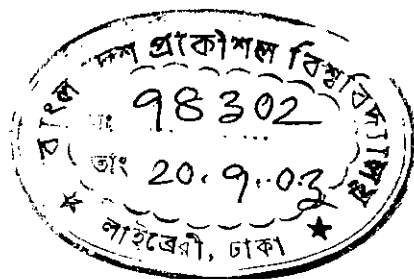
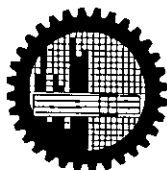


**POLYMERIC ADSORBENT FOR THE REMOVAL OF
ORGANIC AND INORGANIC POLLUTANTS FROM
AQUEOUS SOLUTION**

BY

SYEDA REZINA JESMEEN

**SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENT FOR THE DEGREE OF
M.PHIL IN CHEMISTRY**



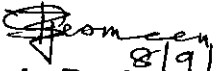
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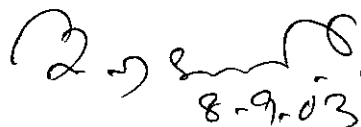
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CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any University or institution.



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Dedicated

TO

My Beloved Parents

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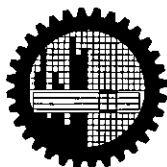
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Certification of Thesis

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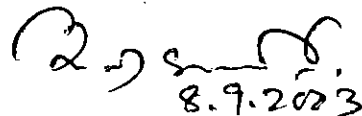
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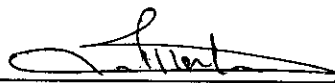
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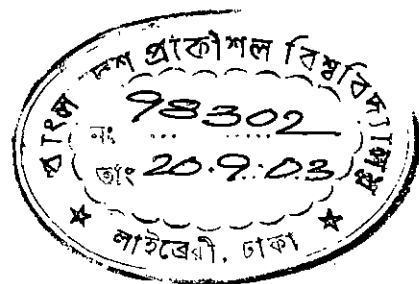
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Abstract



Apart from the use of conducting polyaniline as electronic materials, in the present work, neutral and charged polyaniline are utilized as the effective adsorbents for their possible application in removing organic dyestuff, such as methylene blue, procion red and inorganic species, *viz.*, nickel chloride from their aqueous solutions.

Aniline was polymerized chemically from an acidic solution using an oxidant, ammonium peroxydisulfate. Polyaniline thus obtained was treated with distilled water (pH = 6.86), aqueous hydrochloric acid (pH = 1.71) and aqueous ammonium hydroxide (pH = 10.01) solutions in order to make the polyaniline matrix neutral and charged, respectively.

Polyaniline matrices thus treated were characterized by a wide range of experimental techniques including solid-state d.c. conductance, UV-Vis and IR spectroscopy, X-ray diffraction and SEM measurements. The treated polyaniline matrices were found to be correlated with the idealized forms of polyaniline protonated states proposed by A. G. MacDiarmid [ref. 34 in introduction part]. The acid treated matrix seems to be positively

charged while the other two matrices seem to be either neutral or negatively charged.

UV-Vis and IR spectroscopy studies yielded useful qualitative information on the treated polymer matrices. The strong absorption maxima observed in the ultraviolet region may be attributed to the interband transition; the other intense band in the visible region probably results from the transition between the mid-gap states. From the IR spectra, band characteristics confirmed the differences between the treated polyaniline matrices. The electrical conductivity measurements also provide strong evidence regarding the difference of the electrical properties of the treated polymer. The acid treated polymer shows a conductivity of $\sim 1 \text{ S cm}^{-1}$ while the distilled water and base treated samples show conductivity of 10^{-6} and $10^{-7} \text{ S cm}^{-1}$, respectively.

Surface morphology obtained by SEM provides very interesting results. The acid treated polyaniline seems to consist of agglomerates and stacked over the surface to make a big deposit. On the other hand, distilled water and base treated matrices show granular morphologies. The grain aggregates to a short-pillar like body in the morphology of distilled water treated

polyaniline while in the base treated one, the grains are collected to a body like a broken brick-shaped showing definite size and sharp edges.

The polyaniline matrices thus treated were used as adsorbent and found to be adsorbed the dyestuffs, methylene blue and procion red from their aqueous solutions at various pH. The removal of dyes was monitored spectroscopically by measuring the change of absorbance at their corresponding λ_{\max} . The molar absorption co-efficients of methylene blue and procion red were found to be $59600 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 661 nm and $8518 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 535 nm, respectively. The cationic dye, methylene blue shows a significant adsorption on the base treated polyaniline (negatively charged), while procion red, a negative dye, found to be adsorbed preferentially on the positively charged acid treated polymer. The adsorption isotherms for both methylene blue and procion red seem to follow Langmuir isotherm. However, the inorganic salt, nickel chloride adsorption seems to be very low both on neutral and charged polyaniline matrices suggesting a different mechanism for the adsorption on the polymeric matrices employed.

Chapter 1

INTRODUCTION

1.1 Organic Conductive Polymers

In general, polymers are insulating materials having conductivities ranging from 10^{-10} S cm⁻¹ for poly vinyl chloride to 10^{-18} S cm⁻¹ for poly tetrafluoroethylene (teflon), which are many orders of magnitude below compare to the conductivities associated with metals Fig. 1. As a result, polymers have found widespread acceptance in a myriad of insulating and structural applications throughout the electronic industry. Nevertheless, the discovery in 1973 that poly sulfur nitride (SN)_x was intrinsically conducting provided a proof that polymers could be conducting and thus greatly stimulated the search for other conducting polymer [1]. During the last two decades, a new class of organic polymers has been devised with the remarkable ability to conduct electrical current. These class of materials are called conducting polymers [2].

One of the earliest approaches to make the polymers conductive is to prepare a composite of polymers and conductive filler, such as, metal powder, graphite powder, flake or wire etc. Conductive fillers remain embedded more or less evenly dispersed in the polymer matrix and conduct electric current. But these composites can not be regarded as conducting polymers because the polymers presents in such composites are non-conducting [3-6].

In 1964, W. A. Little [7] synthesized a superconductor at room temperature with polymeric backbone and large polarizable side groups which led the discovery of new organic compounds with high electrical conductivity.

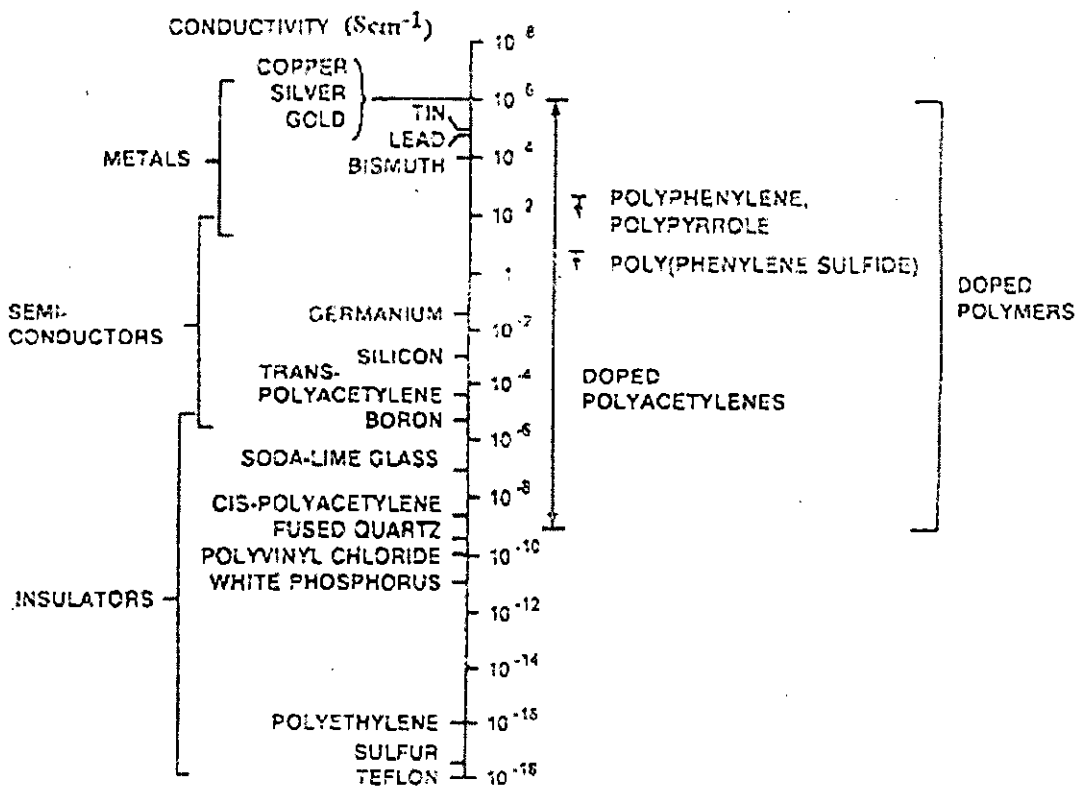


Fig. 1: Conductivity of various metallic, semiconductor and insulating materials.

In the early 1980s, excitement ran high when several prototype devices based on conductive polymers, such as rechargeable batteries and current rectifying p - n junction diodes [8] were announced. Among the many polymers known to be conductive, polyacetylene (PAT), polyaniline (PANI) polypyrrole (PP) and polythiophene (PT), have been studied most intensively [9-15]. However, the conductive polymer that actually launched this new field of research was PAT.

A simple macromolecule with remarkable electrical properties, PAT consists of weakly couple chains of carbon-hydrogen units arranged in a one dimensional lattice. Though PAT was already known as a powder, in 1974 it was prepared as a silvery looking film, using Ziegler-Natta type polymerization catalyst [16]. Oxidative [17] and reductive [18] doping of PAT result in p - and n -type conductance, respectively. The electrical conductivity of PAT can be varied in a controller manner over 12 orders of magnitude through chemical or electrochemical doping and prototype rechargeable batteries have been constructed using PAT as both the cathode and anode [19].

Research has been expanded into the studies of heteroatomic conductive polymers because of their better chemical stability and the interest in the polaron and bipolaron conduction mechanism [20, 21]. Among the heteroatomic polymers PP, PT and PANI have been studies extensively. In 1968, Dall'Olio *et al.* [22] published the first report of analogous electrosynthesis in other system. They observed the formation of brittle, film like pyrrole black on a Platinum (Pt) electrode during the oxidation of pyrrole in dilute sulfuric acid. Conductivity measurements

carried out on the isolated solid state materials gave a value of 8 S cm^{-1} . In addition, a strong ESR signal was evidenced for a high number of unpaired spin. Earlier, in 1961, H. Lund [23] had reported in a virtually unobtainable publication that PP can be produced by electrochemical polymerization.

In 1979, Diaz *et al.* [24] prepared for the first time a flexible, stable PP film with high conductivity (100 S cm^{-1}). The substance was polymerized on a Pt-electrode by anodic oxidation in acetonitrile. The known chemical methods of synthesis [25-27] usually produced low conductivity powders for the monomers. In contrast, electropolymerization in organic solvents formed smooth and manageable films of good conductivity. Thus, this technique soon gained general curiosity, stimulating further electropolymerization experiments with other monomers. PP formed at the electrode surface could be peeled off as a flexible, relatively dense and shiny blue black film. This polymer is characterized not only by its high conductivity but also by its high stability. The potential use of PP film in rechargeable batteries, *p-n* junction diode, photocorrosion protection *etc.* makes it an attractive electronic material. PT and its derivatives can be chemically or electrochemical synthesized. By chemical or electrochemical doping (oxidation or reduction of the polymer), the electrical conductivity of these polymer films can be varied over several orders of magnitude with properties ranging from insulator to semiconductor. PT and its derivatives are considered as the first class of polymers which are chemically and electrochemically stable in air and in moisture in both doped and undoped states [15].

PANI whose structure was first described by English and German chemists at the turn of the century, consists of up to 1000 or more repeating units. It exists in several oxidation states with electrical conductivities progressively from 10^{-11} S cm⁻¹ to more than 10 S cm⁻¹. Different compositions of PANI have different colors and electrical properties. However, only one form, called the “emeraldine salt”, is electrically conducting. Before 1980, little research had been done on PANI. However, it was found in 1980's that the conductivity of PANI increases by several orders of magnitude as the pH of the acid it is doped declines. Its transformation to electronic conducting state by doping, have raised great interest because of their many possible applications.

As a result, during the 1980s, PANI was subjected to intense structural, physical, and electrical characterization, using modern experimental techniques. A brief survey, out of numerous features and studies made on PANI is presented in following section.

1.2 Polyaniline: State of Its Scientific Background.

A. Structural features

Organic conducting polymer, PANI, is being studied more and more, and up to the recent years has been the centre of considerable scientific interest. However, PANI is not really a new material and its existence has been known for the past 150 years or over, since it had already been made by Runge in 1834.

PANI has been described in many papers [28] usually as ill-defined forms such as “aniline black” emeraldine, nigraniline, *etc.* synthesized by the chemical or electrochemical oxidation of aniline. Figure 2 shows the

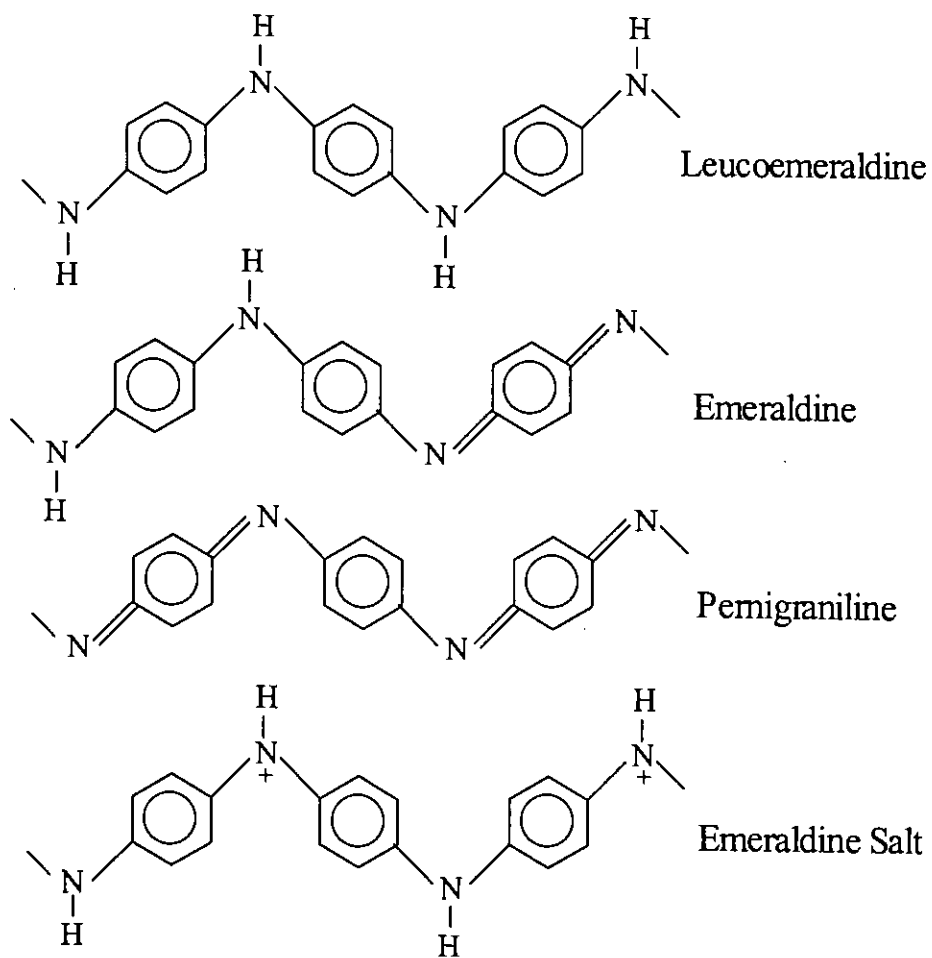
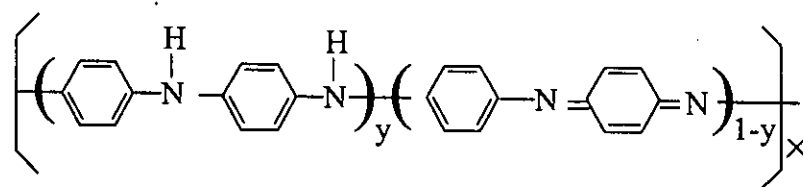
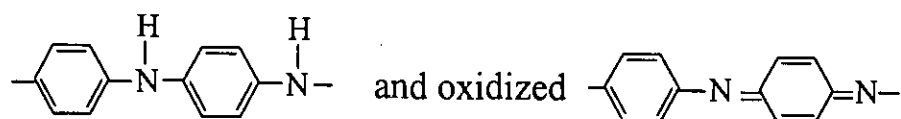


Fig. 2: Representation of idealized oxidation states of PANI.

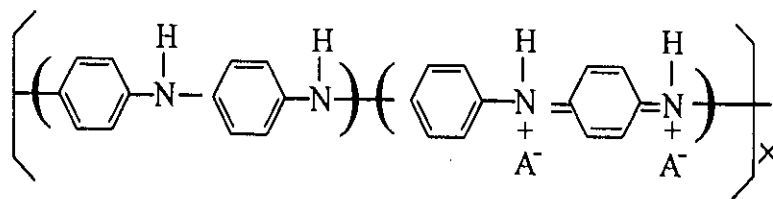
idealized oxidation state of PANI: leucoemeraldine, emeraldine, pernigraniline and emeraldine salt. Different structures result in different electrical behaviours of the material. Emeraldine salt is a partially oxidized compound, protonated, with electrical conducting characteristics. Leucoemeraldine is a fully reduced compound with electrical insulating characteristics. There are no double bonds between the aromatic rings and the N-H groups. Emeraldine base is an insulating compound, partially oxidized with few N-H groups in the main chain. Emeraldine changes from insulator to conductor when it is protonated with proton donor acids, such as, hydrochloric acid. This change is one of the most interesting properties of PANI. The structure of emeraldine PANI can be changed to emeraldine salt by removing an electron from the N-H group. Pernigraniline is a fully oxidized compound without conducting characteristics. There are no N-H groups in the structure. The level of protonation in the structure causes dramatic changes in the conductivity. The base form of the polymer in the emeraldine oxidation state ($y = 0.5$)



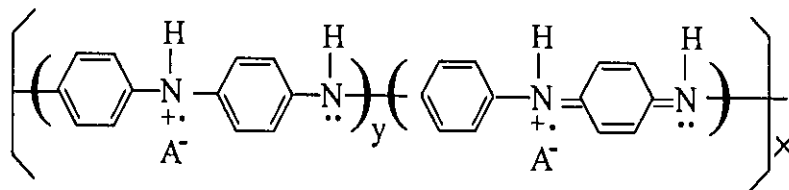
which contains equal number of alternating reduced,



repeat units can be protonated by dilute aqueous acid to produce the corresponding salt (A=anion)



which is believed to exist as polysemiquinone radical cation [29-31].



The polymer exhibits conductivities of $\sim 1\text{-}5 \text{ S cm}^{-1}$ when approximately half of its nitrogen atoms are protonated as shown above.

B. *Methods of preparation*

PANI is generally prepared by direct oxidation of aniline using an appropriate chemical oxidant or by electrochemical oxidation on different electrode materials.

Various chemical oxidizing agents have been used by different authors: potassium bichromate [32, 33], ammonium persulfate or peroxydisulfate [34, 35], hydrogen peroxide, ceric nitrate and ceric sulfate [36, 37]. The reaction is mainly carried out in an acid medium, in particular sulfuric acid, at a pH between 0 and 2 [32, 33]. However, MacDiarmid *et al.* [34, 35] used hydrochloric acid at pH 1. Genies *et al.* [38] used a eutectic mixture of hydrofluoric acid and ammonia, the general formula of which is $\text{NH}_4\text{F} : 2.3 \text{ HF}$, for which the pH is probably less than 0.

When aniline is mixed with the chemical oxidant in a reaction vessel and left for a certain period of time (the duration of which depends on the temperature and the concentration of active species), the solution gradually

becomes colored and a black precipitate appears [39]. The coloration of the solvent is possibly due to the formation of soluble oligomers.

Anodic oxidation of aniline on an inert metallic electrode is the most current method for the electrochemical synthesis of PANI. This method offers the possibility of coupling with physical spectroscopic technique such as visible, IR, Raman, ellipsometry and conductimetry, for *in situ* characterization.

The anodic oxidation of aniline is generally effected on an inert electrode material which is usually Pt [40, 41]. However, several studies have been carried out with other electrode materials: iron [42], copper [43], zinc [44], chrome-gold [45], lead [44], palladium [46] and different types of carbon vitreous, pyrolic or graphite [47] or on semiconductor [48, 49]. When the polymerization is carried out at constant current, a maximum current density of 10 mA cm^{-2} is rarely exceeded.

C. Morphology and structure

The adherence and the homogeneity of a PANI film on an electrode varies according to the method of synthesis employed. Diaz [50] has observed weak adherence for a polymer prepared by electrochemical oxidation at constant potential, whereas good adherence results when potential cycling is employed. Kitani *et al.* [51] have reported that, using the same method, a thin homogenous film is initially deposited on the electrode, followed by the formation of an amorphous powder which eventually becomes detached from the electrode surface. Electrochemical investigations on the polymer growth by Thyssen *et al.* [52] yielded evidence for cross-linking reactions leading to the formation of hemispheres.

