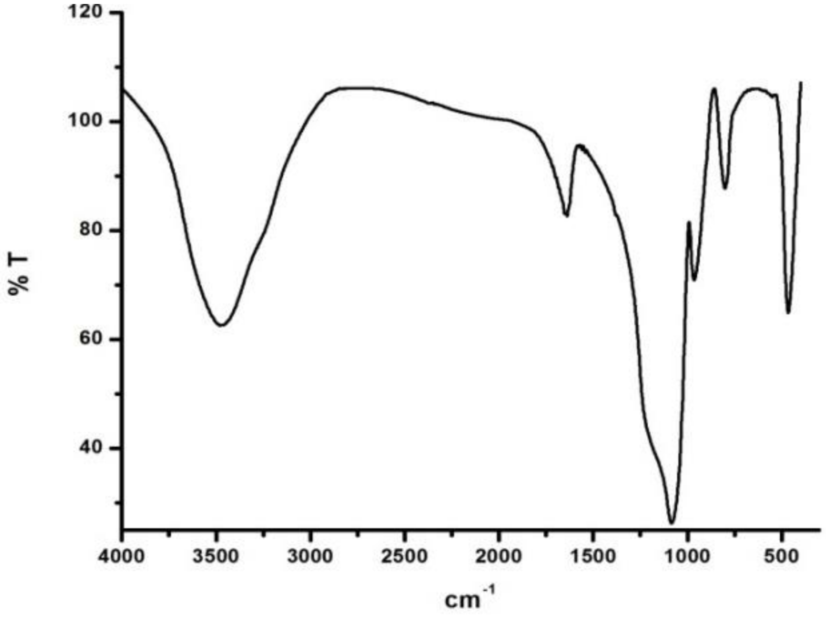


Fig. 5 FTIR spectra of Mesoporous silica synthesised in 1-octyl-3-methylimidazolium chloride.

3.3 Scanning electron microscopy (SEM)

SEM images are usually employed to observe the morphology of nanoparticles or high surface area powders.Fig.5 shows the SEM micrograph of the synthesized mesoporous silica magnified to 5000 times. It is seen that the sample mainly consists of irregular particles with various sizes. However, a few huge particles with larger sizes are also observed.

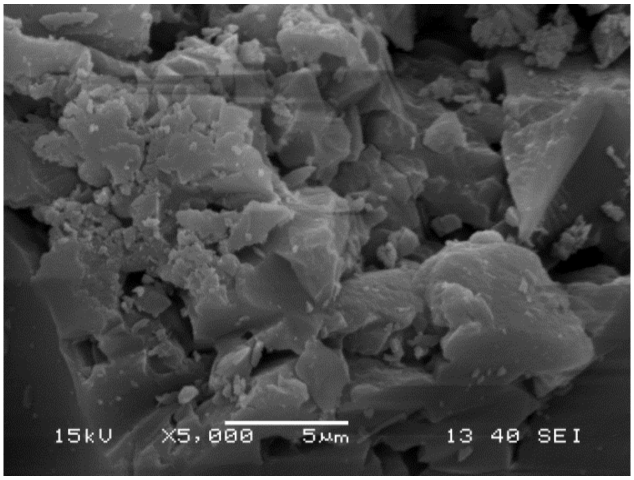


Fig.6 SEM image of mesoporous silica synthesised in 1-octyl-3-methylimidazolium chloride.

3.4 Effect of Contact time on the adsorption of MG

The conventional adsorbents used for dye removal are unstable in environment for long time and the adsorbed dyes can again liberated and pollute the environment. To avoid this problem, environmentally stable adsorbent like mesoporous silica was synthesised in ionic liquid medium and used for adsorption of malachite green which is substantially influenced by contact time and initial concentration. The variation in percentage removal of the dye with contact time at constant initial concentrations of 10mg/L is shown in Fig.7. It is observed from the figure that the removal of MG acquired a maximum at the time of equilibrium i.e 150 min and thereafter becomes steady. This can be justified with the fact that initially all binding sites were vacant as well as high concentration gradient of solute was present. After 150 min, MG uptake becomes almost constant. Fig.8 shows the absorption spectra of mesoporous silica synthesised using ionic liquid medium via modified sol-gel method. The spectra show the adsorption of 10 mg/L malachite green in 300 mg of adsorbent in aqueous solution.

