

Harnessing Magnetic Chitosan Nanocomposites for the Adsorption of Heavy-Metal Ions from Aqueous Medium

PS Jassal^{*1}, Neema Chand² and Sonal gupta³, Rajendra Singh⁴

^{1,2,3}Department of Chemistry, SGTB Khalsa College, University of Delhi, Delhi-110007, India

⁴DRDO, TSO & Head TCP & HR, Brig .S.K .Mazumdar Marg, Timarpur, Delhi-110054, India

^{*1}psj.sgtb57@gmail.com; ²neemaec@yahoo.co.in; ³sonalshruti92@gmail.com; ⁴rajendra58singh@rediffmail.com

Abstract-Chitosan, a biopolymer is a natural polysaccharide showing excellent property of adsorption of toxic metal ions present in wastewater. The use of chitosan (CS) is growing exponentially due to its wide range of application in the field of science and technology. The removal of heavy metal ions from aqueous medium is the reflection of adsorption efficiency of chitosan. We have applied the concept of nanotechnology in the form of Magnetite (Fe₃O₄)- nanoparticles and coated them with our polymer CS to obtain Magnetic Chitosan Nanoparticles (MCNs).

The objective of this review is to focus on the performance of magnetized nanoparticles of chitosans as adsorbents for the removal of heavy metals from aqueous medium. The magnetised nanocomposites of chitosans are with fast rate of adsorption for removal of pollutants as they are easy to recover using an external magnet.

This review outlines the synthesis of MNCs and their subsequent characterization on the basis of spectroscopic techniques namely X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Thermal Gravimetric Analysis (TGA). Adsorption performances of different MNCs for toxic metal ions viz zinc, cadmium, lead and copper etc. were studied by using VA computrace 797, Metrohm (Switzerland). Voltammetric instrument provides both qualitative and quantitative analysis of the metal ions present in the given sample via current-voltage graph.

Keywords- Chitosan; Magnetite (Fe₃O₄); Nanotechnology; Adsorption; Voltammetry

I. INTRODUCTION

Water is the most fundamental requirement of the living beings and also the needs of household, agriculture and industries. However, the unending human activities have polluted and reduced the standard of water resources all over the earth planet. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants that render it unfit for our basic use. The contaminants that include metals, dyes, non-biodegradable waste, phosphates, nitrates and fluorides etc. even in trace amounts lead to enormous pollution problems.

The pushing of even trace amounts of metals in water sources is a serious threat to our aquatic ecosystems because some of these heavy metals are highly toxic even at low concentrations. Additionally, heavy metals are not degraded in living beings and results in the deposition in the different parts of their body organisms thus causing severe problems to both humans and wildlife. Heavy metal ions such as Zn²⁺, Cd²⁺, Pb²⁺, Hg²⁺, Ni²⁺ and Cu²⁺ can cause severe health problems even in small amounts by interacting with proteins, nucleic acids and small metabolites etc [1].

The toxic effects of heavy metals has thus put pressure on the scientific community to develop techniques to monitor and check the concentration of these toxic metal ions in the ecosystem. A number of processes such as electrochemical precipitation, electrodeposition, ion-exchange, filtration and adsorption are being practiced in this regard. Some of these methods are generally expensive, complicated, time consuming and require skilled personnel's. However, among them adsorption has emerged as the most economical and easy to operate technique. The most effective method is the adsorption process as it removes contaminants in wastewater with low and high solute concentration. The adsorption power is related with the design and exploration and also to enhance the separation rate of adsorbents [3]. A review literature reveals that bioadsorbents have found favour owing to their non-toxic and biodegradable nature.