There is, therefore, a myriad of possible chemical structures for the polymeric backbone of PANI. Elucidation of the precise molecular arrangement is complicated by the fact that these structures are affected by both electronic excitation and reduction and by concomitant protonation and deprotonation of the nitrogen atoms in the polymer.

D. Optical properties

A wide range of colors from pale yellow to blue for the PANI is observed. From the optical data obtained for PANI, it is possible to assign three absorption zones which are dependent on the oxidation state of the polymer. In the reduced state, PANI is an insulating material, the energy band structure of which is comparable to that of an intrinsic semiconductor, with the resulting absorption being associated with the transition between the valence band and the conduction band. However, when the potential is increased, the polymer oxidizes and intermediate mid-gap states appear in the forbidden band (radical cations and then dications) and thus results absorption in the longer wave length. Elucidation of band model of a polymer can be made based on optical data.

E. Conductivity

From conductivity measurements, Travers *et al.* [33] have observed that the PANI exhibits a metal-to-insulator transition which is a function of the pH. The conductivity of the polymer is $5 \text{ ohm}^{-1} \text{ cm}^{-1}$ when the polymer is previously equilibrated at pH 6. MacDiarmid *et al.* [34, 35] has also described a variation in the conductivity of both chemically and electrochemically prepared polymers with the pH of the aqueous solution to which the polymer was exposed before drying. The polymer exhibits a

conductivity of $1 \text{ ohm}^{-1} \text{ cm}^{-1}$ when it is equilibrated at a pH between -1 and $+1$, and $10 \text{ ohm}^{-1} \text{ cm}^{-1}$ when it is equilibrated at a pH between 5 and 6 . Elsewhere, they indicates that the conductivity of the polymer is a function of the level of doping, with a value of $1 \text{ ohm}^{-1} \text{ cm}^{-1}$ for 15% doping, and varying from 10^{-10} to $10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ for 0% to 10% doping. Measurements carried out by Brahma [53] revealed that PANI doped with iodine exhibits a conductivity four orders of magnitude greater than the undoped polymer.

F. Solubility

It is generally accepted that PANI is insoluble in most common organic and aqueous solvents, irrespective of the method of synthesis. Nevertheless, Mohilner *et al.* [40] have shown that the polymer is easily dissolved in pyridine and DMF, strongly tinting the solutions blue.

The synthesis of soluble PANI is of great interest since the formation of a soluble material is essential in order to post-synthesis processing. There are two possible methods for preparing soluble polymers: (i) formation of the polymer salt using an anionic dopant which favors dissolution, or (ii) prefunctionalization of the starting monomer with a suitable group prior to polymerization. Chemical synthesis of soluble PANI by the former method has been successfully accomplished by Li *et al.* [54] and involves proton acid dopants of large molecular size such as toluene-*p*-sulfonic acid, sulfanilic acid or polymeric electrolyte-polystyrene sulfonic acid.

G. Applications

PANI can be used as material for modified electrodes [47, 50], as a corrosion inhibitors for semiconductors in photoelectrochemical assemblies [58], in microelectronics [55] and as electrochromic material [56]. The

application which has inspired most interest is in the area of electrochemical batteries. The possible use of PANI as active anodic material is in rechargeable batteries [57].

More recent systematic studies have been undertaken by numerous groups [34, 35, 58] on the possible use of PANI as an active electrode material. These investigations deal with the behaviour of PANI in aqueous and organic media as a function of the mode of synthesis.

1.3 Theoretical Aspects of Experimental Techniques

A. *d.c. pellet conductance*

The direct current (d.c.) conductivity of a polymeric material depends on dopant level, protonation level, morphology and moisture content of the sample. Electrical conductance of the polymer sample may be measured by two-and four-point probe techniques. The electrical conductivity is measured based on Ohm's law [59].

$$E/I=R \tag{1}$$

where I is the current in amperes, E is the potential difference in volts and R is the resistance in ohms. The reciprocal of resistance is termed as the conductance, that expressed in siemens (S) which is reciprocal of ohm (ohm^{-1}). The resistance of a sample of length L , and cross-sectional area A , is given by

$$R = \rho L/A \tag{2}$$

Where ρ is a characteristic property of the material termed as resistivity. If L and A are measured, in cm and cm^2 , respectively, then ρ refers to cm^3 of the material, and

$$\rho = RA/L \tag{3}$$

The reciprocal of resistivity is the conductivity (specific conductance),

$$K = 1/\rho \quad \text{or} \quad K = L/RA \quad (4)$$

which in SI units is the conductance of one cm^3 of the substance and has the units in $\text{ohm}^{-1}\text{cm}^{-1}$ or S cm^{-1} .

In this experiment, the pellets of solid samples are made by pressing with a pressure of 10^4 pounds per square inch. Two electrodes of microvolt are pressed tightly on the pellet prior to measurement. The resistivity could measure directly using the microvolt employed.

B. UV-Vis spectral feature

Ultraviolet – visible (UV-Vis) spectra is a useful tool to measure the impurity level, band gap energy, *etc.* of a polymeric material. The electronic spectra of the studied samples were recorded on a UV-Vis spectrophotometer in the wave length range 200 – 800 nm. Electromagnetic radiation of suitable frequency can be passed through a sample so that photons are absorbed by the samples and changes in the electronic energies of the molecules can be brought about. So it is possible to effect the changes in a particular type of molecular energy using appropriate frequency of the incident radiation. When a beam of photons passes through a system of absorbing species, then we can write

$$-\frac{dI}{dx} = \alpha I \quad (5)$$

where, I = intensity of photon beam

dI = reduction of intensity

dx = rate of photon absorption with distance (x) traversed

α = absorption co-efficient of the material

Now if I_o is the initial intensity at thickness $l = 0$ and I is the transmitted radiation at $x = l$, then by integration, we can write

$$\ln \frac{I_o}{I} = \alpha l \quad (6)$$

C. IR spectroscopy

Emission or absorption spectra arise when molecules undergo transition between quantum states corresponding to two different internal energies. The energy difference ΔE between the states is related to the frequency of the radiation emitted or absorbed by the quantum relation

$$\Delta E = h\nu \quad (7)$$

where h is Planck's constant and ν is frequency. Infrared (IR) frequency have the wave length from 1 μm to 50 μm are associated with molecular vibration and vibration-rotation spectra. Detection of chemical groups and bonding are done by the typical spectra.

In polymer, the IR absorption spectrum is often surprisingly simple, if one considers the numbers of atoms involved. This simplicity results first from the fact that many of the normal vibrations have almost the same frequency and, therefore, appear in the spectrum as one absorption band and second, from the strict selection rules that prevent many of the vibrations from causing absorptions. In our experiment, we try to observe the change in frequency of different PANI samples. IR spectra of all the compounds were recorded on IR spectrophotometer in the region of 4000-400 cm^{-1} . Samples were introduced as KBr pellets in the IR instrument.

D. X-ray diffraction

The X-ray diffraction (XRD) provides substantial information on the crystallinity of a solid. This method is applied for the investigation of orderly arrangements of atoms or molecules through the interaction of electromagnetic radiation to give interference effects with structures comparable in size to the wave length of the radiation. A study on the crystal structure is performed based on methods using single crystals after the discovery of XRD [60]. Now a days, XRD is used not only for the determination to crystal structure but also for chemical analysis, such as chain conformations and packing for polymers, for stress measurements and for the measurements of phase equilibriums and the measurement of particle size, for the determination of the orientation of the crystal and the ensemble of orientations in a polycrystalline material. X-ray is the electromagnetic radiation whose wavelength is in the neighborhood of 1 \AA . The wavelength of an x-ray is thus of the same order of magnitude as the lattice constant of crystals, and, it is this, which makes x-ray so useful in analysis of crystals whenever x-ray are incident on a crystal surface they are reflected from it. The reflection abides by the celebrated Bragg's law as given below:

$$2d \sin\theta = n\lambda \quad (8)$$

where d is the distance between crystal planes, θ is the incident angle, λ is the wave length of x-ray and n is the positives integer. The diffracted x-ray may be detected by their action on photographic films or plates or by means of a radiation counter or electronic equipment feeding data to a computer.

The main purpose of using XRD technique is the analysis of PANI samples in order to study the change in crystallinity of the PANI upon post-synthesis treatment.

E. SEM technique

The scanning electron microscope (SEM) uses a finely focused beam of electrons to scan over the area of interest. The beam-specimen interaction is a complex phenomenon. The electrons actually penetrate into the sample surface, ionizing the sample and cause the release of electrons from the sample. These electrons are detected and amplified into a SEM image that consists of Back Scattered Electrons and Secondary Electrons. Since the electron beam has a specific energy and the sample a specific atomic structure, different image will be collected from different samples, even if they have the same geometric appearance.

The specimen stage allows movement of the specimen along 5 axis as indicated in Fig.3. The basic stage is controlled manually by micrometers and screw-type adjusters on the stage door. The motorized stage has motors driving the X, Y, Z and rotation controls, all with manual override.

The stage can be tilted over 90° . The tilt axis always intersects the electron optical axis of the column at the same height (10 mm). When the specimen positioned at this height, the specimen can be tilted in the eucentric plane. This means that during tilt, almost no image displacement occurs. The tilting mechanism can be locked for more stability at high magnification.

F. Adsorption characteristics

Adsorption is a surface phenomenon. It may be defined as a process in which the concentration of a chemical species is greater on the surface than

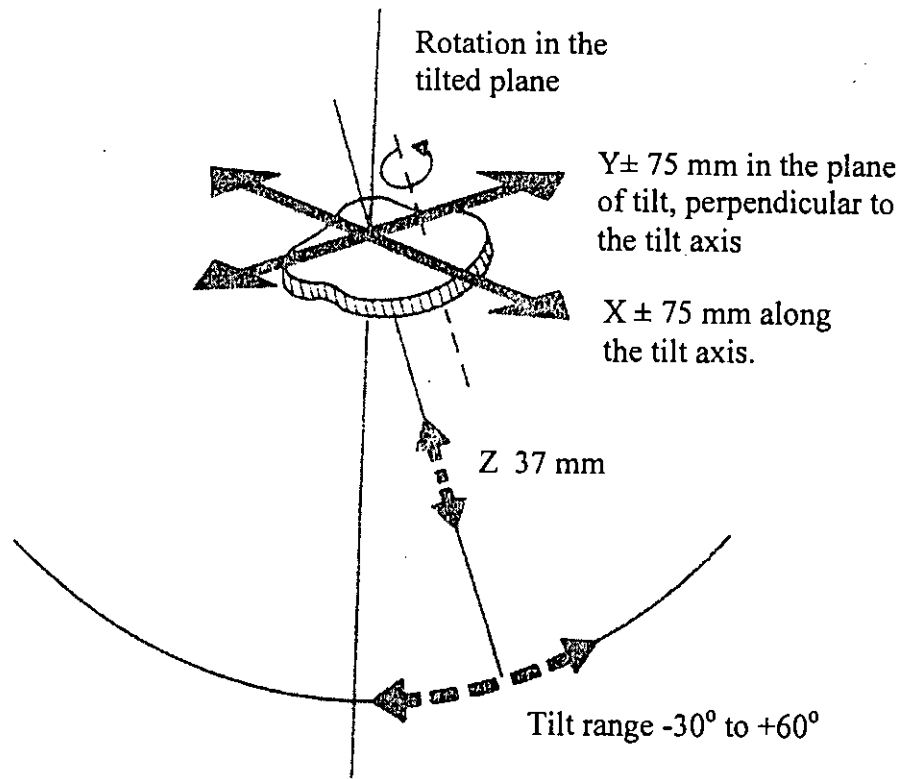


Fig. 3a: Illustration of specimen stage movement in SEM arrangements.

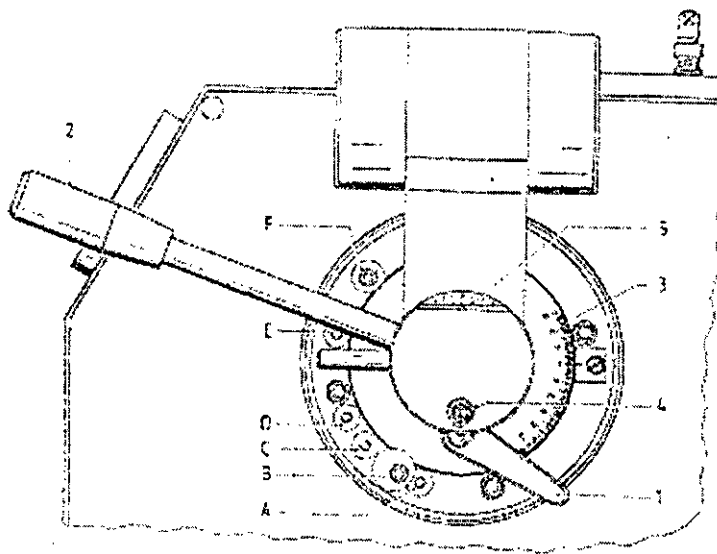


Fig. 3b: Mechanical controls and tilt stops on the stage door of SEM.

in the bulk resulting from inelastic collision suffered by molecules on the surface. The species that is adsorbed is called adsorbate and the material of the surface on which adsorption takes place is called adsorbent. Adsorption strictly refers to accumulation of adsorbates on the surface only due to residual field of force.

The adsorption surface is generally a solid or liquid. Surface of solid or liquids have certain properties and characteristic that makes them different from the bulk of matter. Although there is no chemical distinction between the molecules or atoms on the surface and the molecules or atoms in the bulk, energy considerations lead to quite dissimilar properties.

When two immiscible and chemically non reactive phases are brought into contact with each other, adsorption is a common observation which means that the concentration of one phase is greater at the interface than the bulk. This occurs due to unsaturation of the surface atoms. Most studies of adsorption from solution have been concerned with equilibrium conditions and predominantly with the adsorption isotherm. Generally two types of adsorption have been distinguished: (a) Physical adsorption (Physisorption) and (b) Chemical adsorption (Chemisorption). Physical adsorption results purely from physical forces like van der Waals forces and chemical adsorption is due to formation of chemical bonds.

a) Adsorption isotherms: There are three adsorption isotherms are known which are used most frequently:

i) Langmuir adsorption isotherm: Langmuir derived a relation between gas pressure and amount of gas adsorbed at a constant temperature. The Langmuir equation can be written as

$$X = \frac{X_m bp}{(1 + bp)} \quad (9)$$

$$\text{or, } \frac{1}{X} = \frac{1}{X_m bp} + \frac{1}{X_m} \quad (10)$$

where X = amount adsorbed at a definite concentration, $X_m = k_1 / k_2$; k_1 and k_2 are the rate constant for adsorption and desorption, respectively.

ii) Freundlich adsorption isotherm: The variation of adsorption with concentration of the substance in solution is usually represented by Freundlich isotherm as follows:

$$y = kC^{\frac{1}{n}} \quad (11)$$

$$\text{Or, } \log y = \log k + \frac{1}{n} \log C \quad (12)$$

Where, y = mass of substance per unit mass of adsorbent, C = equilibrium concentration of solid in solution, k and n are the empirical constants.

iii) BET adsorption isotherm: The theory of Brunauer, Emmett and Teller (BET) is an extension of the Langmuir treatment to allow for multilayer adsorption on non-porous solid surface. The BET equation is usually written as:

$$\frac{P}{X(P_o - P)} = \frac{1}{X_m C} + \frac{C - 1}{X_m C} \cdot \frac{P}{P_o} \quad (13)$$

where, P_o = saturation vapor pressure, X_m = the monolayer capacity and $C = \exp [(\Delta H_L - \Delta H_1) / RT]$.

b) Adsorption from solution: Adsorption from solution is much simpler than that of gas adsorption. A known mass of adsorbent is kept in touch with a

known volume of solution at a given temperature until there is no further change in the concentration of the supernatant solution. This concentration can be determined by a variety of methods involving chemical or radiochemical analysis such as colorimetry, refraction index, *etc.* The experimental data are usually expressed in terms of an apparent absorption isotherm in which the amount of solute adsorbed at a given temperature per unit mass of adsorbents calculated from the decreases of solution concentration.

c) Adsorption of dyes: By far, the most widely method of determining the amount of dye adsorbed by a substrate is spectroscopy in the visible region. The following types of forces either singly or combined are attribute for the adsorption affinity of dyes for solid adsorbents: ionic and ion-dipole, hydrogen bond, van der Waals, hydrophobic and covalent bond. Because of the intense color of dyes, it is very easy to monitor the adsorption by observing its color change at various intervals of adsorption process.

d) Adsorption of inorganic salt: The strongly dissociated salts, *viz.*, sodium chloride or potassium nitrate are essentially not at all absorbed by the activate carbon while the non-dissociating solute like mercuric chloride are very well adsorbed. The key factor is the form of the solute, whether it exists in ionized or non-ionized form. The solubility of a compound in a queous solution is often regarded as a good indicator of whether or not the compound is likely to be well adsorbed. The reason is that solubility reflects the degree of attraction of the solute by the solvent.

G. Molar conductance

The conductance of an electrolyte solution at any temperature depends only on the ions present, and their concentration. When a solution of an electrolyte is diluted, the conductance will decrease, since fewer ions are present per milliliter of solution to carry the current. If all the solution be placed between two electrodes 1 cm apart and large enough to contain the whole of the solution, the conductance will increase as the solution is diluted. This is due largely to a decrease in inter-ionic effects for strong electrolytes and to an increase in the degree of dissociation for weak electrolytes.

The molar conductivity (Λ) of an electrolyte is defined as the conductivity due to one mole and is given by:

$$\Lambda = 1000 k/C = k \cdot 1000 V \quad (14)$$

where, C is the concentration of the solution in mole L^{-1} , and V is the dilution in L (i.e. the number of liters containing one mole). Clearly, since specific conductance, k has the dimension $\Omega^{-1} \text{ cm}^{-1}$, the units of Λ are $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, or in SI units, $\Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$.

For strong electrolytes the molar conductivity increases as the dilution is increased, but it appears to approach a limiting value known as the molar conductivity at infinite dilution.

To measure the conductivity of a solution it is placed in a cell carrying a pair of platinum electrodes which are firmly fixed in position. It is usually very difficult to measure precisely the area of the electrode and their distance apart, and so if accurate conductivity values are to be determined the cell constant must be evaluated by calibration with a solution of accurately known conductivity, e.g. a standard potassium chloride solution. It is now a common practice for the cell constant to be determined by the

manufacturer, and to allow for measurements which solutions of widely differing conductivities, different cells can be obtained offering a range of a cell constants.

The measurements are made by connecting the cell to a conductivity meter which supplied alternating current at a frequency of about 1000 Hz to the cell. The use of alternating current reduces the possibility of electrolysis occurring and causing polarization at the electrodes, but it introduces the complication that the cell has a capacitance in addition to its resistance. The modern conductivity meter has a sophisticated electronic circuit which eliminates capacitance effects, can measure a wide range of conductivities (e.g. $0.001 \mu\Omega^{-1} \text{ cm}^{-1}$ - $1300 \text{ m}\Omega^{-1} \text{ cm}^{-1}$), and with provision for automatic range switching. By operation of a balancing control, the instrument is adjusted so that the constant of the cell in use is displayed on the digital meter which records the conductivities values. The clean conductivity cell is rinsed with, and then charged with, the solution whose conductivity is to be measured, and the required result is immediately displayed on the meter.

The purity of distilled or de-ionized water is commonly checked by conductimetric measurements. The conductivity of pure water is about $5 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$, and the smallest trace of ionic impurity leads to a large increase in conductivity.

H. Solution pH

The pH concept was originated in 1909 by the Danish biochemist S. P. L. Sorensen while he was working on the control of acidity during the brewing of beer. The p in pH stands for puissance (in French), potenz (in German), or power in English; the H stands for hydrogen ion. L. Sorensen introduced the hydrogen ion exponent pH defined by the relation:

$$\text{pH} = \log_{10} 1/[\text{H}^+] \quad (15)$$

$$\text{or } [\text{H}^+] = 10^{-\text{pH}} \quad (16)$$

The quantity pH is thus the logarithm (to the base 10) of the reciprocal of the hydrogen ion concentration, or is equal to the logarithm of the hydrogen ion concentration with negative sign. This method has the advantage that all states of acidity and alkalinity between those of solutions containing, on the one hand, 1 mol L⁻¹ of hydrogen ions, and on the other hand, 1 mol L⁻¹ of hydroxide ions, can be expressed by a series of positive numbers between 0 and 14. Thus, a neutral solution with $[\text{H}^+] = 10^{-7}$ has a pH of 7; a solution with a hydrogen ion concentration of 1 mol L⁻¹ has a pH of 0 ($[\text{H}^+] = 10^0$); and a solution with a hydroxide-ion concentration of 1 mol L⁻¹ has $[\text{H}^+] = K_w/[\text{OH}^-] = 10^{-14}/10^0 = 10^{-14}$, and possesses a pH of 14. A neutral solution is therefore one in which pH= 7, an acid solution one is which pH < 7, and an alkaline solution one is which pH > 7. An alternative definition for a neutral solution, applicable to all temperatures, is one in which the hydrogen ion and hydroxide ion concentrations are equal. In an acid solution the hydrogen ion concentration exceeds the hydroxide ion concentration, whilst in an alkaline or basic solution, the hydroxide ion concentration is greater.