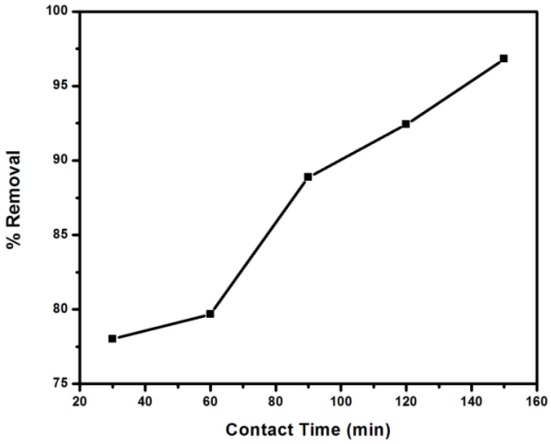


Fig. 7 Effect of Contact time on adsorption of malachite green on mesoporous silica synthesised in 1-octyl-3-methylimidazolium chloride.

Fig.8. displays the absorption band of MG at around 617nm and the peak intensity decreased rapidly in 150 min. It was observed that after 150 min the mesoporous silica synthesised in ionic liquid medium shows around 97 % adsorption of malachite green. The high adsorption capacity of malachite green on mesoporous silica was because of the high surface area of mesoporous silica synthesised from ionic liquid. The use of long-chain ionic liquids like 1-octyl-3-methylimidazolium chloride corresponds to high surface area of the mesoporous silica. Antoinetti and group proved that how long-chain ILs are gives rise to high surface area silica [34].

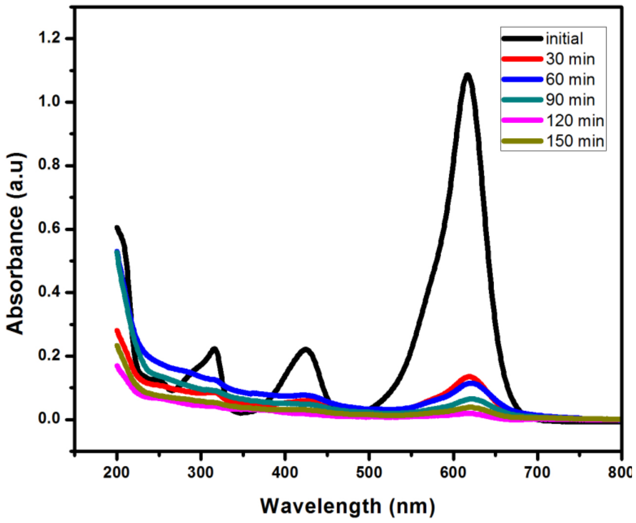


Fig. 8 Adsorption of malachite green in mesoporous silica synthesised in 1-octyl-3-methylimidazolium chloride.

Chapter-4

CONCLUSIONS AND FUTURE WORK

Mesoporous silica having surface area of 898 m^2 g^{-1}, pore diameter of 2.8 nm and pore volume of 0.84 cc g^{-1} were successfully synthesized using 1-octyl-3-methylimidazolium chloride ionic liquid as template by a modified sol-gel method. The silica adsorbent was characterized by N_2 adsorption-desorption, SEM and FTIR analysis. The maximum adsorption of malachite green dye was found to be 97% on mesoporous silica prepared from 1-octyl-3-methylimidazolium chloride in 150 min and 10 mg/L initial concentration of dye. From the above results, it could be concluded that mesoporous silica synthesized in 1-octyl-3-methylimidazolium chloride ionic liquid was an efficient adsorbent for removal of malachite green from aqueous solution due to its simple preparation, and high adsorption capacity.

As mesoporous silica was successfully synthesised in 1-octyl-3-methylimidazolium chloride ionic liquid, further studies will be carried out by using different ionic liquids including acidic ionic liquids for preparation of mesoporous silica. One possible research direction would be the studies on the removal efficiency of heavy metals such as Arsenic, Chromium, Lead and Mercury from synthetic and actual contaminated water by this adsorption media.

REFERENCES

[1] A.B.D. Nandiyanto, F. Iskandar, *Chem. lett.,* 37 (**2008**) 1040.

[2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature*, 359 (**1992**) 710.