Chitosan (Fig. 1) is a well known biopolymer which is typically obtained by chemical deacetylation of chitin under alkaline conditions. Chitin being the most abundant polymer standing second only to cellulose has made the use of this bioadsorbent cost friendly and easily accessible. Chitosan is a waste by-product of the shellfish processing industries and offers the additional advantage of being inexpensive, plentiful, non-toxic, renewable and biodegradable [4]. This natural biomass represents an attractive alternative to other biomaterials because of its physico-chemical characteristics. The chemical stability, high reactivity, excellent coordination with heavy metals and reactions towards a wide range of pollutants, makes it right substance for adsorption [5]. Chitosan is shown to have properties like high hydrophilic property, non-toxicity, biocompatibility and biodegradability that make it a desirable adsorbent.

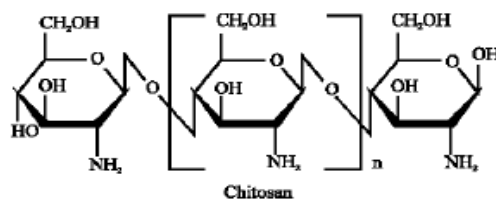


Fig. 1 Chitosan unit

Chitosan has excellent properties for the adsorption of heavy metal ions, principally due to the presence of $-NH_2$ group, in the polymer matrix of chitosan which primarily attracts metal ions in solution by ion-exchange change as well as by coordination linkage [6]. Therefore the prime chemical application lies with waste water treatment as chitosan carries a partial positive charge and binds to metal ions.

Ordinarily, 0.015 micron and sub micron-sized particles, adsorption rate and available capacity increases with increase in internal porosities. The nano-sized adsorbing substances demonstrate better performance to the traditional micro-sized supports used in separation process [7].

Chitosan-based nano-sized adsorbents, it is difficult for them to separate from the aqueous solution with the usual sedimentation or filtration methods due to their extremely small sizes. The magnetic separation has the advantage of using a large amount of wastewater and can be purified in a short period of time and in using less energy and with no contaminations [8].

Iron oxides from technological importance are i.e. $Fe(OH)_3$, $Fe(OH)_2$, $Fe_5OH_8 \cdot 4H_2O$, Fe_3O_4 , FeO , five polymorphs of $FeO(OH)$ and four of Fe_2O_3 . All these oxides include trivalent iron, low solubility and brilliant colors [9]. Fe_3O_4 is used extensively for the magnetization of chitosan nanoparticles [10]. The attractive property of magnetic nanoparticles is due to large volume of surface area, low toxicity, high recoverability and high ligand binding capacity [11].

In the present work, magnetic nanoparticles were synthesised by chemical co-precipitation modified with chitosan. Co-precipitation technique involves mixture of Fe^{2+} and Fe^{3+} ion being precipitated in the presence of a base. These particles are then coated with chitosan under constant stirring to yield magnetic chitosan nanoparticles (MCNs) [12].

The atomic absorption spectrometry (AAS) or mass spectrometry with inductively coupled plasma (ICP-MS) for detection of trace metal require complex laboratory equipment, expensive chemicals and their availability is very limited. Instead the electrochemical methods can be used (differential pulse voltammetry and/or cyclic voltammetry). These techniques are one of the best for metal detection because of their low detection limits, metal selectivity, high sensitivity, mobility and low cost [13]. Determination of heavy metal ionse is done using differential pulse anodic stripping voltammetry (DPASV) using hanging mercury drop electrode.

II. MATERIALS

A. Chemicals

Chitosan (Low Molecular Weight, LMW) was purchased from Sigma-Aldrich chemicals. monium hydroxide (NH_4OH) (AR) and salts of Ferric Chloride ($FeCl_3$) (AR) and errous sulphate ($FeSO_4 \cdot 7H_2O$) (AR) were purchased from CDH, New Delhi. Double distilled water (DDW) was used throughout the experiment. Salts of $ZnCl_2$, $Pb(NO_3)_2$, $CdCl_2 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$, all being of AR grade were purchased from CDH, New Delhi. These salts were used to prepare 5ppm stock solutions of Zn, Pb, Cd and Cu respectively. For buffer, KCl and Sodium acetate (NaAc) were also of AR grade.