There are several methods for determining the pH of a solution. One of the most familiar techniques for measuring pH is the litmus paper test. An acidic solution turns blue litmus red, and basic solution turns red litmus blue. However, the very elementary and inaccurate measurement determines only whether the pH is greater or less than 7. Other pH-indicating papers enable one to estimate pH to about ± 0.5 to 1 unit. Mixture of indicators, which are often colored plant extracts, change color with pH, and can be used to determine pH calorimetrically. Several instrumental colorimetric methods and electrical methods are also available. In one electrical method, a voltage

proportional to the pH develops when appropriate electrodes are dipped into a solution, and the pH is displayed on a pH meter. For solution of fairly high concentration, the most accurate technique for determining the acid or base concentration is titration.

The glass electrode is the most widely used hydrogen ion responsive electrode, and its use is dependent upon the fact that when a glass membrane is immersed in a solution, a potential is developed which is a linear function of the hydrogen ion concentration of the solution. The basic arrangement of a glass electrode is shown in Fig. 4(a); the bulb *B* is immersed in the solution of which it is required to measure the hydrogen ion concentration, and the electrical circuit is completed by filling the bulb with a solution of hydrochloric acid (usually 0.1 M), and inserting a silver-silver chloride. Provided that the internal hydrochloric acid solution is maintained at constant concentration, the potential of the silver-silver chloride electrode inserted into it will be constant, and so too will potential between the hydrochloric acid solution and the inner surface of the glass bulb. Hence the only potential which can vary is that between the outer of the glass bulb and the test solution in which it is existing immersed, and so the overall potential of the electrode is governed by the hydrogen ion concentration of the test solution.

Glass electrode are now available as combination electrodes which contain the indicator electrode (a thin glass tube) and a reference electrode (silver-silver chloride) combined in a single unit as depicted in Fig. 4(b) The thin glass bulb *A* and the narrow tube *B* to which it is attached are filled with hydrochloric acid and carry a silver-silver chloride electrode *C*. The wide tube *D* is fused to the lower end of tube *B* and contains saturated potassium chloride solution which is also saturated with silver chloride; it carries a

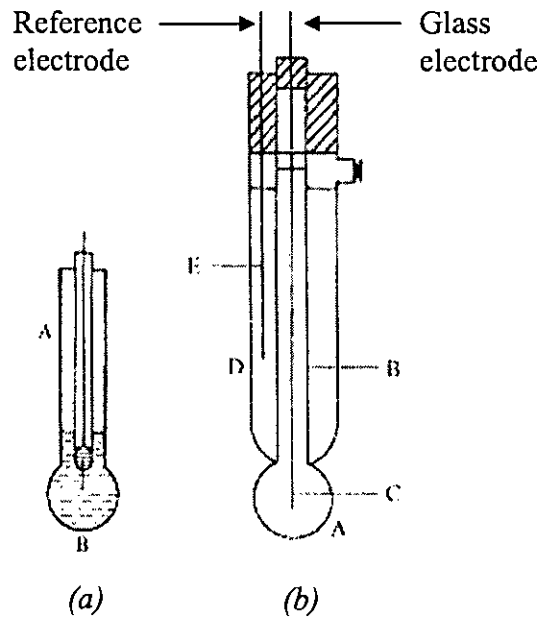
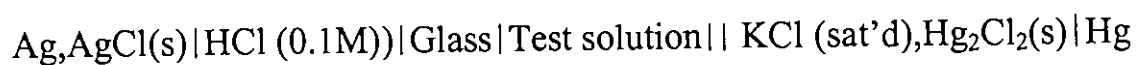


Fig. 4: (a) Basic arrangement of (a) glass electrode; (b) glass electrode in combination with a reference electrode.

silver-silver chloride electrode E. The assembly is sealed with an insulating cap.

To measure the hydrogen ion concentration of a solution the glass electrode must be combined with a reference electrode, for which purpose the saturated calomel electrode is most commonly used, thus giving the cell:



The e.m.f. of the cell may be expressed by the equation:

$$E = K + (RT/F) \ln a_{\text{H}^+} \quad (17)$$

or at a temperature of 25°C by the expressed:

$$E = K + 0.0591 \text{ pH} \quad (18)$$

In these equations, K is a constant partly dependent upon the nature of the glass used in the construction of the membrane, and partly upon the individual character of each electrode; its value may vary slightly with time.

The glass electrode should be thoroughly washed with distilled water after each measurement and then rinsed with several portions of the next test solution before making the following measurement. The glass electrode should not be allowed to become dry, except during long period of storage: it will return to its responsive condition when immersed in distilled water for at least 12 hours prior to use.

1.4 Aim of the Present Work

Taking into account the works cited in the review, it is evident that much important progress has been made on the study of PANI. A good progress has also been made in preparing polymers with more well-defined structures and which possess the lowest possible degree of irregularity. PANI is unique among conducting polymers that its electrical properties can be reversibly controlled both by charge-transfer doping and by protonation. The wide range of associated electrical, electrochemical and optical properties coupled with good stability make PANI potentially attractive for application as an electronic material. Indeed, a good number of papers already reported the application of PANI as electronic materials. PANI and PP are the type of conductive polymers that can be made charged (positively or negatively) and discharge (neutral) by doping and dedoping, respectively. Furthermore PANI and PANI-based composites have also been reported to exhibit relatively high surface area [61]. These results prompted us to undertake the present study.

The main aim of the present work is to address the application of conducting polymeric materials, *viz.*, PANI as an effective adsorbent for surface processes. Secondly, to examine surface processes of PANI towards adhesion of organics and inorganics onto its surface. Experimental design for the development of charged and discharged PANI adsorbent is also another important object of this work.

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Chapter 2

EXPERIMENTAL

2.1 Materials and probes

A. Chemicals

The chemicals and reagents used in this work are listed below. These are analytical grade and used as received except for the aniline which was distilled twice prior to use. Doubly distilled water was used as solvent to prepare most of the solutions of this work. However, N,N-dimethyl formamide (DMF) was employed as solvent for the few spectral analysis.

- (i) Aniline [E. Merck, Germany]
- (ii) Hydrochloric acid (32%) [E. Merck, Germany]
- (iii) Ammonium peroxydisulfate [E. Merck, Germany]
- (iv) Dimethyle formamide [E. Merck, Germany]
- (v) Ammonium hydroxide (25%) [E. Merck, India]
- (vi) Methylene blue [Fluka, England]
- (vii) Procion red [Fluka, England]

B. Instruments

The instruments and probes employed in this work are mentioned below:

- i) Infra red spectrophotometer [IR-470, Shimadzu, Japan]
- ii) UV-visible spectrophotometer [UV-1601PC, Shimadzu, Japan]
- iii) Automatic X-ray diffractometer [JDX – 8P, JEOL Ltd., Japan]
- iv) Scanning electron microscope [Philips XL 30, Holland]
- v) Autoranging microvolt [Keithley 197A, USA]
- vi) pH meter [HM –16s, TOA, Japan]

- vii) Centrifuge machine [Universal 16A, Hettich. Germany]
- viii) 100 mesh sieve [Endecotts test sieves limited, England]
- ix) Digital balance [FR -200, Japan]
- x) Controlled heating vacuum oven [Gallencamp, England]

2.2. Synthesis of polyaniline substrates

Polyaniline (PANI) was prepared by a chemical method at room temperature, 30°C ($\pm 2^{\circ}$) following the procedure described elsewhere [1– 3]. In brief, the procedure is as follows: 2.5 mL of aniline, 5 mL of hydrochloric acid (HCl) and 3.0g of ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) were added to distilled water maintaining the total volume of the mixture 400 mL. The reaction mixture was turned into deep blue polymeric sediment instantaneously. However, the content was left over night for the completion of polymerization. The deep blue sediment was then filtered and treated separately with aqueous solutions having pH of 1.71, 6.86 and 10.01 in order to get three different PANI substrates – described below:

- i) The polymeric sediment as obtained was washed with distilled water (pH=6.86) until the pH of the supernatant reaches 6.86. The mass was then kept in contact with the distilled water for over night and then filtered. The PANI thus treated is called neutral PANI (*n*-PANI) in this work.
- ii) In other case, the sediment was washed with aqueous 0.1M HCl (pH=1.71) solution and continued washing as before until the supernatant shows a pH value 1.71. The content was

then left over night in the acid solution. PANI treated in this way is called acidic PANI (*a*-PANI).

- iii) And in another case, the sediment was washed with 0.1M aqueous ammonium hydroxide (NH_4OH) solution ($\text{pH}=10.01$) until the supernatant attains the pH value 10.01. The sediment was then kept over night in the ammonia hydroxide solution. The PANI thus treated is called basic PANI (*b*-PANI) throughout the work.

The PANI substrates thus treated were then dried initially in air followed by vacuum drying at 40°C . The dried mass was grounded and then sieved using 100 mesh sieves and stored in a vacuum desiccator.

2.3 Solid state conductance

Compressed pellet d.c. conductivity of the PANI matrices thus treated were measured by a conventional two-point probe method [4, 5]. PANI samples were mechanically compressed with pressure to a rigid pellets having diameter 7 mm and thickness 3 mm. These pellet forms of the PANI samples were used in the conductance measurements.

An auto ranging microvolt was employed to get the voltage drop between the arbitrary two points on the pellet surface. The distance between the two points for all the samples were maintained constant for all the measurements. The observed resistance for each sample could

read directly from the microvolt and thus corresponding specific conductance of the sample was just calculated out. The conductivity measurements were performed under ambient atmospheric condition.

2.4 Spectral analysis

A. IR spectra

IR spectra of all the dried samples were recorded on an IR spectrometer in the region of 4000 - 400 cm^{-1} . IR spectra of the solid samples were frequently obtained by mixing and grinding a small amount of materials with dry and pure KBr crystals. Thorough mixing and grinding were done in a mortar by a pestler. The powdered mixture was then compressed in a metal holder under a pressure of 8-10 tons to make a pellet. The pellet was then placed in the path of IR beam for measurements.

B. UV-Vis spectra

The ultra violet-visible (UV-Vis) spectral analysis of the sample solutions employed a double beam spectrophotometer. The PANI solutions were prepared by dissolving its small amount of mass in 50 mL DMF. The sample solution was diluted with DMF to a visible extent in such a way that the optical density did not exceed 2. In these experiments, DMF was used as reference solvent. UV-Vis spectroscopic analysis for the adsorption studies involved the aqueous solution of different pH. The references in these cases were the corresponding aqueous solutions that used for preparing the adsorbate

solutions. Detail UV-Vis measurements during adsorption processes will be discussed in the later sections.

2.5 X-ray diffraction

PANI substrates thus treated were analyzed for their x-ray diffraction pattern in the powder state. For this purpose, the samples were prepared as the procedure described in section 2.2. The powder samples were pressed in a square aluminum sample holder (40 mm × 40 mm) with a 1 mm deep rectangular hole (20 mm × 15 mm) and pressed against an optical smooth glass plate. The upper surface of the sample was labeled in the plane with its sample holder. The sample holder was then placed in the diffractometer.

X-ray diffraction pattern were recorded on an automatic X-ray diffractometer using Mo(K α) radiation of wave length 1.54 Å. The diffractometer was operated at 30 KV and 20 mA with a scan speed of 2° min⁻¹.

2.6 Surface morphology

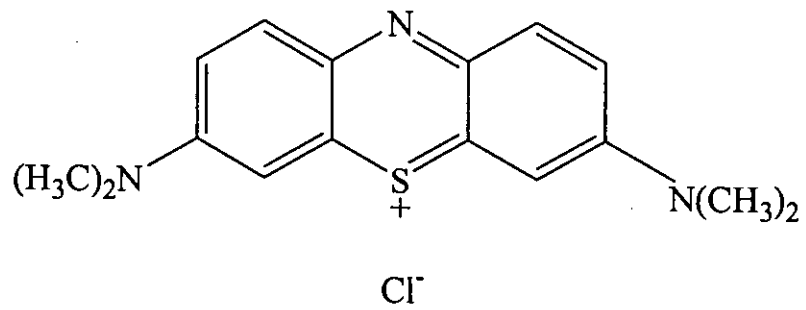
PANI matrices thus prepared and treated following the methods described in section 2.2 were examined for their surface morphology. For this purpose, scanning electron microscopy technique was adopted. The dried powder PANI samples were dispersed on a conducting carbon glued strip. The sample loaded strip was then mounted to a chamber that evacuated to $\sim 10^{-3}$ to 10^{-4} torr and then a very thin gold

layer (~ few nanometers thick) was sputtered on the sample to ensure the conductivity of the sample surface. The sample was then placed in the main SEM chamber to view its surface. The system was computer interfaced and thus provides recording of the surface images in the computer file for its use as hard copy.

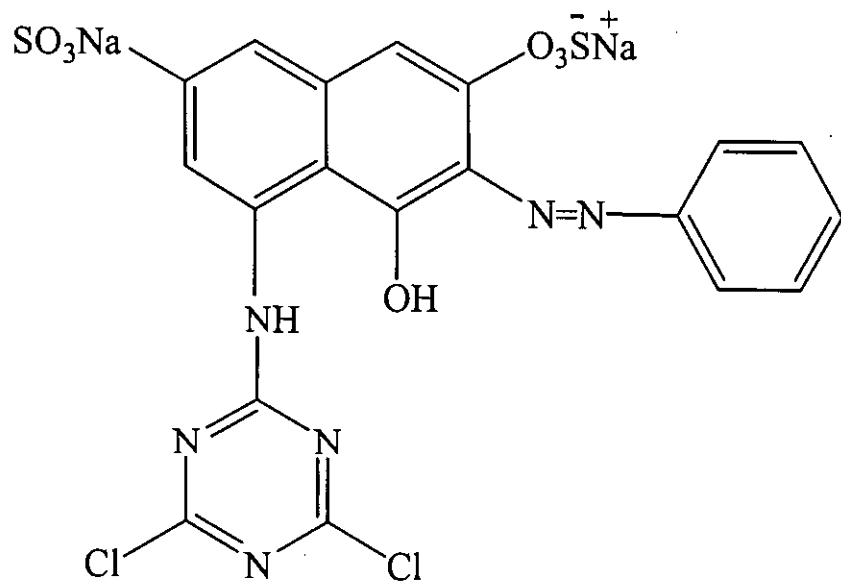
2.7 Adsorption study

For adsorption studies, polymeric matrices, *viz.*, *a*-PANI, *n*-PANI and *b*-PANI, were used as adsorbents. Their preparation and post-synthesis treatments with aqueous solution of various pHs are described in section 2.2. On the other hand, organic dyes such as methylene blue (MB) and procion red (PR) and an inorganic salt, hydrated nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were used as adsorbate. The chemical structure of MB and PR are shown in Fig. 1.

Adsorption of MB and PR on *a*-PANI, *n*-PANI and *b*-PANI matrices were studied spectroscopically from their aqueous solution of pH 1.71, 6.86 and 10.01, respectively. The distilled water used in this work has the pH=6.86. On the other hand, when 1.92 mL of concentrated NH_4OH (25%) was diluted to 500 mL by adding the distilled water, it gives an aqueous solution of pH= 10.01. An aqueous solution of pH=1.71 was made by adding 1.6 mL of concentrated HCl (32%) to distilled water and making the total volume 500 mL. Indeed, the concentration of the aqueous NH_4OH and HCl solution were calculated to be 0.1 M for each.



(a)



(b)

Fig. 1: Chemical structure of (a) MB and (b) PR.

MB and PR were found to be quite stable in the solution pH ranging from 1.71 to 10.01 employed at least for 2h as evidenced experimentally. Figures 2 and 3 show the UV-Vis absorbance spectra of MB and PR solutions taken immediately (0h) and 2h after its preparation.

Adsorption was performed by charging 350 mL of stock solution of the adsorbates to a known mass of the adsorbents and then follows the change in absorbance of the stock solution with time. Corresponding concentration for the observed absorbance was obtained from a calibration curve. Calibration curve represents absorbance of stock solution at its different concentration. Figures 4-6 show the calibration curves of MB solution prepared in aqueous HCl (pH= 1.71), distilled water (pH=6.86) and aqueous NH_4OH (pH=10.01) solutions, respectively. In each cases, stock solution of MB was made by dissolving 0.18 g MB in 500 mL the aqueous solutions employed to give a concentration of 9.63×10^{-5} M. 100 mL of 9.63×10^{-5} M MB solution was then diluted again to 500 mL to result a concentration of 1.93×10^{-5} M which was used as the stock solution of MB.

Figures 7-9 show the calibration curve of PR solution in aqueous HCl (pH = 1.71), distilled water (pH=6.86) and aqueous NH_4OH (pH=10.01) solutions, respectively. Stock solution of PR in different solvents used were made by dissolving 0.03 g of PR in 500 mL aqueous solution to show a concentration of 9.63×10^{-5} M. It's 100 mL was then diluted to 500 mL solution to yield a concentration of 1.93×10^{-5} M that

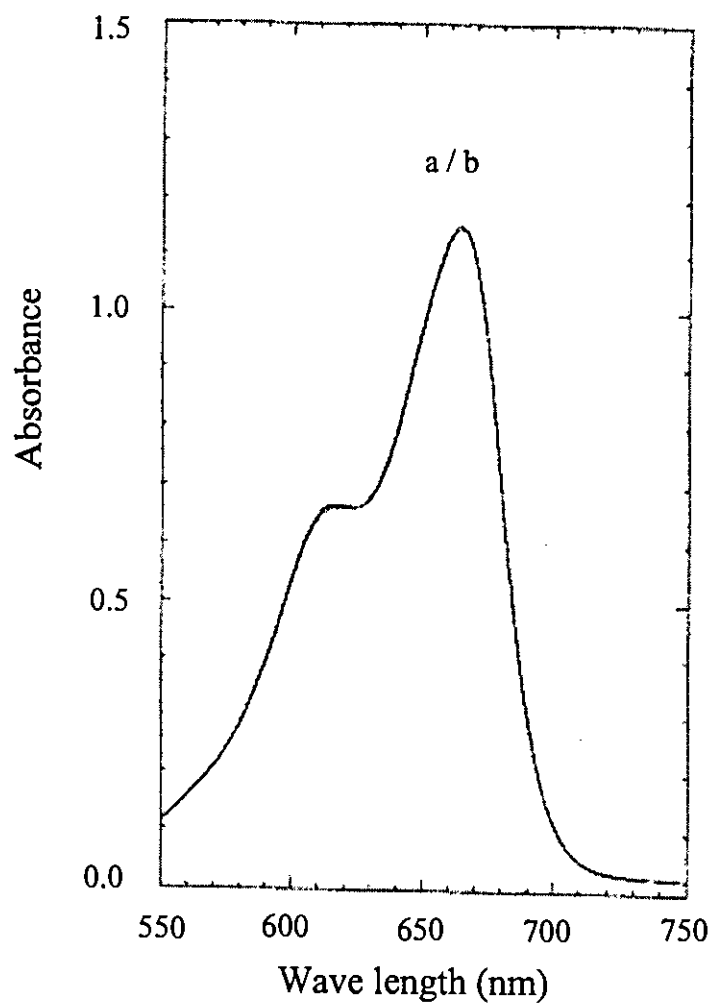


Fig. 2: UV-Vis absorption spectra of MB solution (pH=10.01) taken (a) immediately (0h) and (b) 2h after its preparation.

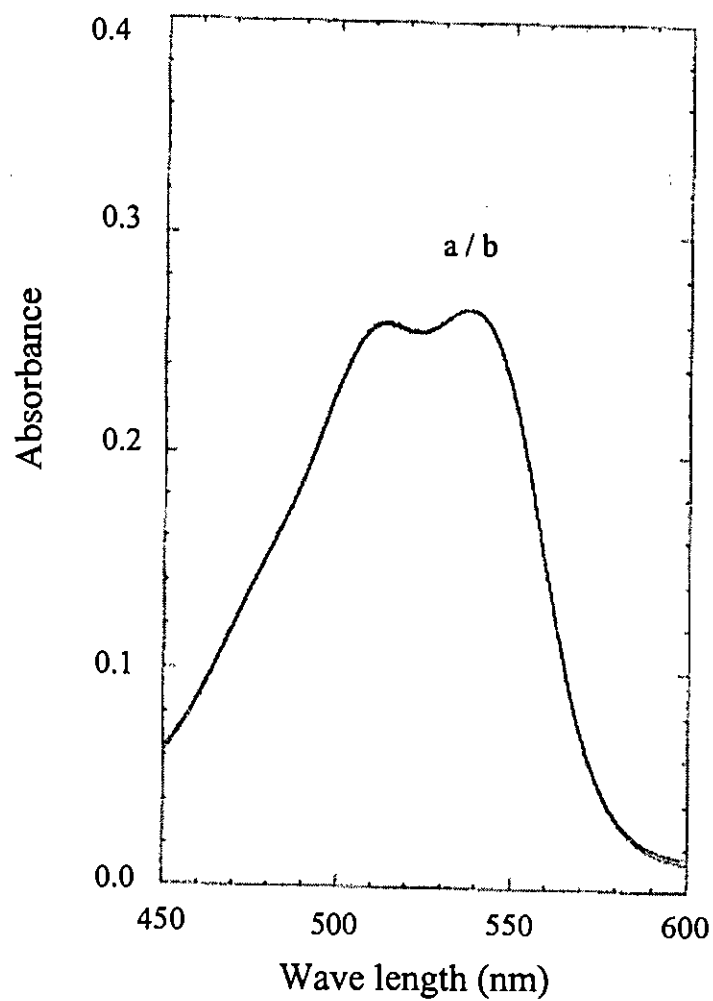


Fig. 3: UV-Vis absorption spectra of PR solution (pH=10.01) taken (a) immediately (0h) and (b) 2h after its preparation.