[3] T. Blasco, A. Corma, M.T. Navarro, J.P. Pariente, *J. Catal.*, 156 (**1995**) 65.

[4] P.T. Tanev, T. Pinnavaia, *J. Chem. Mater.*, 8 (**1996**) 2068.

[5] A. Liepold, K. Roos, W. Reschetilowski, *Chem. Eng. Sci.*, 51 (**2001**) 3007.

[6] K.R. Seddon, *J. Chem. Tech. Biotechnol.*, 68 (**1997**) 351.

[7] C.L. Hussey, *Adv. Molten Salt Chem.*, 5 (**1983**) 185.

[8] H. Zhao, S.W. Malhotra, *Aldrichim Acta.*, 35 (**2002**) 75.

[9] S.V. Volkov, *Chem. Soc. Rev.*, 19 (**1990**) 21.

[10] P. Afanasiev, C. Geantet, *Coord. Chem. Rev.*, 178 (**1998**) 1725.

[11] P. T. Anastas, E.S. Beach, *Green Chem. Lett. Rev.,* 1 (**2007**) 9.

[12] N.V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.*, 37 (**2008**) 123.

[13] H.M. Luo, S. Dai, P.V. Bonnesen, *Anal. Chem.*, 76 (**2004**) 2773.

[14] J.F. Huang, H.M. Luo, C.D. Liang, D.E. Jiang, S. Dai, *Ind. Eng. Chem. Res.*, 47 (**2008**) 881.

[15] S.H. Zhou, Z. Ma, G.A. Baker, R.J. Rodinone, Q. Zhu, H. M. Luo, Z.L. Wu, S. Dai, *Langmuir,* 25 (**2009**) 7229.

[16] J.S. Lee, X.Q. Wang, H.M. Luo, G.A. Baker, S. Dai, *J. Am. Chem. Soc.*, 131 (**2009**) 4596.

[17] M. Kruk, M. Jaroniec, *Chem.Mater.*, 13 (**2001**) 3169–3183.

[18] S. Oliver, A. Kuperman, N. Coombs, A. Lough, G. Ozin, *Nature,* 378 (**1995**) 47.

[19] L. Mercier, T.J. Pinnavaia, *Chem. Mater.*, 12 (**2000**) 188.

[20] C.J. Adams, A.E. Bradley, K.R. Seddon, *Aust. J. Chem.*, 54 (**2001**) 679.

[21] Y. Zhou, J.H. Schattka, M. Antonietti, *Nano. Lett.,* 4 (**2004**) 477.

[22] Z. Li, L. Yu, B. Dong, F. Geng, *J. Disper. Sci. Technol.,* 29 (**2008**) 1066.

[23] T. Welton, *Chem. Rev.*, 99 (**1999**) 2071.

[24] J.S. Beck, J.C. Vartuli, W.J. Roth, *J. Am. Chem. Soc.,* 114 (**1992**) 10834.

[25] C.K. Lee, H.H. Peng, I.J.B. Lin, *Chem. Mater.*, 16 (**2004**) 530.

[26] A.A. Pujari, J.J. Chadbourne, A.J. Ward, *New. J. Chem.,* 33 (**2009**) 1997.

[27] Y. Guo, H. Zhang, N. Tao, Y. Liu, J. Qi, Z. Wang, H. Xu, *Mater. Chem. Phys.*, 82 (**2003**) 107.

[28] M. A, *J. Hazard. Mater.*, 133 (**2006**) 196.

[29] F. Kandag, D. Sanaydin, F. Aydin, *Turk. J. Chem.,* 22 (**1998**) 227.

[30] Y.C. Sharma, *J. Chem. Eng. Data*, 56 (**2011**) 478.

[31] E. Bulut, M. Ozacar, I.A. Sengil, *Microporous Mesoporous Mater.,* 115 (**2008**) 234.

[32] Y. Zhou, M. Antonietti, *Chem. Mater.*, 16 (**2004**) 544.

[33] L. Viau, M.A. Neouze, C. Biolley, S. Volland, D. Brevet, P. Gaveau, P. Dieudonne, A. Galarneau, A. Vioux, *Chem. Mater.,* 24 (**2012**) 3128.

[34] M. Antonietti, D.B. Kuang, B. Smarsly, Z. Yong, *Angew. Chem., Int. Ed.,* 43 (**2004**) 4988.