III. METHOD

A. Synthesis of Magnetic Nanoparticles

Magnetite (Fe_3O_4) core had been first synthesised by chemical co-precipitation technique. 0.5 M of $FeSO_4$ solution is mixed with 1M of $FeCl_3$ with constant stirring till it forms a transparent solution. Then, NH_4OH is added slowly drop by drop to the solution along with stirring till the pH of the solution becomes 10. A dark colored precipitate is formed at the end of this duration and this precipitate is actually the Fe_3O_4 nanoparticles. The particles are separated using an external magnet and then dried in the oven. The magnetite particles are stored for further use.

B. Synthesis of Magnetic Chitosan Nanoparticles

In suspension cross-linking technique, 5% chitosan solution was prepared by dissolving 0.25g of low molecular weight (LMW) chitosan in 50 ml of 2% CH_3COOH solution. The solution is thoroughly stirred to form the chitosan solution. To this solution 2g of previously prepared Fe_3O_4 nanoparticles are added, and the resulting solution is again stirred for about 2 hrs to facilitate maximum coating of the magnetite particles with chitosan. The magnetic chitosan nanoparticles are separated and

stored for further use.

C. Characterization of Magnetic Chitosan Nanoparticles

The surface homogeneity and morphologies was observed by scanning electron microscopy (SEM). Fourier transform infrared Spectra (FTIR) of MCNs was recorded on a Perkin-Elmer FTIR spectrometer. Phase identification and structural analysis of the bare MCNs were studied by X-Ray Diffraction (XRD) in the 2θ range from 2° to 100° were the structural and phase identification. Thermal Gravimetric Analysis (TGA) was also performed to estimate the homogeneity and thermal stability of MCNs.

IV. ANALYTICAL EXPERIMENT

A. Voltammetric Measurement

The voltammetric measurements with Metrohm, 797 VA Computrace (Switzerland) and three-electrode system, including hanging mercury dropping electrode (HMDE), a platinum plate as the auxiliary electrode, and KCl (3.01M) as the reference electrode was to find the metal ion concentration. DPASV accounts for measuring the oxidation current of metal ions deposited in on HMDE, as a function of added standard metal-ions solution. Deposition period afterwards, potential on Hg- electrode is ramped positive, and the current from amalgamated metal is measured [14].

B. Anodic Stripping Voltammetry

10 ml ultra pure water and 1 ml of acetate buffer of pH 4.6 (50 ml of 1.0M HCl +20.0 ml of 1.0 M sodium acetate) was taken in polarographic vessel and then the measurement was carried under the given parameters (Table 1), voltammograms of the standard solution of Zn, Cd, Pb, Cu and sample solution were recorded (Fig. 2).