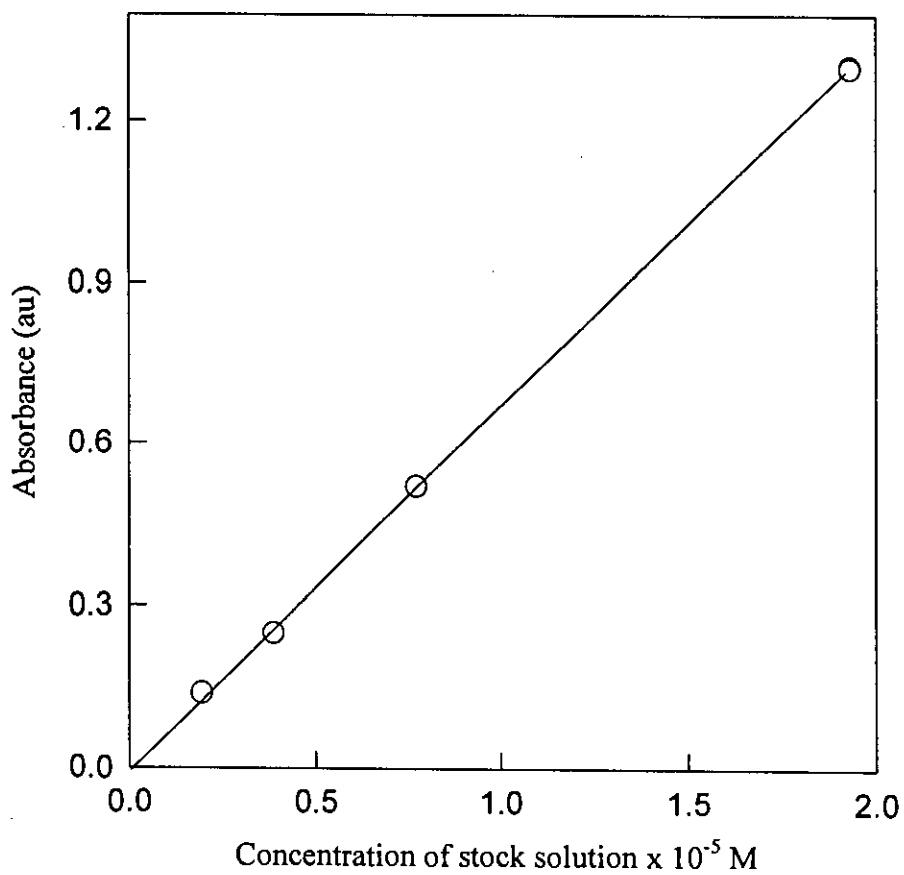


Fig. 4: Calibration curve of MB in aqueous HCl solution (pH = 1.71).

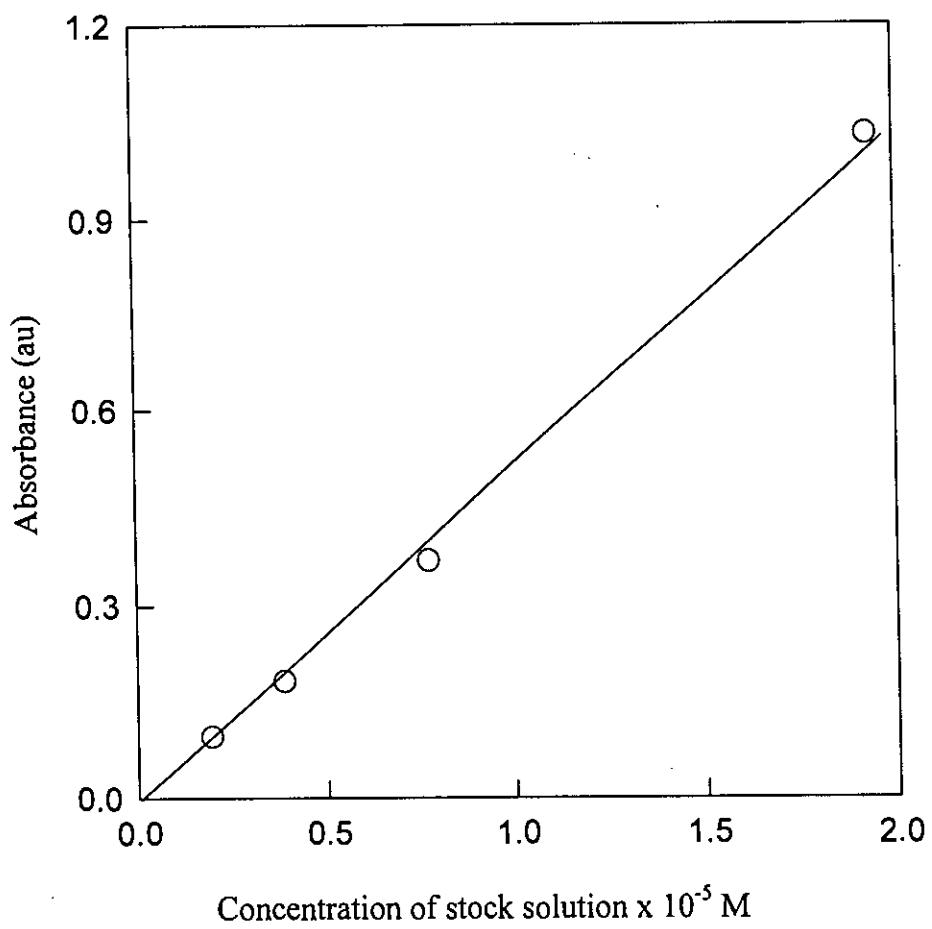


Fig. 5: Calibration curve of MB in distilled water (pH = 6.86).

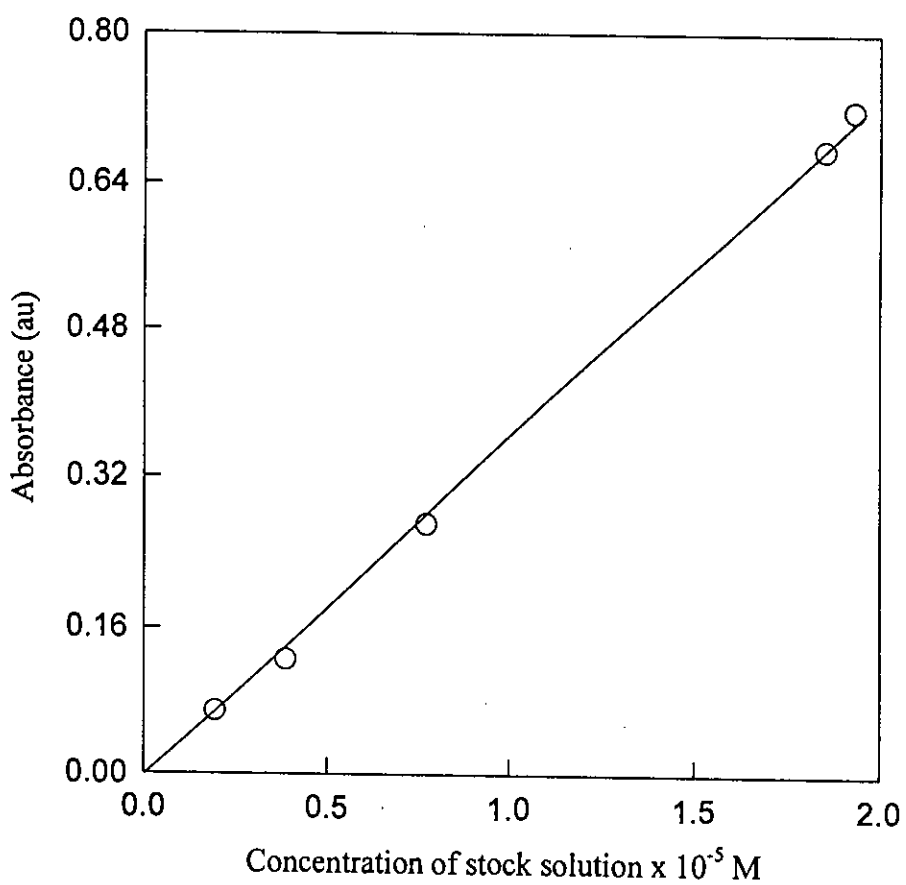


Fig. 6: Calibration curve of MB in aqueous NH_4OH (pH = 10.01).

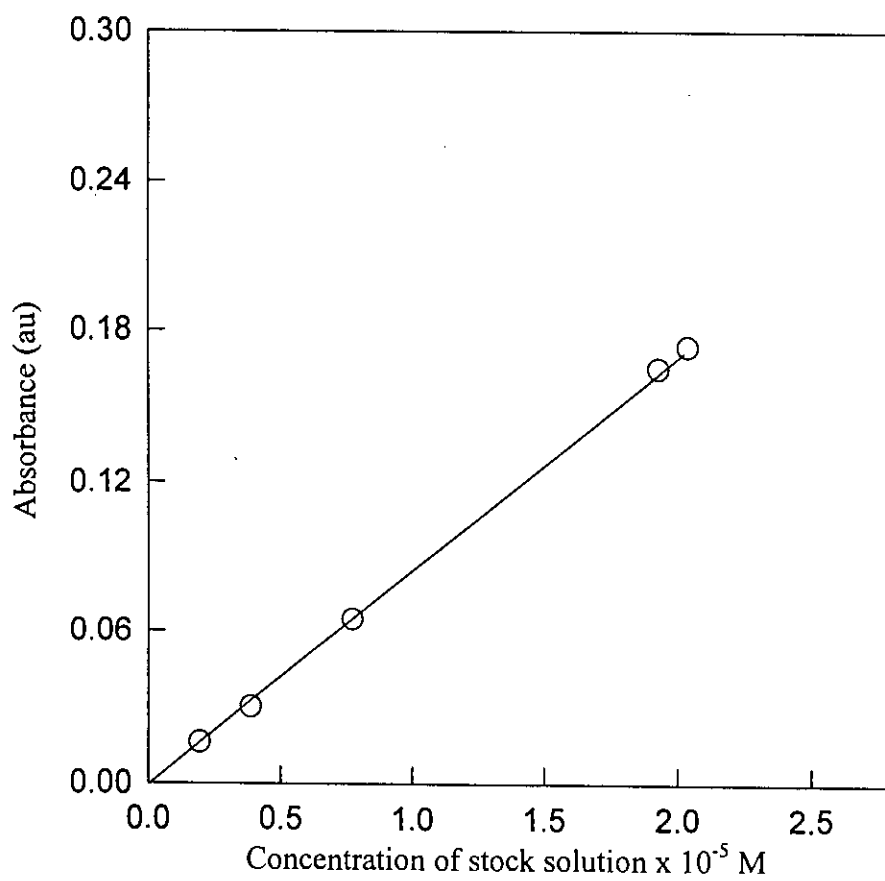


Fig. 7: Calibration curve of PR in aqueous HCl solution (pH = 1.71).

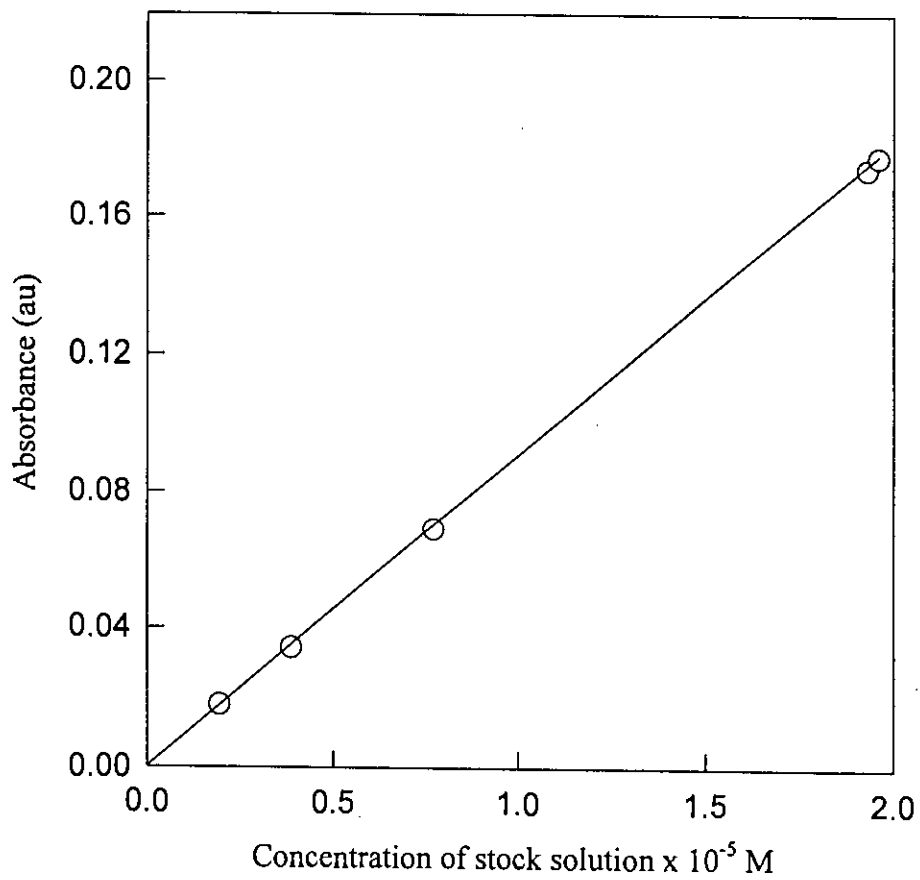


Fig. 8: Calibration curve of PR in distilled water (pH = 6.86).

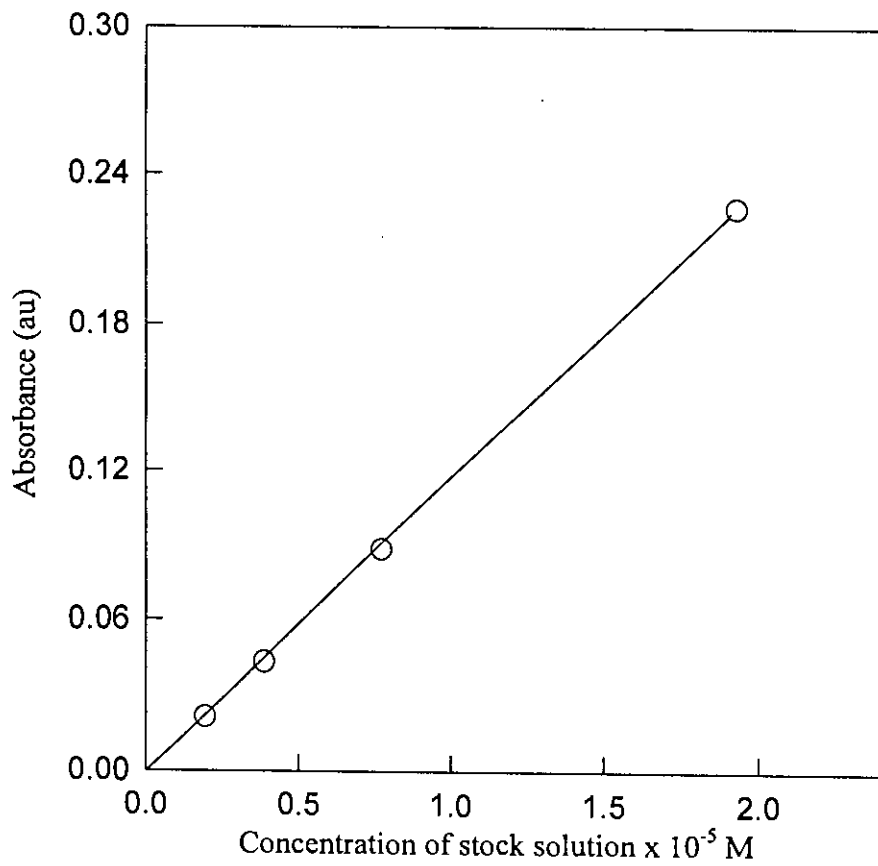


Fig. 9: Calibration curve of PR in aqueous NH₄OH (pH = 10.01).

used as the stock solution of PR. For each adsorption run, both for MB and PR, 0.464 g of PANI adsorbent was employed.

Adsorptions of MB and PR on *a*-PANI, *n*-PANI and *b*-PANI matrices were followed simply by withdrawing the solution at different time intervals, centrifuged and then monitoring the absorbance of the solution. In all the case, equilibrium time of adsorption was seen to be reached within ~2h. Thus, from this equilibrium state, total amount adsorbed was calculated out. Experiment for the MB adsorption isotherm was performed as follows: 9.63×10^{-5} M MB stock solution was prepared in aqueous NH_4OH solution (pH=10.01). From this solution, 5, 10, 15, 20, 25, 30 and 35 ml solution were withdrawn separately and diluted all the solutions up to 100 ml with the same aqueous NH_4OH solution. These solutions were then charged to ~ 0.133 g of *b*-PANI matrices until equilibrium condition reached after 2h. Small portion of each solution was then withdrawn and centrifuged to record its absorbance. The concentration difference between the stock and the solution withdrawn after 2h gives the total amount of MB adsorbed and utilized for the isotherm plots.

PR adsorption isotherm was obtained similarly. In this case, 5, 10, 15, 20, 30, 40, 50 and 60 ml of 9.63×10^{-5} M PR stock solution of aqueous HCl (pH=1.71) were withdrawn and diluted to 100 ml each with the same HCl solution. These were then charged to ~ 0.1g of *a*-PANI sample and allowed to adsorb for 2h until equilibrium was

reached. The solution was then decanted and centrifuged for their absorbance measurements. The concentrations of the solutions were then calculated out as before for the isotherm data.

Since NiCl_2 solution is not stable in a solution of $\text{pH} = 10.01$, adsorption of this salt was attempted only with the *a*-PANI and *n*-PANI matrices. For this purpose, 0.2 M NiCl_2 solutions were prepared in aqueous HCl ($\text{pH}=1.71$) solution and distilled water ($\text{pH}=6.86$). In both the solutions, NiCl_2 was found to be stable for 2h as can be seen in Fig. 10. However, the solutions were then charged to 0.466 g of *a*-PANI and *n*-PANI matrices separately and then adsorption was monitored spectroscopically as before for 2h until the equilibrium is reached.

2.8 Molar conductance and pH measurements

Molar conductance of the solutions was just calculated out from the observed specific conductance of the solutions. About 50 ml of the solution was charged in the cell and this volume of solution was just sufficient to immerged the electrodes of the conductance bridge for specific conductance measurement.

For pH measurement also 50 ml of solution was placed in the cell where the electrode of the pH meter was immerged for the quantification of H^+ concentration (pH) of the solution being under investigation. The pH data can be read directly from the display of the instrument.

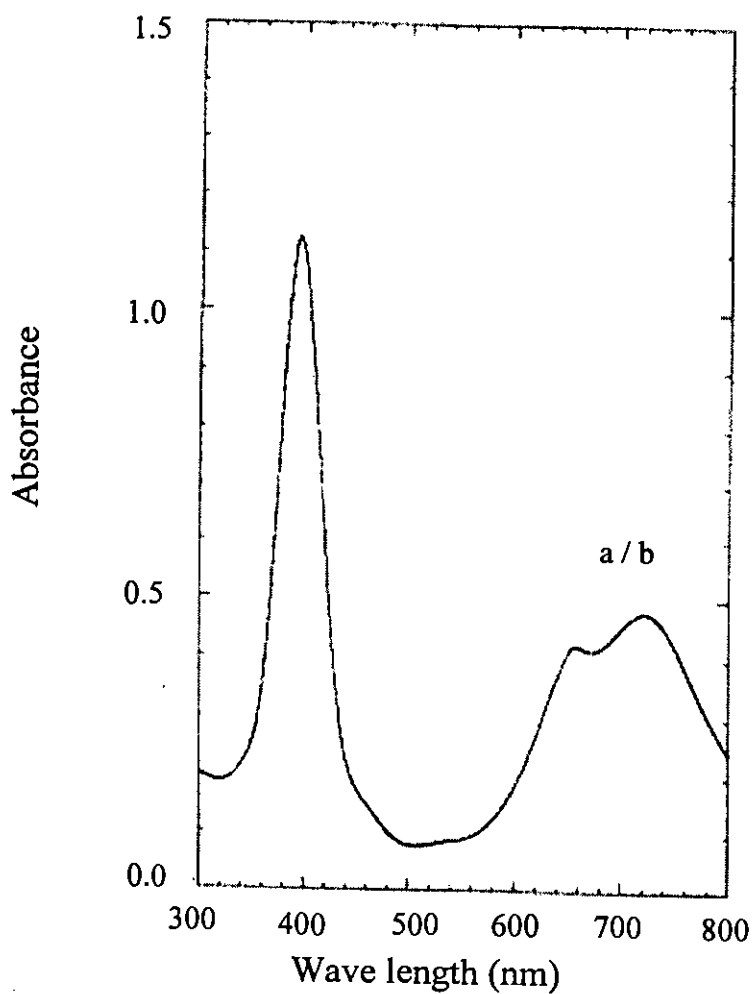


Fig. 10: UV-Vis absorption spectra of NiCl_2 solution ($\text{pH} = 1.71$) taken (a) immediately (0h) and (b) 2h after its preparation.

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2. M. Gill, S. P. Armes, D. Fairhurst, S. N. Emmett, G. C. Idzorek and T. Pigott, *Langmuir*, **8** (1992) 2178.
3. N. J. Terrill, T. Crowley, M. Gill and S. P. Armes, *Langmuir*, **9** (1993) 2093.
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5. J. Lange, *J. Appl. Phys.*, **35** (1964) 2659.

Chapter 3

RESULTS AND DISCUSSION

3.1 Polymerization mechanism and structure of PANI

The wide variety of methods [1-12] employed for the preparation of PANI leads to the formation of products whose nature and properties differ greatly. According to most authors, the first step in the oxidation of aniline is the formation of a radical cation, which is independent of the pH of the synthesis medium (be it acidic or basic), and is the governing criteria for the polymerization reaction. In the subsequent steps, radical cation coupling of aniline leads to the formation of PANI (Fig. 1).

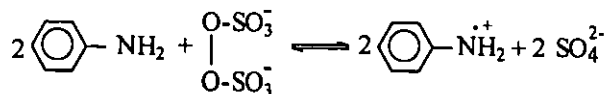
PANI can be prepared in the four idealized forms [13] shown in Fig. 2, at least when it's synthesis and any subsequent treatment are carried out in aqueous media. These forms may be interconverted at will by chemical and/or electrochemical oxidation or reduction. A given "A" form, *e.g.* 1A, may be converted to a given "S" form, *e.g.* 1S by treatment with an aqueous protonic acid, such as HCl. The acid may be removed to regenerate the "A" form by treating the "S" form with an aqueous solution of a base, such as NH₄OH.

In the present investigation, PANI was synthesized chemically as a dark blue/black powder $[(\text{C}_6\text{H}_4)=\text{N}-(\text{C}_6\text{H}_4)-\text{N}(\text{H})=\text{N}^+\text{Cl}^-]_x$, (form 2S) by treating a solution of aqueous HCl containing dissolve aniline, with the oxidizing agent, ammonia peroxodisulfate, (NH₄)S₂O₈. Protonation was

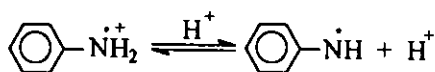
Step 1: Formation of the anilinium cation



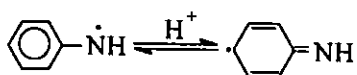
Step 2: Formation of the anilinium radical cation 1



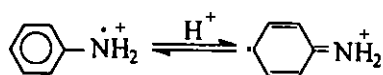
Step 3: Formation of the anilinium radical 1



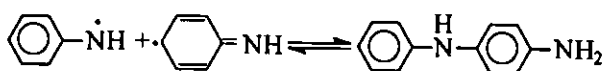
Step 4: Formation of the anilinium radical 2



Step 5: Generation of benzidine *via* the anilinium radical cation 1 and its resonance structure, *i.e.* the anilinium radical cation 2



Step 6: Coupling of the anilinium radicals 1 and 2
(Generation of *p*-aminodiphenylamine)



Step 7: Growth of aniline oligomers and polymers
(Growth *via* *p*-aminodiphenylamine and the anilinium radical 2)

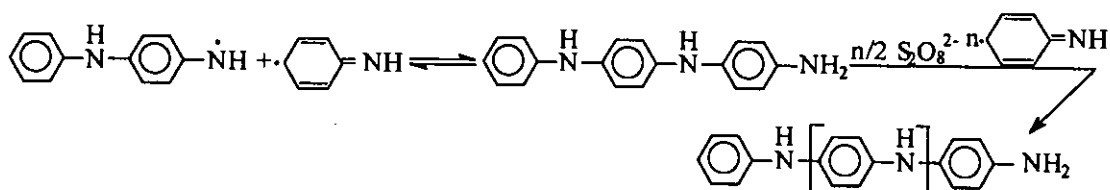
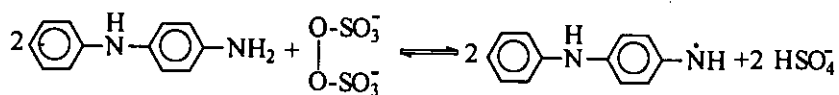


Fig. 1: Possible mechanism for the chemical oxidation of aniline in acid media to yield PANI.

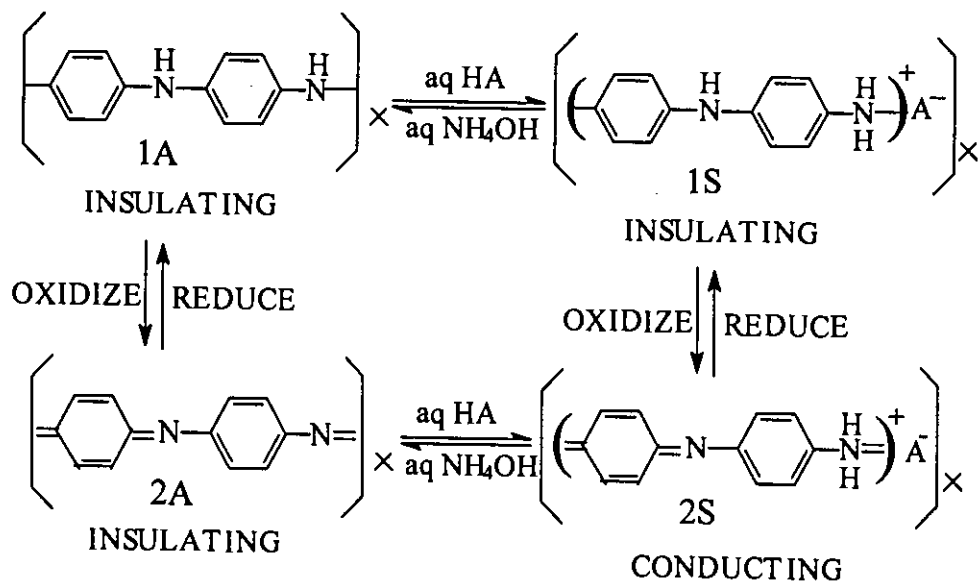


Fig. 2: Illustration of the idealized forms of PANI.

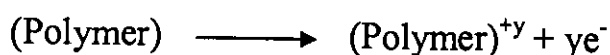
completed by treating the powder with 0.1M aqueous HCl solution (pH = 1.71) for over night followed by drying initially in air and then under vacuum at room temperature for 3 days to remove water and free HCl. Hence, we designated this powder "*acidic PANI*". The "2S" form was converted to the "2A" form, a dark purple / black powder by treating over night with a 0.1M NH₄OH solution (pH = 10.01) followed by drying in air and under vacuum as mentioned for the pervious sample. This sample is term as "*basic PANI*". The 2S form was washed with distilled water (pH=6.86) until the pH of the washed out water reached the pH value of 6.86 and then kept over night in the distilled water. This sample is termed as "*neutral PANI*" and may correspond to any form in between 2A and 2S. The 2A form (*basic PANI*) fully de-protonated, the "*neutral PANI*" could be less de-protonated compared to that of *basic PANI* that treated with NH₄OH. Level of protonation in its structures results in different electrical and optical behaviors. The electrical and optical characterizations of the studied PANI samples are discussed in the following sections.

3.2 Characterization of PANI samples

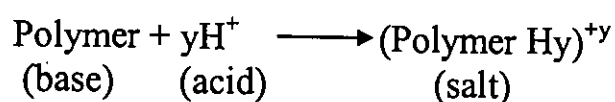
A. *Solid-state d.c. conductance*

Electrical conductance of a material depends generally on the doping level. The conductivity of PANI usually depend somewhat on the

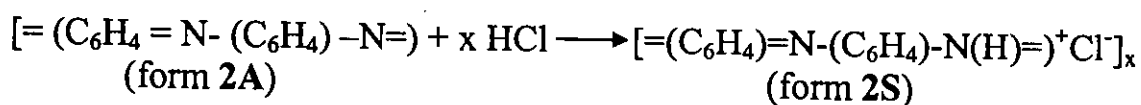
polymerization and protonation conditions [12, 13]. The conventional method of *p*-doping (oxidizing) an organic polymer involves removal of electrons from the *pi* system of the polymer by chemical or electrochemical oxidation:



In principle, it should be possible to *p*-dope a conducting polymer by adding a proton, which may interact with and hence partly depopulated the *pi* system with concomitant increase in conductivity of the polymer:



It is found that when PANI is treated with an aqueous protonic acid, such as HCl, it undergoes an insulator to metal transition involving a dramatic increase in the conductivity.



This transition is readily reversed by treatment with either of distilled water or aqueous NH_4OH solution.

The extreme sensitivity of the PANI to the pH of the aqueous solution with which it is equilibrated is illustrated in Fig.3. The plot shows what is necessary to achieve the electrically conductive or doped state of PANI powder. It is seen in this figure that it is necessary to keep the pH value of the PANI samples after synthesis in the range 0 to 2-3 to get its electrical

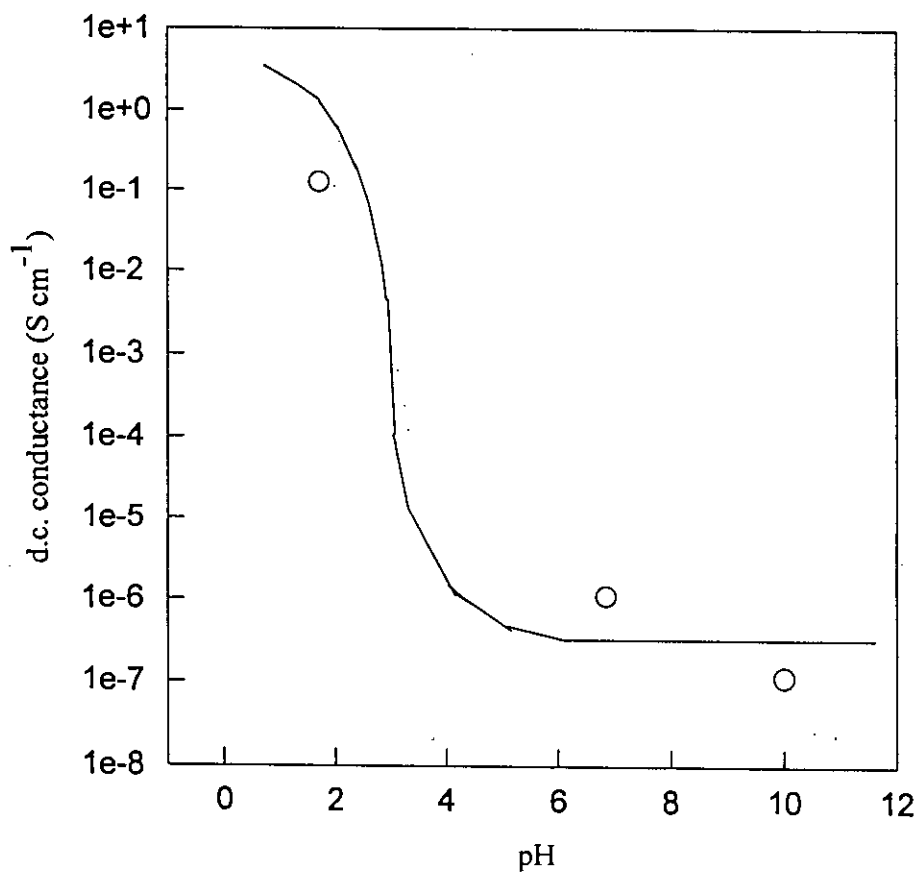


Fig. 3: Dependence of the d.c. conductivity of PANI on pH.

conductivity in the range 10^{-2} to 10 S cm^{-1} . If the pH value is increased above the value of 2-3, the PANI becomes insulating with a typical d.c. conductivity in the range 10^{-10} to 10^{-7} S cm^{-1} . The conductivity of the present PANI sample reaches a maximum value of 1.26×10^{-1} S cm^{-1} when it is treated with an aqueous HCl solution (pH=1.71). On the other hand, its conductivity drastically fall to 1.10×10^{-6} and 1.14×10^{-7} S cm^{-1} when treated with distilled water (pH = 6.86) and aqueous NH_4OH (pH = 10.01), respectively. Different structures result in different electrical behaviour of the polymer. PANI is protonated in the acid media, with electrical conducting characteristics while in the basic media, it is fully deprotonated or reduced with electrical insulating characteristics. The observed conductance of the present PANI samples treated in different pH media seems to be consistent with previous studies reported earlier [12-18].

The conduction mechanism has not been cleared up until now. However, Wnek [19] has proposed a conduction mechanism for PANI. During protonation of the polymer (which is in basic emeraldine form) the cations become involved in disproportionation reactions forming semiquinon radical cations which are subsequently responsible for the increase in the conductivity. On the other hand, investigation by Salaneck *et. al.* [20, 21] on conduction mechanism of PANI has shown that the temperature dependence of the electrical conductivity of the polymer is indicative of one-dimensional variable range hopping or three-dimensional fluctuation-induced tunneling.

B. UV-Vis absorption spectra

The UV-Vis absorbance spectra of PANI treated with different pH media ranging from 1 to 10.01 are shown in Fig.4. In principle, the absorbance in the UV-Vis range is due to allowed electronic transition

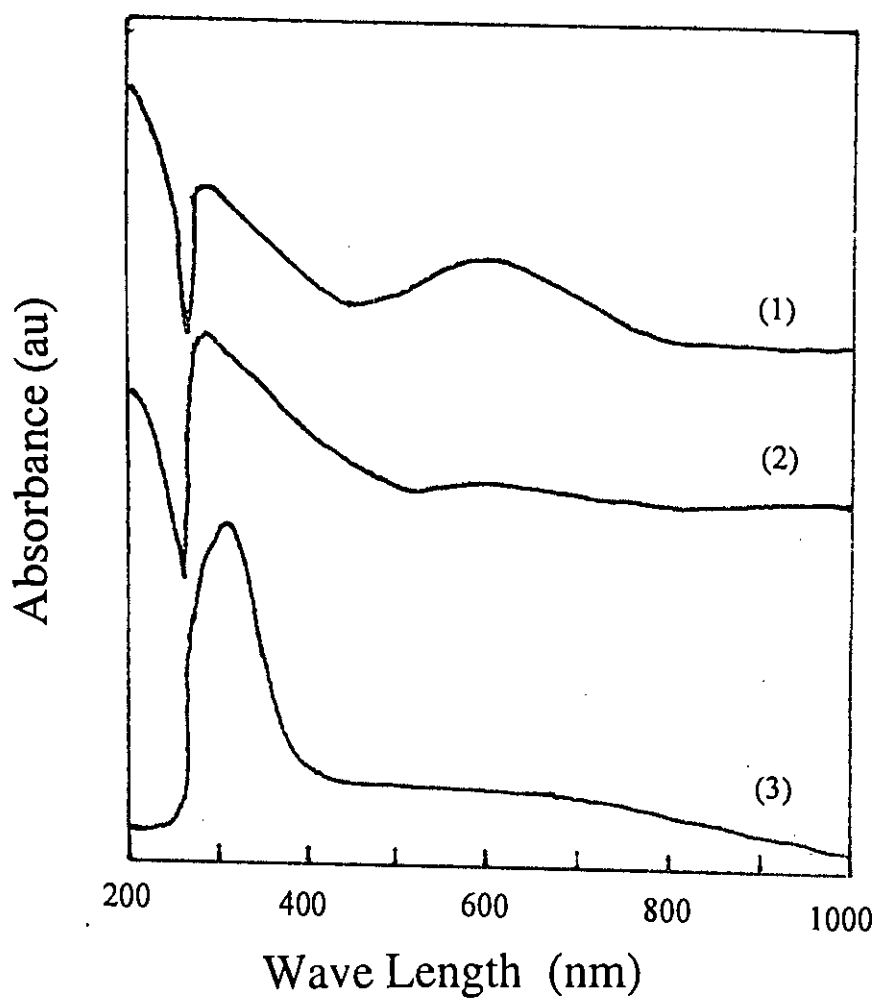


Fig. 4: UV-Vis absorption spectra of (1) α -PANI, (2) n -PANI and (3) b -PANI in DMF solution.

between the electronic levels of the polymer. Electronic absorption chromophores corresponding to the aromatic amine, the radical cation and the quinone-diimine forms are correlated to the reduced – insulating, the conductive and the oxidized – insulating forms of the polymer, respectively [22, 23].

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The spectra depicted in Fig. 4(1) are similar to those for doped conducting polymer films [24]. For the acid treated PANI, a strong absorption band in the ultra violet region at ~ 305 nm and a weak absorption in the visible region at ~ 601 nm are observed. On the other hand, spectra for the PANI treated with distilled water (2) and aqueous NH_4OH (3) show a strong band at around ~ 284 nm although a weak shoulder is seen at ~ 600 nm in (2). The peak observed at ~ 283 to 305 nm may corresponds the interband π - π^* (valance band to conduction band) transition. The other peak observed at ~ 600 nm may responsible for the polymer conductivity by forming polaron and bipolaron as mid-gap states. This is due to the oxidation of neutral or reduced PANI to cation radical (polaron), which absorbs here, and then oxidation of this cation to dication (bipolaron). The absorbance at this wave length can be attributed to a transition of the radical cation NH-NH^{\ddagger} (or the protonated form, between the bonding level of the polaron to the conduction band [25, 26]. The weak shoulder at ~ 600 nm for (2) may arises from the possibility of little protonation, since the pH of the distilled water with which the PANI was treated was 6.86.

As the doping or protonation happens, the originally filled valance band of the polymer become partially empty. The Fermi level lowers to the valance band which ensures a metallic behavior of the polymer. In this respect, it can be expected that the more doped (protonated) the polymer,

will be, the more empty the valance band become and as a consequence, that the free carrier concentration (polaron and bipolaron) and hence the conductivity will increase. Hence, the increase conductivity for the acid treated PANI and lower conductivity for the base or distilled water treated PANI, as described in Fig.3 seems to be consistant with the present spectral data (Fig. 4)

C. IR spectral analysis

IR spectra of the solids provide useful qualitative structural information. In order to get some insight about the structure of PANI treated under different condition of pH, IR spectral analyses were performed.

Figures 5-7 give IR spectra of the PANI obtained after treating with various aqueous solutions having (a) pH = 6.86, (b) pH = 1.71 and (c) pH = 10.01, while the tentative assignment of the spectra are listed in a tabular form presented later. The main absorption peaks are almost at the same position but their relative intensities obviously change with the solution pH with which PANI was treated. It can be seen form Fig.5 that the main effects of HCl treatment are: (i) The base line over 4000-2000 cm^{-1} is raised remarkably, (ii) The intensity of the 1315 cm^{-1} peak is increased (iii) with the 1160 cm^{-1} peak growing, another peak appears at 1140 cm^{-1} . After treating with NH_4OH , the spectrum substantially returns to the original shape except the additional bands formed at 3150 and 1400 cm^{-1} due to the NH_4Cl .

It is the worthwhile to mention here that the observed IR spectra are consistant with the previous studies [27-33] and discuss below according to the frequency region:

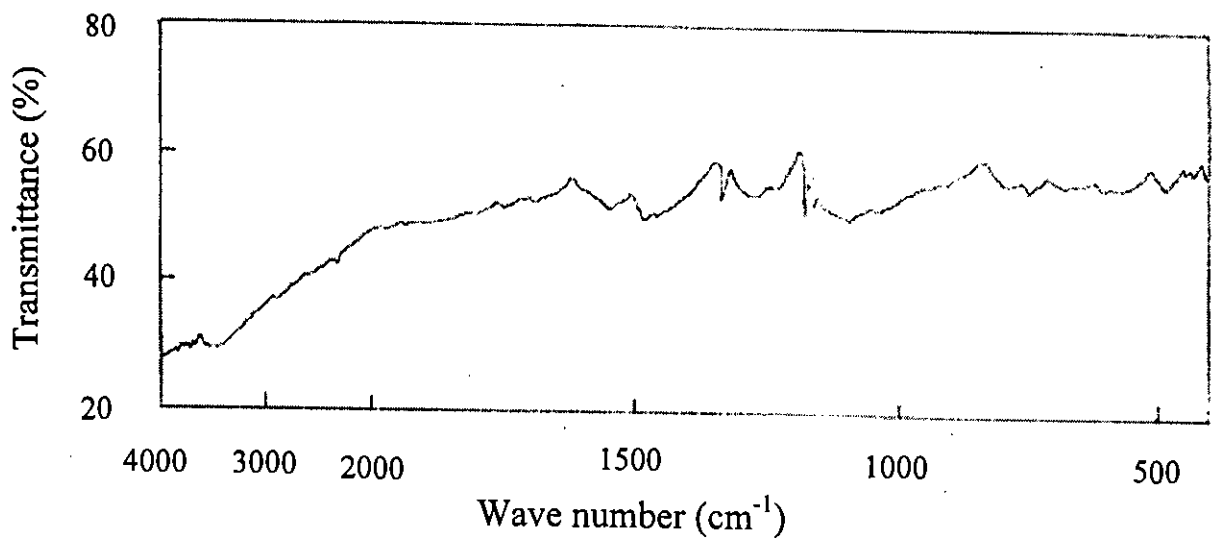


Fig. 5: IR spectrum of α -PANI.