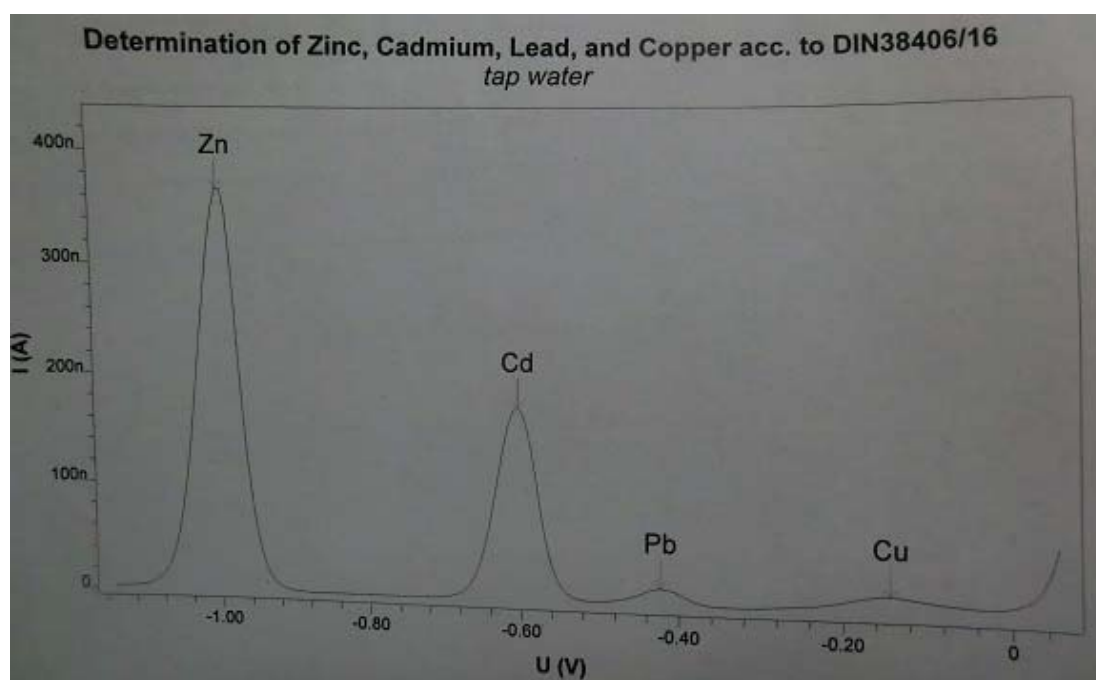


Fig. 2 Voltammograms of Zn, Cd, Pb and Cu

V. RESULT AND DISCUSSION: CHARACTERIZATION

A. X-Ray Diffraction

Structural analysis of the bare MNPs was done by XRD with Cr-K radiation (2.2897 Å) in the 2θ range from 2° to 100° . The XRD of Fe_3O_4 particles and magnetic Fe_3O_4 -CS particles show six characteristic peaks of Fe_3O_4 confirming that the resultant nanoparticles consists of pure Fe_3O_4 with a spinel structure. The results confirm that the coating process did not result in the phase change of Fe_3O_4 . The peaks corresponding to (hkl) values of (220), (311), (400), (422), (511) and (440) located at 30.22, 35.56, 43.22, 53.70, 57.12 and 62.72 degrees were characteristic of Fe_3O_4 with a face-centred-cubic structure. The peaks of Fe_3O_4 in MCNs indicating both chitosan and Fe_3O_4 particles are there as shown in Fig. 3.