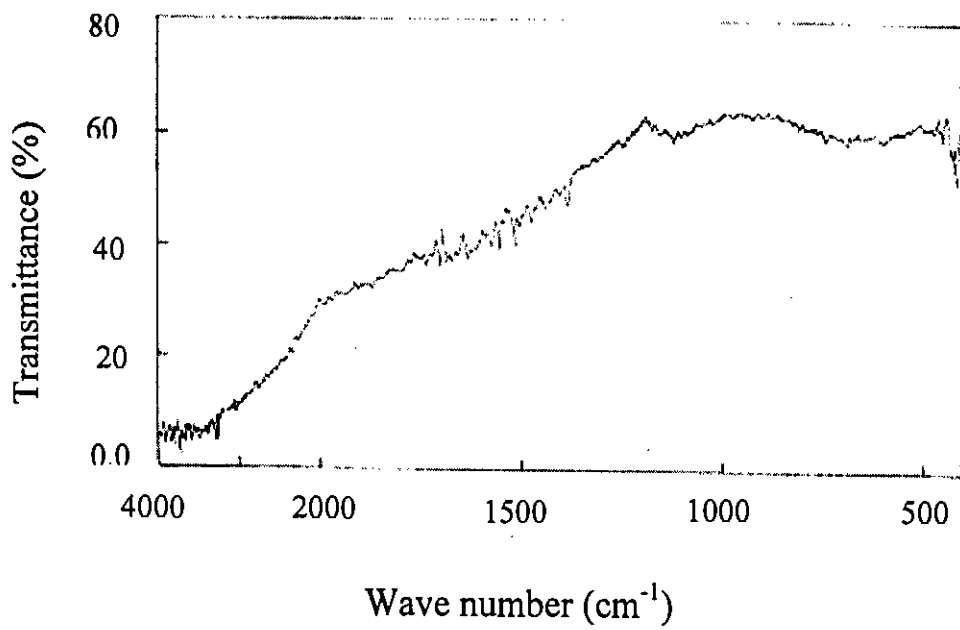


Fig. 6: IR spectrum of *n*-PANI.

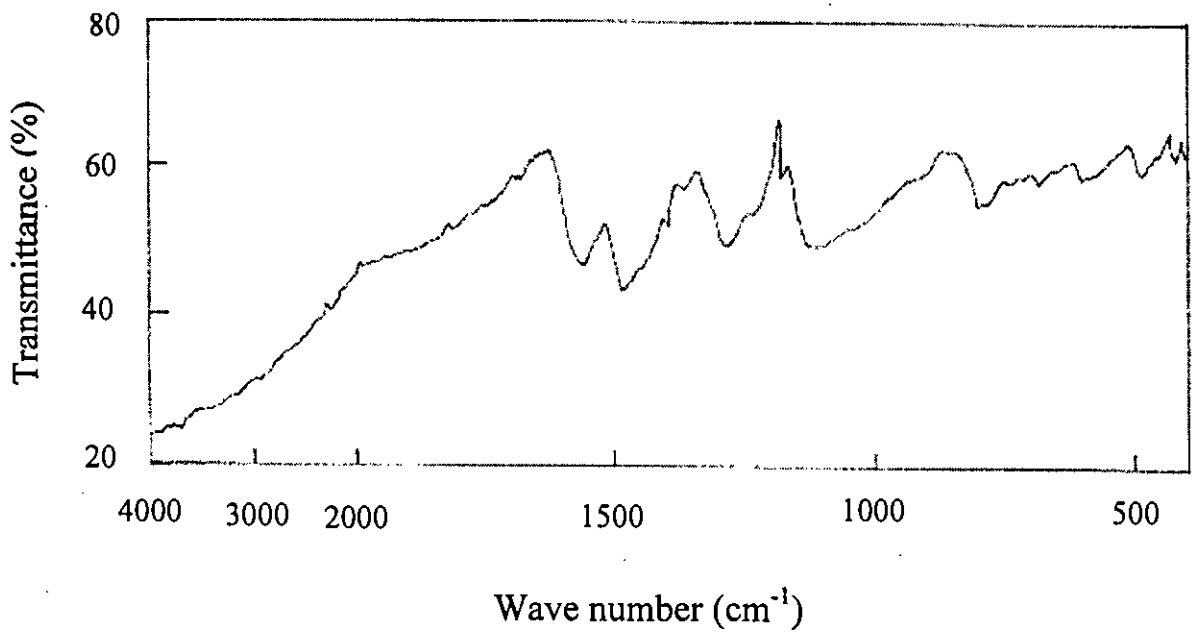


Fig. 7: IR spectrum of *b*-PANI.

(a) 3500-3100 cm^{-1}

This is the N-H stretching region. The absorption of PANI in this region is rather weak. The main absorption peaks are located at 3380 and 3310 cm^{-1} , with shoulders at 3460 and 3170 cm^{-1} . With increasing HCl concentration in the polymerization system, the peak at 3380 cm^{-1} increases and the shoulder at 3170 cm^{-1} decreases.

(b) 3100- 2800 cm^{-1}

This is the C-H stretching region. The absorption of PANI in this region is even weaker, but it is observable at 3050 – 3030 and 2960 – 2850 cm^{-1} . With increase of HCl concentration in the polymerization system, the relative intensity of the 3040 cm^{-1} decreases indicating that the number of H atoms bonded to benzene ring is reduced. This implies that Cl substitution occurs and thus strengthening of the C-Cl stretching band at 810 cm^{-1} occurs.

(c) 1600-1450 cm^{-1}

Aromatic ring breathing, N-H deformation and C=N stretching all give absorption in this region. In general, The N-H deformation band is very weak. A 1, 4- substituted benzene ring may give absorption band at 1600-1580 and 1510-1500 cm^{-1} . However, the former is very weak and even observable if the two substituents are the same and the latter is strong in the IR in this range. Therefore, it is reasonable to assign the band at 1510 cm^{-1} mainly to benzoid ring (B) stretching in PANI. Based on the following arguments, we consider the 1587 cm^{-1} band as a characteristic band of nitrogen quinone (Q).

(d) 1400-1240 cm^{-1}

This is the C-N stretching region for aromatic amines. The intrinsic PANI shows three peaks: medium absorption at 1240 cm^{-1} and weak ones at

1380 and 1240 cm^{-1} . The 1315 cm^{-1} peak is rapidly strengthened by HCl treatment. Here it would be worthy to point out that the reaction mechanism of PANI with HCl may involve the structure $=\overset{+}{\text{N}}\text{H}$ and $-\overset{+}{\text{N}}\text{H}$. The introduction of the positive charge leads to a great increases in molecular dipolar moment and thus IR activity. This is why all peaks in this region grow obviously during HCl doping or treatment. The band at 1160 and 1140 was referred as "electronic like band" and was considered as a measure of the degree of delocalization of electrons on PANI and thus are the characteristic peaks of PANI conductivity [34, 35]. The band at 1160 and 1140 cm^{-1} be assigned separately: 1160 cm^{-1} to intrinsic structure and 1140 cm^{-1} to the doped (HCl treated) structure. The 1140 cm^{-1} band is a vibrational mode of $\text{B-NH} = \text{Q}$ or $\text{B}-\overset{+}{\text{N}}\text{H}-\text{B}$ which is formed in doping reactions. This may be attributed to the existence of the positive charge and the distribution of the dihedral angle between the B and Q rings [36].

(e) 1220-500 cm^{-1}

This is the region of in-plane and out-of-plane bending of C-H bonds on aromatic rings. The main absorption bands for intrinsic PANI are located at 1160 and 830 cm^{-1} and some weak bands can be observed. It is easy to judge the substitution pattern on the benzene ring from the frequencies of these peaks. For example, 1220, 1105, 1010 and 830 cm^{-1} stands for 1,4-substitution, 1115, 1060, 960, 895 and 850 cm^{-1} for 1, 2, 4-substitution and 740 and 690 cm^{-1} for 1,2- or mono-substitution.

In summary, tentative assignment of the IR spectra of intrinsic PANI are listed in Table-1.

Table-1: Tentative assignment of the IR spectra of PANI sample.

Frequency (cm^{-1})	Assignment*
3710	presence of H_2O
3470	NH_2 asym. str.
3360	NH_2 sym. str., NH str
3175	$=\text{NH}$ str.
1563	str. of $\text{N}=\text{Q}=\text{N}$
1538	str. of $\text{N}-\text{B}-\text{N}$
1450	str. of benzene ring
1368	$\text{C}-\text{N}$ str. in QB_tQ
1315	$\text{C}-\text{N}$ str. in QB_cQ , QBB , BBQ
1245	$\text{C}-\text{N}$ str. in BBB
1160	a mode of $\text{N}=\text{Q}=\text{N}$
1140	a mode of $\text{Q}=\overset{+}{\text{N}}\text{H}-\text{B}$ or $\text{B}-\overset{+}{\text{N}}\text{H}-\text{B}$
1225	
1104	$\text{C}-\text{H}$ <i>ip</i> on 1,4-ring
1128	
1046	$\text{C}-\text{H}$ <i>ip</i> on 1,2,4-ring
952	
917	
875	$\text{C}-\text{H}$ <i>op</i> on 1,2,4-ring
847	
807	$\text{C}-\text{H}$ <i>ip</i> on 1,4-ring
759	
690	$\text{C}-\text{H}$ <i>ip</i> on 1,2-ring
659	
534	aromatic ring deformation
494	

* Abbreviations: asym = asymmetric, sym = symmetric, str = stretching, *ip* = in-plane bending, *op* = out-of-plane bending, Q = quinoid unit, B = benzoid unit, B_t = *trans* benzoid unit, B_c = *cis* benzoid unit.

D. X-ray diffraction pattern

Structural analysis by X-ray can provide information on the intermolecular arrangement, i.e. the level of crystallinity of a material. The PANI samples prepared chemically were examined for their structural analysis in the powdered state by using wide angle X-ray diffraction. The scattering patterns as function of the Bragg angle, 2θ at $\lambda = 1.54 \text{ \AA}$ for the studied PANI powders are presented in Fig. 8-10. The results show that the patterns consist of only diffuse x-ray scattering i.e., the peaks appear in the pattern are responsible for the amorphous nature of the sample. Most of the conducting polymers are reported to be extremely poor crystalline. During polymerization, although most of the aniline units are linked through the 1,4-position, a significant units are couple through other positions. This introduces defects in the hypothetical ideal linear chain arrangement of the polymer and also causes some cross-linking of the polymer and consequently results in a significant decrease in the crystallographic order of the chain [37, 38]. As a result, the polymer loses its crystallinity and leads diffuse diffraction pattern as exhibited in Fig. 8-10. Other well studied conducting polymer PP, has also been reported to be amorphous in nature [40]. The importance of a better intermolecular arrangement, i.e., a level of crystallinity in the PANI samples for obtaining a higher conductivity has become a well-accepted factor all around the world, and this idea is not restricted to PANI but involves most of the more prominent electronically conductive polymers. The observation that the conductivity of PANI films and fibre can be increased upon stretching is direct evidence for the importance of a good intermolecular arrangement. Effort is still paying for achieving the better PANI structure. Indeed, results of few studies have

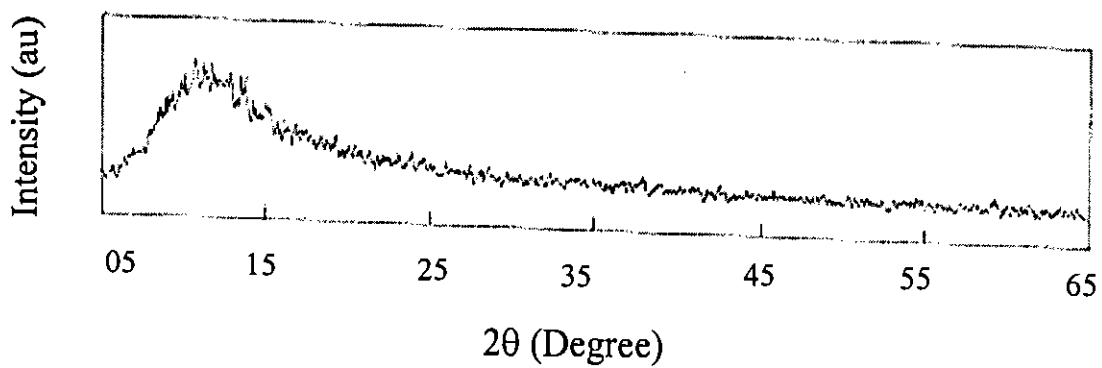


Fig. 8: XRD pattern of *a*-PANI.

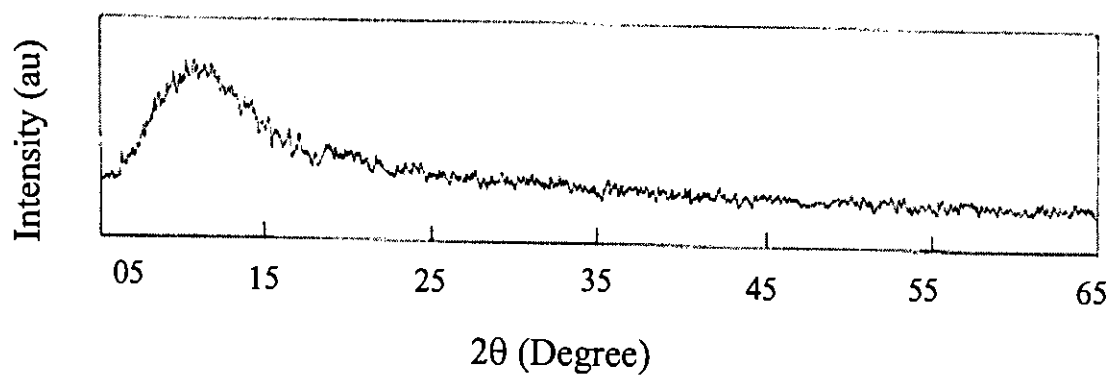


Fig. 9: XRD pattern of *n*-PANI.

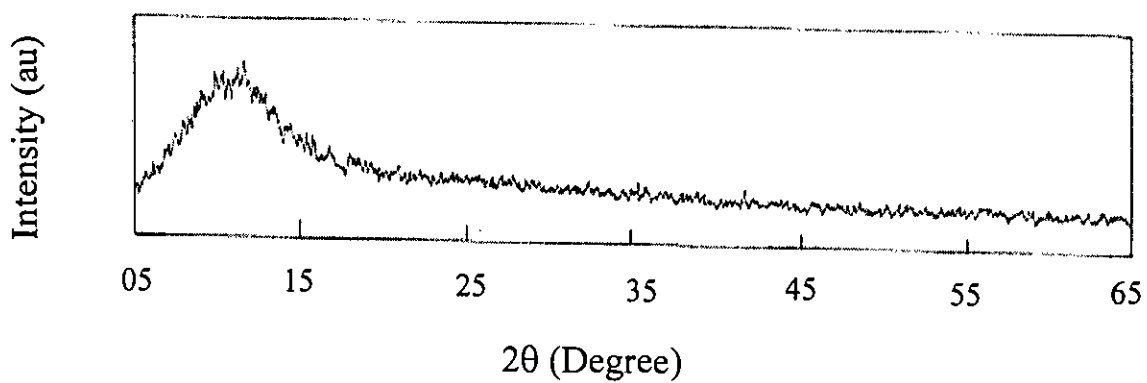


Fig.10: XRD pattern of *b*-PANI.

already been appeared and reported to be claimed the crystalline structure of PANI [40-42].

E. Surface morphology

Chemical composition and morphological structure of a material strongly depends on the mode of synthesis, be it chemical or electrochemical, on the synthesis conditions such as pH, concentration of reactants and products, chemical nature of oxidant, oxidation potential etc. Thus, there is a variety of possible chemical structure and morphology of a material may possible. Instead of varying the conditions of synthesis, in this study, PANI samples were synthesized under the same condition but a post-treatment of the PANI was made under different condition to examine if any change occurs in its physico- chemical and morphological properties. The morphology of the dried PANI powder thus treated was investigated using SEM. Figure 11 shows the SEM images of a PANI samples after treated with (1) aqueous HCl (pH=1.71), (2) distilled water (pH =6.86) and (3) aqueous NH₄OH (pH=10.01). It can be seen that on treatment, the morphology of the PANI affected considerably. In (1), acid treatment of PANI results in a hierarchy of agglomerates and piled up over the substrate. When the PANI is treated with distilled water, the aggregates seem to exhibit granular morphology that assembled in a short body and distributed non-uniformly over the substrate. On treatment of the PANI with a basic solution, granular morphology of the PANI also results. The granular particles aggregate in a body like a broken brick showing, at least few of them, regular size with sharp edges. Thus, the present result clearly demonstrates that surface morphology can be controlled by post-synthesis treatment of the PANI with the solution of different pH. Modification of the

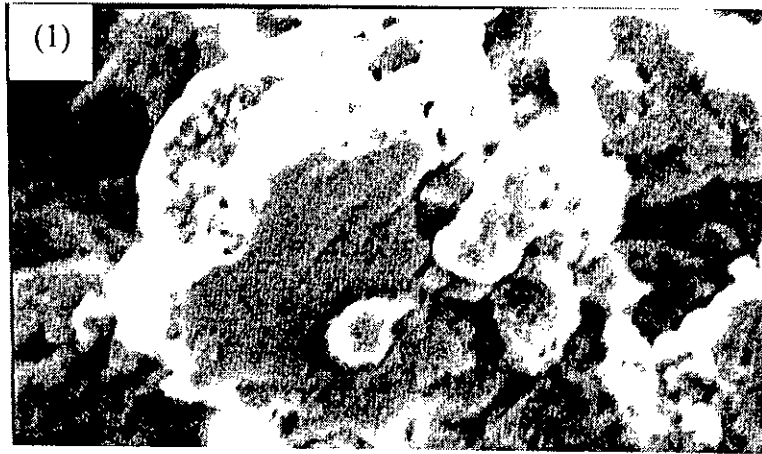


Fig. 11: SEM micrographs of (1) *a*-PANI, (2) *n*-PANI and (3) *b*-PANI. Magnification: 2000x.

PANI surface morphology is also reported by the various works [37, 38] by varying synthesis conditions. From the observed dissimilar morphological features of the acidic, basic and neutral PANI studied in this work, it may be expected that their surface behaviors toward adsorption could be different.

3.3 Surface processes on PANI substrates

Conducting polymers can be made charged and discharged by doping (oxidation / protonation) and undoping, respectively. Thus, it is expected that the charged polymer matrix could bind oppositely charged species on its surface and hence, removal of that species could be possible from the phase under investigation. From this point of view, chemically synthesized PANI was treated with aqueous solution of various pH expecting the PANI to be charged positively and negatively and can effect removal of oppositely charged particle from a solution phase. On treatment, interestingly, significant differences in the morphological feature of the PANI were also observed. These observations made us interested to study surface processes on the PANI matrices. In this respect, aqueous solutions of organic dyes, viz. cationic MB and anionic PR and inorganic salt, such as NiCl_2 were prepared in various pH and examined their removal by using PANI substrates. The results are summarize below:

A. Removal of MB from its aqueous solution

The amount of the dye, MB removal with time by PANI substrates in contact with the dye solutions containing 1.93×10^{-5} M MB was determined. Figure 12 shows the change in absorbance of MB solution (pH=1.95) with time after charging it to the absorbent, *a*-PANI (0.464g). The result shows a

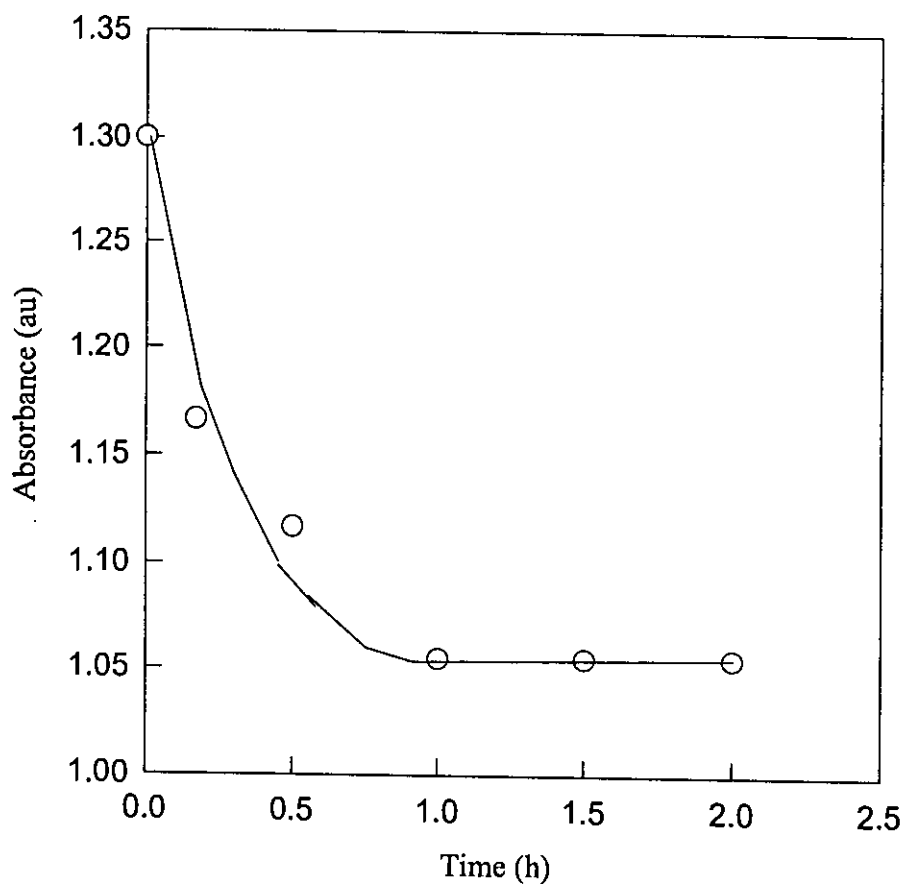


Fig.12: Absorbance vs time during MB adsorption on α -PANI.

decrease in absorbance at various intervals of time. The decrease in absorbance obviously account for a decrease in the dye concentration of original solution. Thus, the result indicates that MB is removed or uptaken as a consequence of the adsorption of the MB by *a*-PANI. The result was further analyzed by converting the observed absorbance to the corresponding concentration. This is presented in Fig.13. Indeed, Y-axis gives the concentration of MB unadsorbed at different time. It can be seen from the result that at the beginning, there is a rapid decrease in the MB concentration followed by a gradual equilibrium condition reached within approximately 2h.

Removal process of the cationic MB by *n*-PANI and *b*-PANI was also examined. The *n*-PANI and *b*-PANI matrices were treated with aqueous solutions of pH 6.86 and 10.01, respectively. Thus, these substrates may differ from *a*-PANI which was treated with an aqueous solution of pH =1.71. We assume that, since *a*-PANI is positively charged [43-44], the *n*-PANI and *b*-PANI should be oppositely charged or at least neutral. However the removal of cationic MB was also attempted using these matrices. Figures 14-15 describe the removal of the cationic MB by the *n*-PANI substrate while the Figures 16-17 represent the removal of the same MB using *b*-PANI one.

The results of the amount of cationic MB taken up by *a*-PANI, *n*-PANI and *b*-PANI are compared and described below: Figure 18 shows the spectral feature of the MB solution before and after 2h adsorption by the matrices. The spectra clearly suggest that the extent of the adsorption is largely depends on the nature of the PANI employed as adsorbents. With the *b*-PANI, the dye shows a large amount of adsorption whereas, the adsorption on the *a*-PANI and *n*-PANI substrates are less significant.

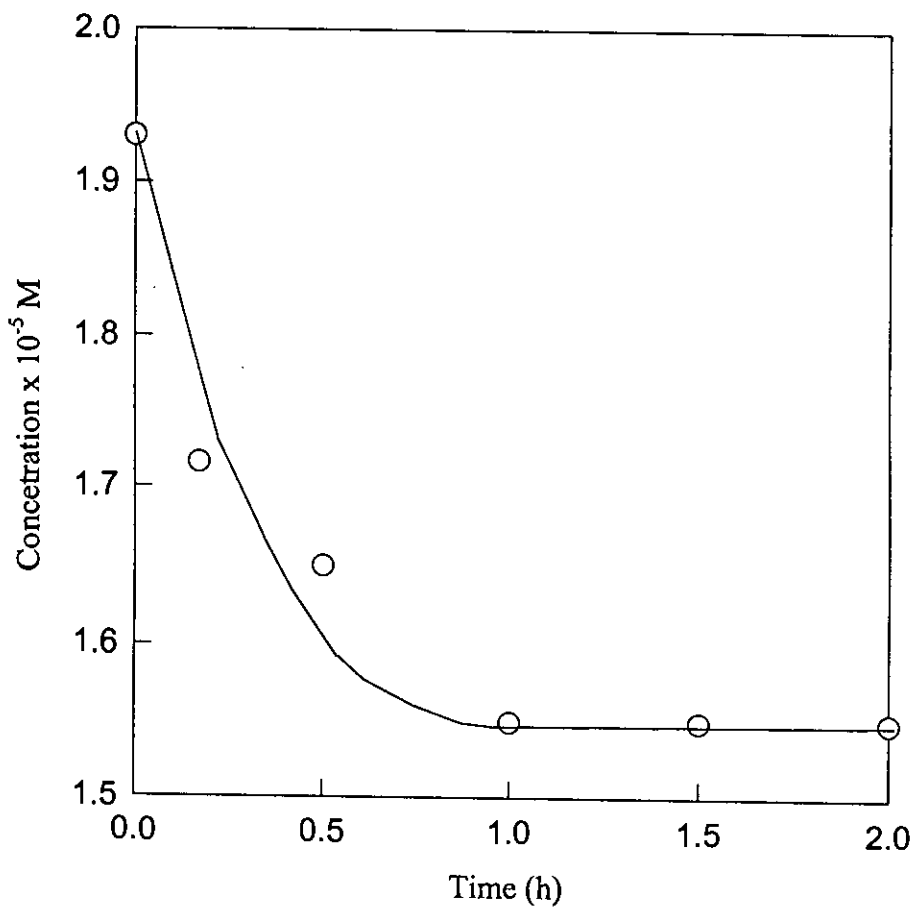


Fig.13: Concentration vs time during MB adsorption on *a*-PANI.

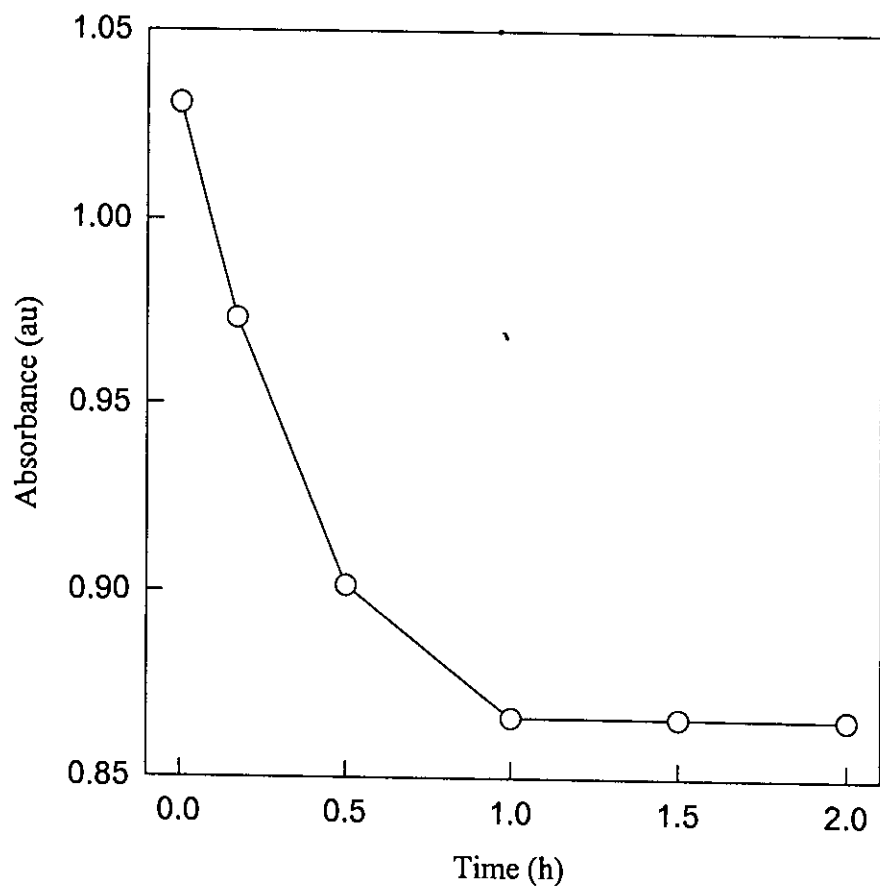


Fig.14: Absorbance vs time during MB adsorption on *n*-PANI.

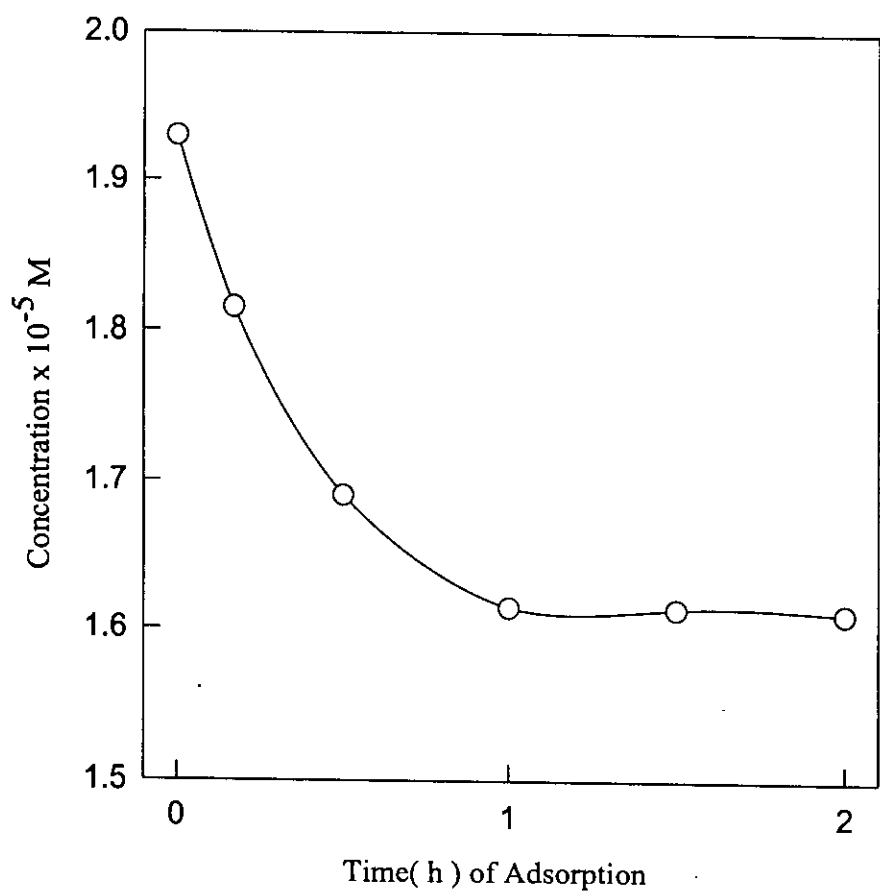


Fig.15: Concentration vs time during MB adsorption on *n*-PANI.

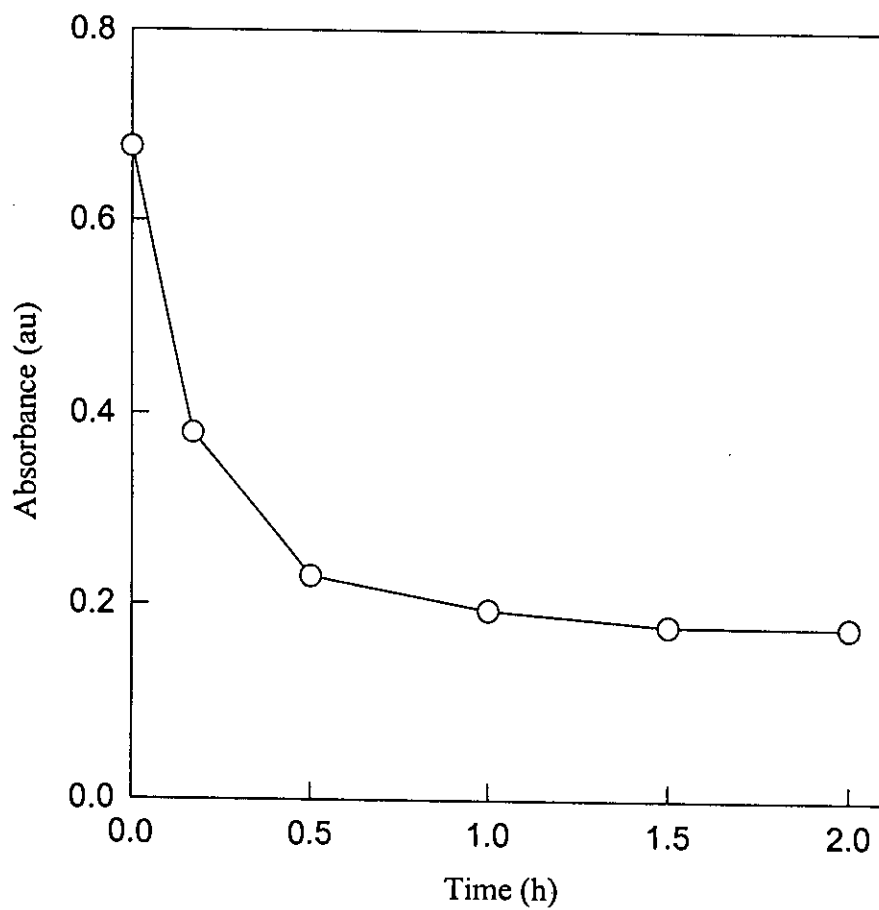


Fig.16: Absorbance vs time during MB adsorption on *b*-PANI.

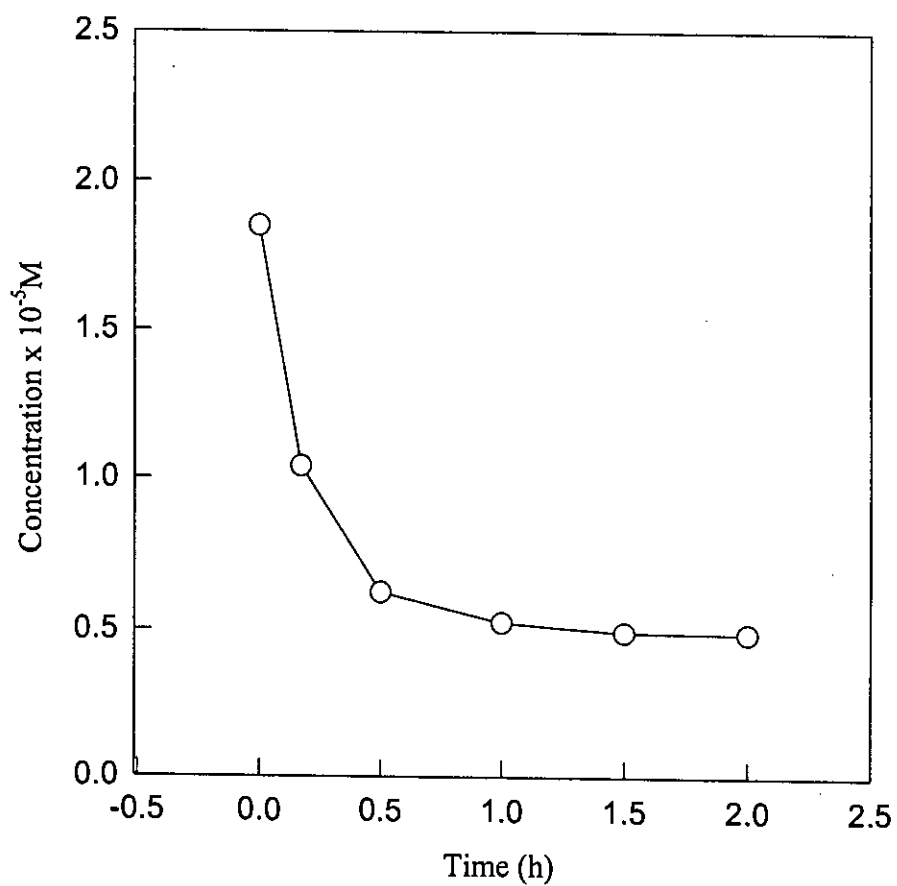


Fig.17: Concentration vs time during MB adsorption on *b*-PANI.

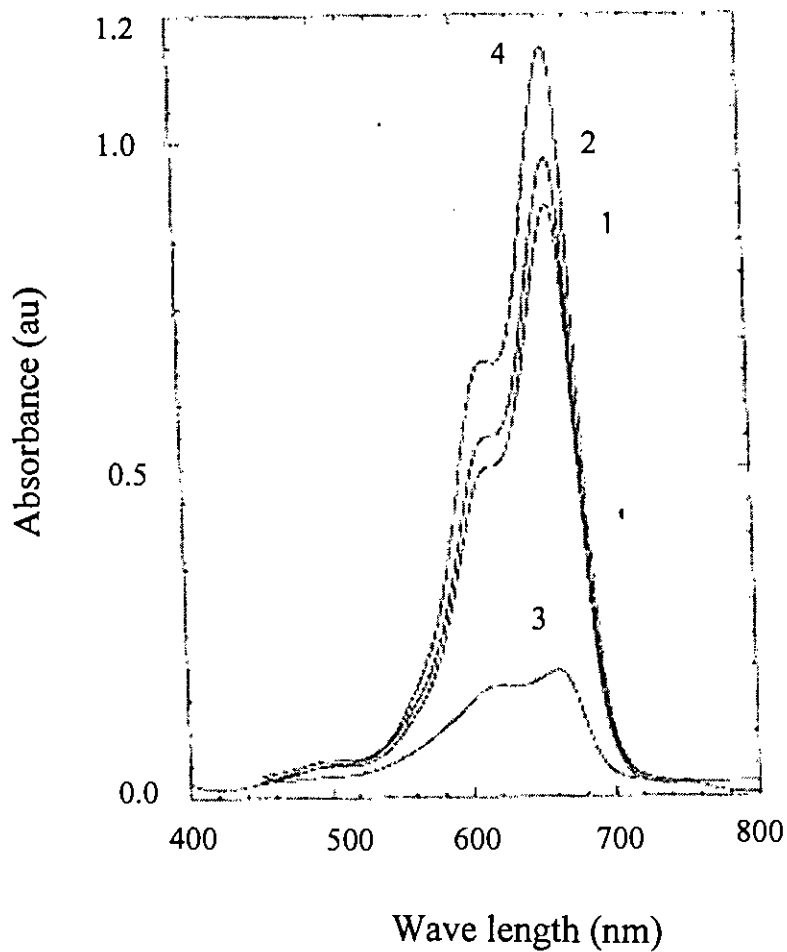


Fig.18: Typical spectral feature after 2h of MB adsorption on (1) *a*-PANI, (2) *n*- PANI, (3) *b*-PANI and (4) stock solution of MB before adsorption.

Figure 19 shows the amount of MB adsorption with time. For all the substrates employed, removal of the dye by adsorption increases rapidly for the initial 30 min and attain the state of equilibrium within 2h. It is worth noticing that the rate of adsorption and also the amount of cationic MB adsorbed on the *b*-PANI is significantly higher than that of *a*-PANI and *n*-PANI. This result clearly indicates that adsorption process is largely depend on the nature of the electrical charge of the adsorbate and adsorbent employed.

Since *a*-PANI is considered to be positively charged, the insignificant adsorption of cationic MB on such a positively charged adsorbent seems to be likely, if one consider the electrostatic repulsion between the adsorbate and adsorbent. However, a very small amount of adsorption still takes place. This may be due to trapping of the MB molecules by the porous sites of the matrix. The adsorption on *n*-PANI is seen to be the lowest one. The porosity in this case may be less and thus provides a smaller surface area. Accordingly, a small amount of adsorption is expected for *n*-PANI. A considerable amount of MB adsorbed on *b*-PANI suggests that the surface charge on the polymer at this pH (~10.01) should be negative. For inorganic semiconducting oxides, there is a pH called pH_{zpc} , at which the surface charge is zero. Above and below the pH_{zpc} the surface charge is negative and positive, respectively [45, 46]. The observed finding also seems to suggest the same kind of behaviour for polymeric semiconductor like PANI.