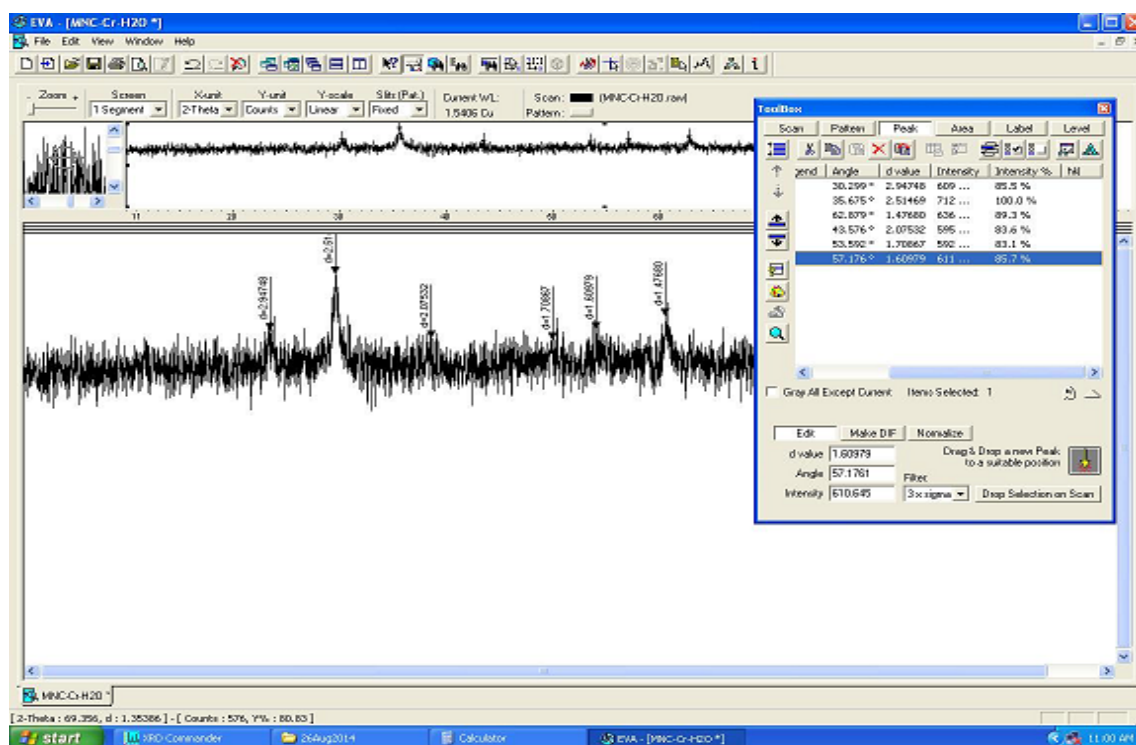


Fig. 3 XRD Pattern of magnetic chitosan nanoparticles (MCNs)

B. Fourier Transform Infrared Spectra (FTIR)

An infra red studies of magnetic chitosan nanocomposite show the following characteristic peak at around: 3145cm^{-1} for O-H bond stretching N-H bond stretching, 2363 cm^{-1} for C-H stretching, 1127 cm^{-1} for C-O stretching, 1630 cm^{-1} for C=O of -NH=C=O bond stretching, 600cm^{-1} for Fe-O group due to pure Fe_3O_4 . The characteristic peaks of functional groups present in MCNs are displayed in Fig. 4.

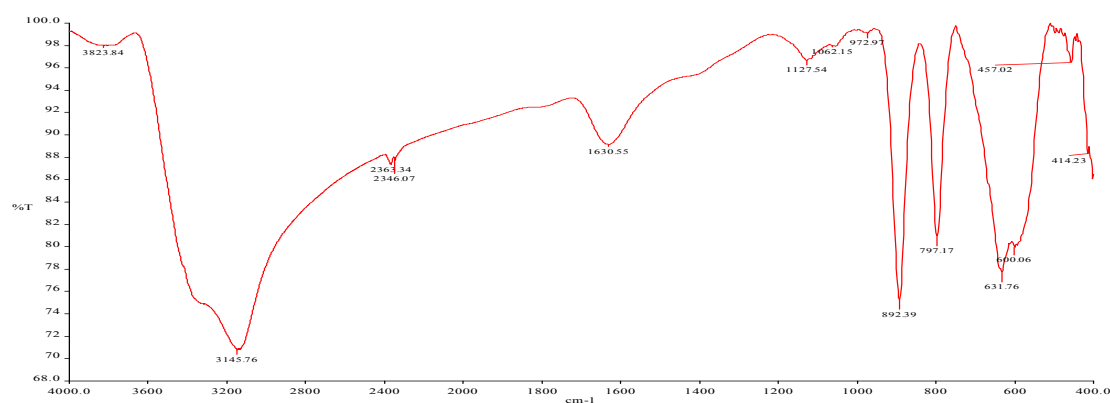
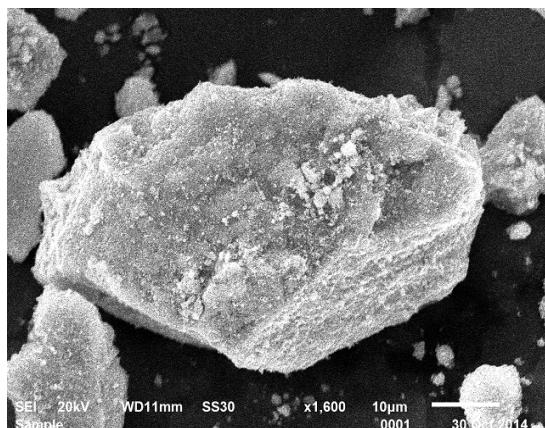
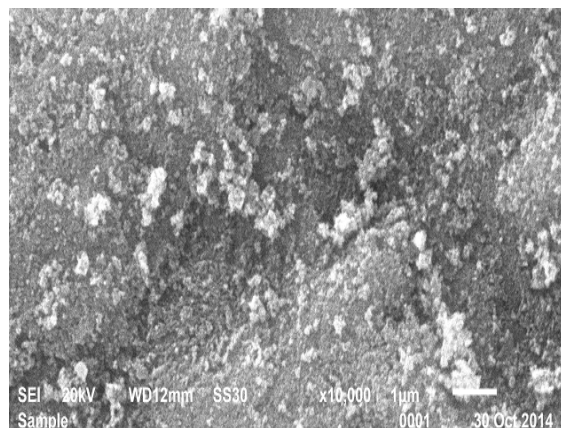


Fig. 4 FTIR peaks of magnetic chitosan nanoparticles

C. Scanning Electron Microscopy

The surface homogeneity and morphologies of Fe_3O_4 and Chitosan coated Fe_3O_4 particles have been investigated using the SEM. SEM image of MCN indicate that the composite is structurally layered on which some tiny particles can be seen which are attributed to the attached Fe_3O_4 nanoparticles. The shape of MCN is irregular, and spherical Fe_3O_4 microspheres are anchored on the surface of Mg-Ch-Fe particles with a high density. The scanning electron microscopic analysis MCNs are shown in the magnification of 1.6k (Fig. 5I) and 10k (Fig. 5II).

Fig. 5(I) SEM Image of MCN($\times 1,600$)Fig 5(II) SEM Image of MCN($\times 10,000$)

D. Thermal Studies (TGA)

TGA provides a quantitative evidence of the coating of CS on NPs. The MNCs are heated to 600 under flowing N_2 and changes in the mass loss of organic material are recorded. This is an extremely valuable technique for surface characterization of NPs. For Fe_3O_4 nanoparticles coated with chitosan, after a gradual loss of water molecules in the polymer matrix, a great weight loss started at $200^\circ C$ at which the decomposition of chitosan occurred. When the chitosan was decomposed, the residual substance left was chitosan magnetic nanoparticles. The TGA curve obtained is shown in Fig. 6.

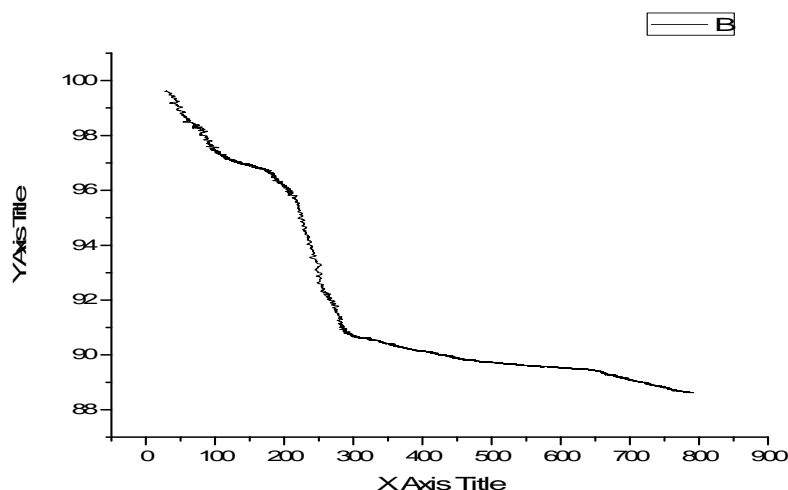


Fig. 6 TGA Graph of magnetic chitosan nanoparticles

E. Adsorption Study

Initially metal ion solutions were prepared and analysed in the instrument to mark the initial concentration of the specific metal ion. Then Magnetic Chitosan nanoparticles were added to the solution and periodic readings were taken after 10-10 mins for a total time of around 50 mins to study the effect on the concentration of metal ion (Table 1).

TABLE 1 CONCENTRATION OF METAL IONS AT DIFFERENT TIME INTERVALS

Time (sec $\times 10^{-2}$)	Concentration of Metal ions in ppm			
	Zn	Cd	Pb	Cu
Initial	0.453	0.002	0.788	0.122
6.0	0.123	0.001	0.027	0.053
12	0.119	0.001	0.011	0.043
18	0.104	0.001	0.008	0.042
24	0.099	0.0009	0.001	0.033
30	0.086	0.0007	0.0002	0.013

VI. CONCLUSION

According to the spectroscopic study using the above mention techniques, we conclude that using the chemical co-precipitation process we were successful in synthesizing magnetic chitosan nanoparticles (MCNs), which show the desired properties.

The adsorption study using 797 VA Computace also confirms that the prepared MCNs also have the capacity to absorb toxic metal ions namely zinc (Zn^{+2}), cadmium(Cd^{+2}), lead(Pb^{+2}) and copper(Cu^{+2}) etc. After the experiment it was observed that with the course of time, concentration of above mentioned metal ions keeps decreasing due to their adsorption by magnetic chitosan nanoparticles which are put in the solution. Therefore it is evident from the concentration result that the magnetic chitosan nanoparticles synthesised in the above mention process are capable of removing toxic metal ions aqueous medium and can therefore be applied in the field of water purification for the elimination of toxicity from industrial wastewater.

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Dr. PS Jassal did graduation and post graduation from University of Rajasthan, Jaipur in 1977 and 1979. He completed the MPhil and PhD in Chemistry from University of Delhi, Delhi, India in 1983 and 1986. Centre of Advanced Study, Chemistry Department of Delhi University awarded me research fellowship (JRF) for PhD work. Dr Jassal was also given the meritorious award in MSc (chemistry) for getting a position. Presently I am teaching as Associate Professor in Chemistry Department of SGTB Khalsa College, University of Delhi, Delhi, India for the last 28 years.



Ms. Neema Chand Graduated from, Ewing Christian College, Allahabad. For Masters in Chemistry, she joined St John's College, Agra in 2009 and became the member of the Chemical society. Bagged the Eric Ford Award during her M.Sc (2011) for the Best Performance in the class. She has also undergone a training in advanced Analytical Instrumentation.

At present, Neema Chand is a research student pursuing her PhD degree in a DRDO sponsored project, in the Chemistry Department, SGTB Khalsa College, University of Delhi, Delhi, India.



Ms. Sonal gupta did M.Sc. from Agra University. She is a project research fellow pursuing her PhD degree in a DRDO sponsored project, in the Chemistry Department, SGTB Khalsa College, University of Delhi, Delhi. She has also attended the International Conference, "20th I.S.C.B International Conference on Chemistry and Medicinal Plants in Transnational Medicine for Health Care" in Department of Chemistry, University of Delhi. She has also participated in Antardhwani Program, University of Delhi, Delhi, India.



Dr. Singh graduated with honours degree in 1976 from Meerut University, India. Post graduation in Chemistry with Ist class in 1979. He has been awarded Ph.D in chemistry in 1986 from University of Delhi. In 1992 he joined DRDO as Scientist and worked on metal alkyls. As former joint director in ER&IPR DRDO HQ he has interacted with most of academic and R&D Institutions in India to promote the S&T programmes relevant to DRDO.