The measurements of pH and molar conductance of the MB solution with time gives further evidence for the selectivity of the adsorbents for the removal of MB. Figure 20 shows the change of pH of MB solution at different time of its removal. The result shows that although not significant, some changes in pH occur during the removal process. The pH of the MB

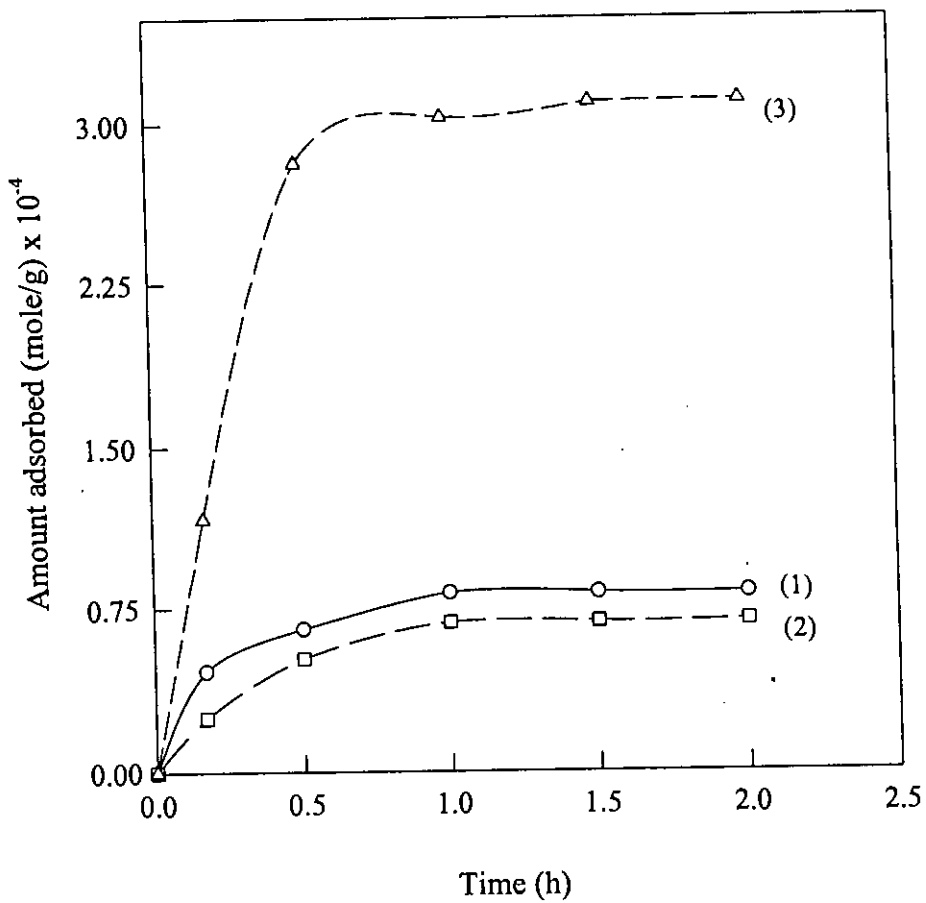


Fig.19: Amount of MB adsorbed with time on (1) *a*-PANI, (2) *n*- PANI and (3) *b*-PANI.

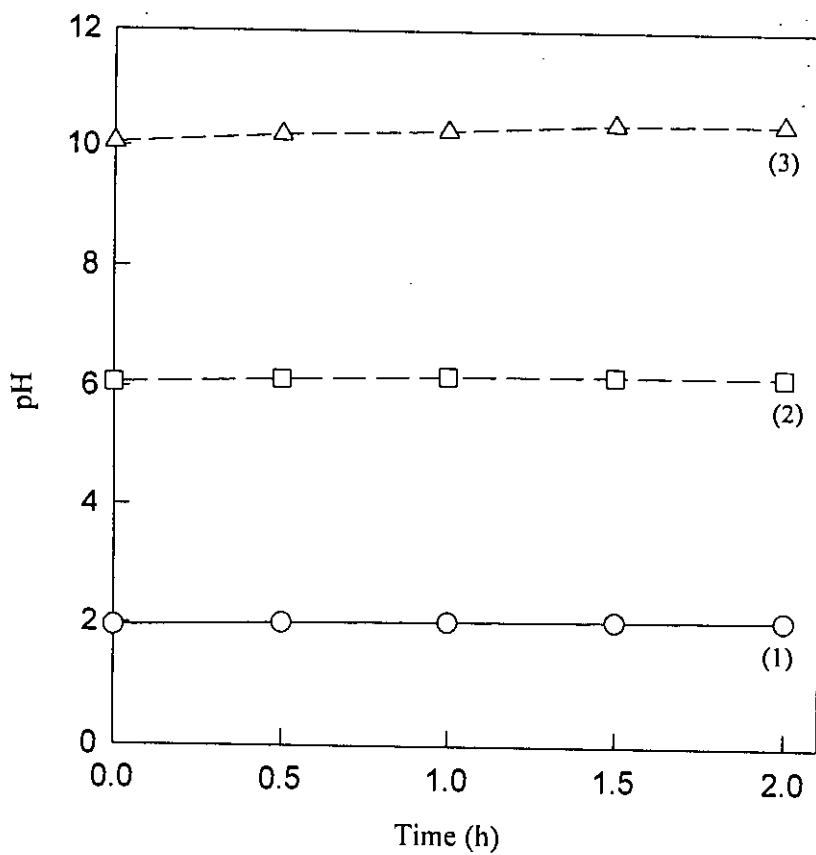


Fig. 20: Change of pH during MB adsorption on (1) α -PANI, (2) n -PANI and (3) b -PANI.

solution enhanced by ~ 0.36 after 2h adsorption on *b*-PANI while its increase is comparatively much less, when adsorbed on either of *a*-PANI or *n*-PANI substances. The increases of pH of the MB solution can easily be realized if one considers the removal of cationic species from the solution. The result in Fig.19 clearly demonstrated that *b*-PANI can adsorb highest amount of MB compared to those of *a*-PANI and *n*-PANI. Thus, the magnitude of pH changes depicted in Fig.20 seems to be consistent with the previous results described in Fig.19. Figure 21 shows the change in molar conductance of MB solution during its adsorption on *a*-PANI, *n*-PANI and *b*-PANI. It is evident from the result that with the progress of adsorption, molar conductance of the MB increases. In principle, molar conductance of a solution should increase if the concentration of the solution decreases. Thus, the observed increment of molar conductance with time as seen in Fig.21 indicates that concentration of MB is decreasing with time. The decrease of MB concentration could be the consequence of its adsorption on the adsorbents employed. The relative larger increment of molar conductance with *b*-PANI, thus indicates further that amount of MB adsorbed on *b*-PANI is greater than that with *a*-PANI and *n*-PANI. The larger amount of cationic MB adsorption on the *b*-PANI may be ascribed due to adsorption influence by the electrostatic force of attraction between the adsorbate and adsorbent. The observed change in molar conductance data seems to be consistent with the findings described in Fig.19.

With respect to the cationic MB adsorption by the *b*-PANI, Fig.22 shows the amount of MB, '*x*' gram adsorbed on, '*m*' gram of *b*-PANI, as a function of the equilibrium concentration C_e . Where '*K*' is the adsorption co-efficient and '*k*' is the proportionality constant. The isotherm seems to

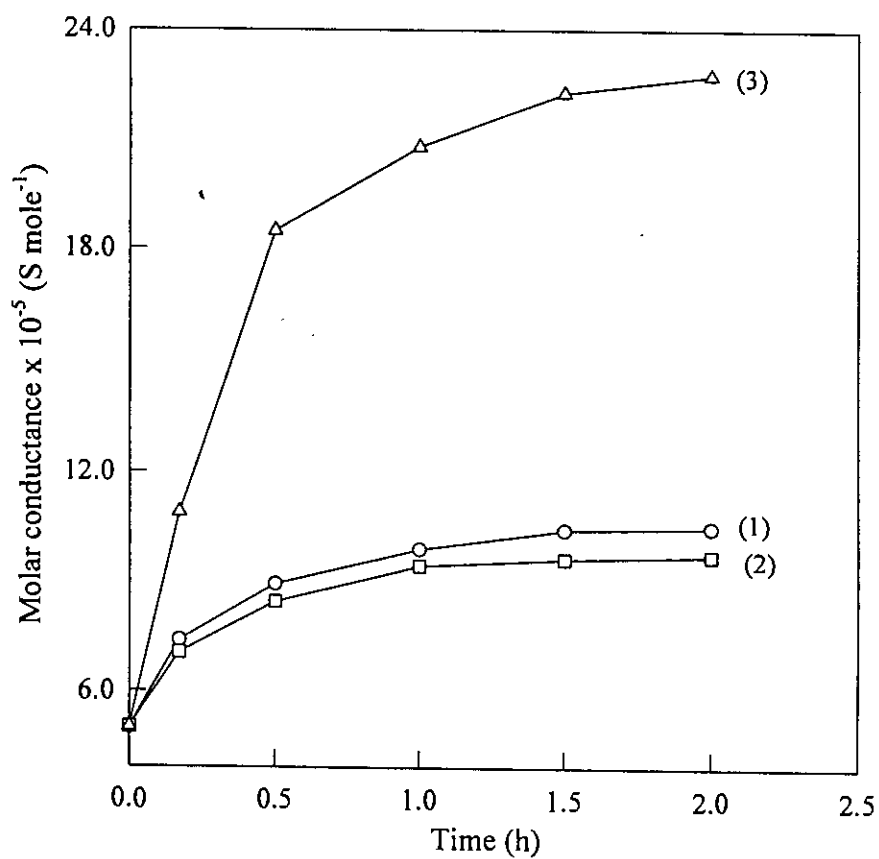


Fig. 21: Change of molar conductance during MB adsorption on (1) α -PANI, (2) n -PANI and (3) b -PANI. The quantity 24.43 and 1224.43 are subtracted from the original molar conductance data of curve (1) and (3), respectively.

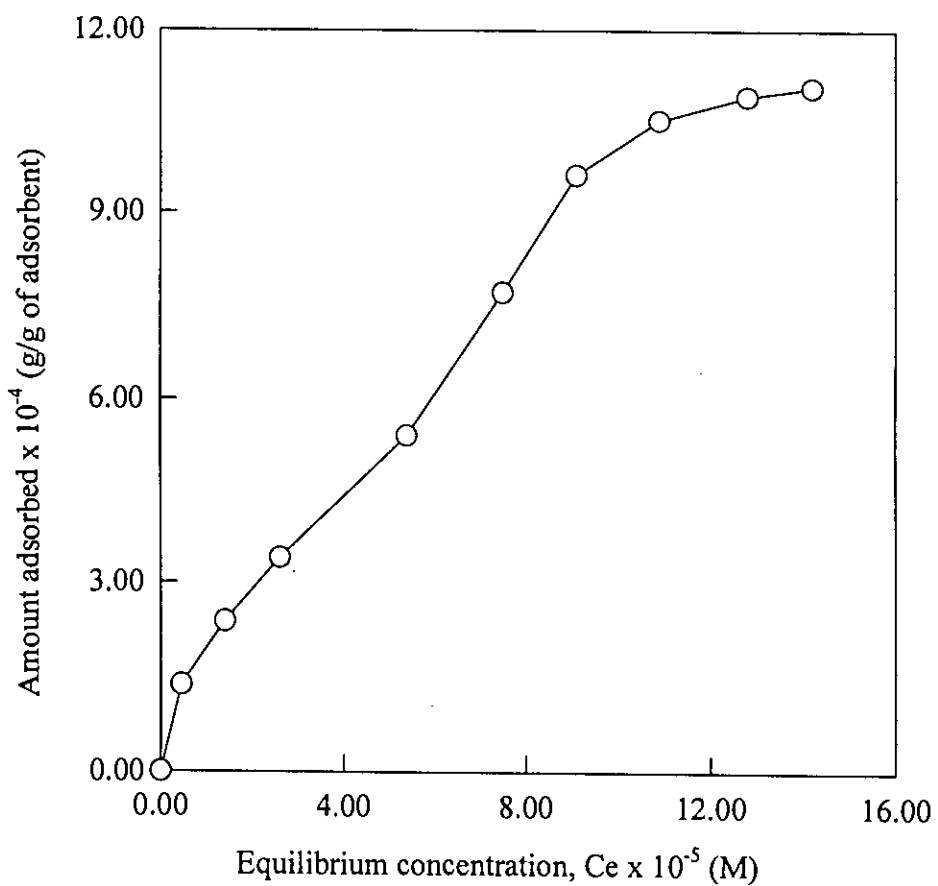


Fig. 22: MB adsorption isotherm on *b*-PANI substrate at 30°C.

follow Langmuir equation. The following equation is used to draw the isotherm.

$$\frac{x}{m} = \frac{C_e kK}{1 + KC_e}$$

B. Removal of PR from its aqueous solution

The uptake of the anionic dye, PR by PANI substrates having different surface charge was also studied. A definite concentration of PR ($1.93 \times 10^{-5} \text{M}$) was allowed to be in contacted with different substrates, *viz*, *a*-PANI, *n*-PANI and *b*-PANI of a known mass ($\sim 0.464 \text{g}$). The PR solution was withdrawn at various intervals of time for its spectroscopic measurements. The result are presented in Fig. 23-28.

The different surface charge on the PANI at different pH becomes much more evident, if the adsorption of the anionic dye, PR on PANI is studied. Figure 29 shows the spectral feature for the stock solution of PR and the solutions withdrawn after 2h of adsorption on the PANI matrices. The amount of the anionic PR adsorbed on the *a*-PANI, *n*-PANI and *b*-PANI are plotted against time in Fig.30. The time to reach equilibrium is seen to be about 2h, in this case too. The result shows that the amount of PR uptaken by *a*-PANI is significantly higher compared to that amount by *n*-PANI and *b*-PANI. Since PR is a negative dye and *a*-PANI is believed to be positively charged, the considerably large amount of adsorption on the *a*-PANI might be influence by the electrostatic attraction between the PR and *a*-PANI. Cationic MB was also found to be adsorbed preferentially on *b*-PANI, assume to be negatively charged substrate, possibly influence similarly by the electrostatic force of attraction. Considerably lower amount of PR

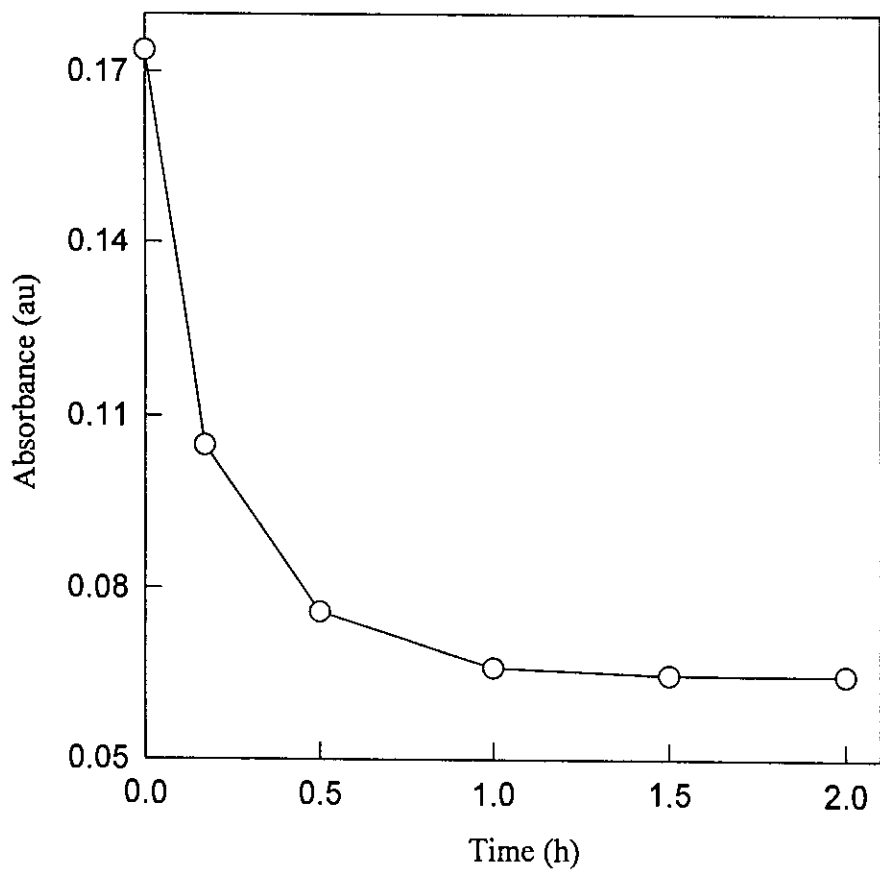


Fig. 23: Absorbance vs time during PR adsorption on α -PANI.

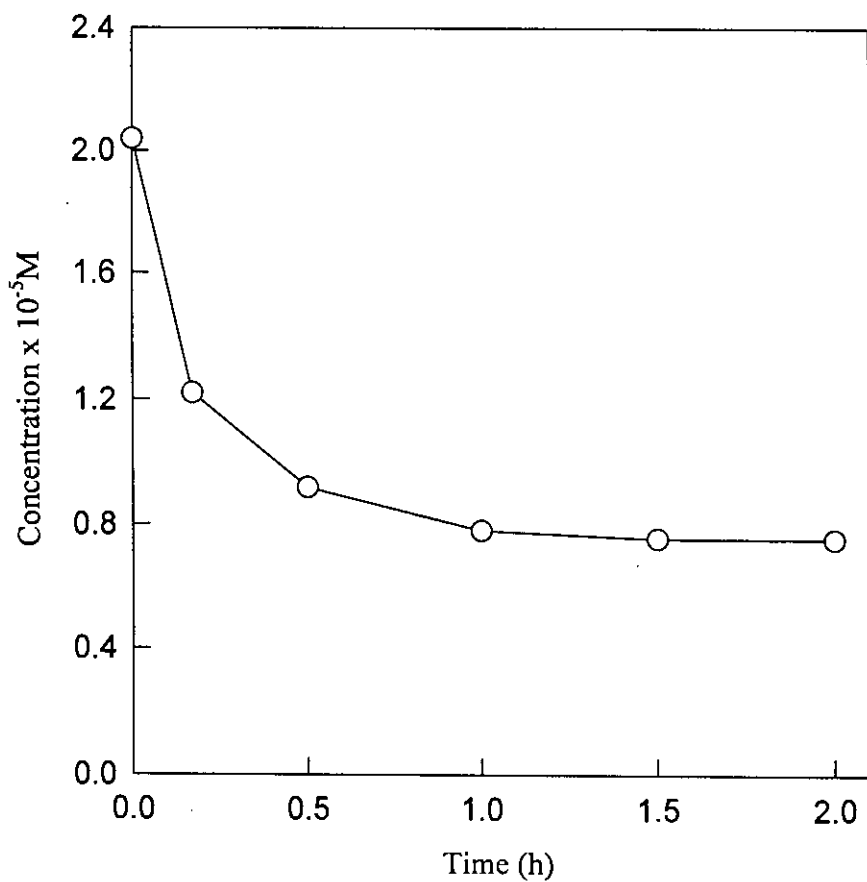


Fig. 24: Concentration vs time during PR adsorption on α -PANI.

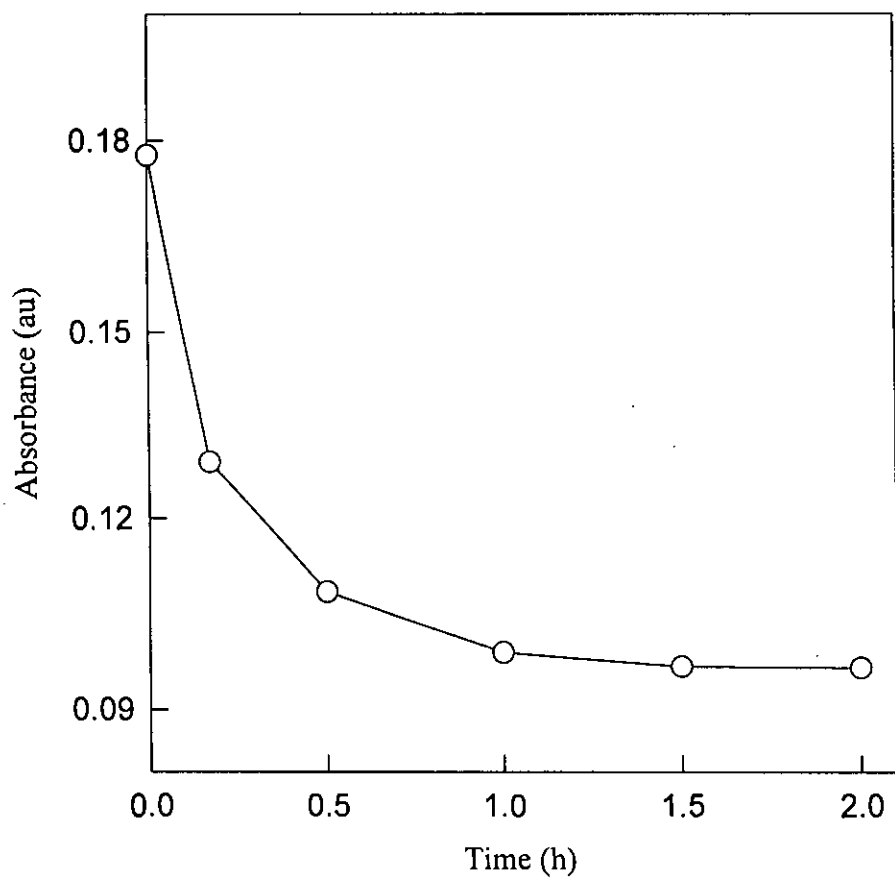


Fig. 25: Absorbance vs time during PR adsorption on *n*-PANI.

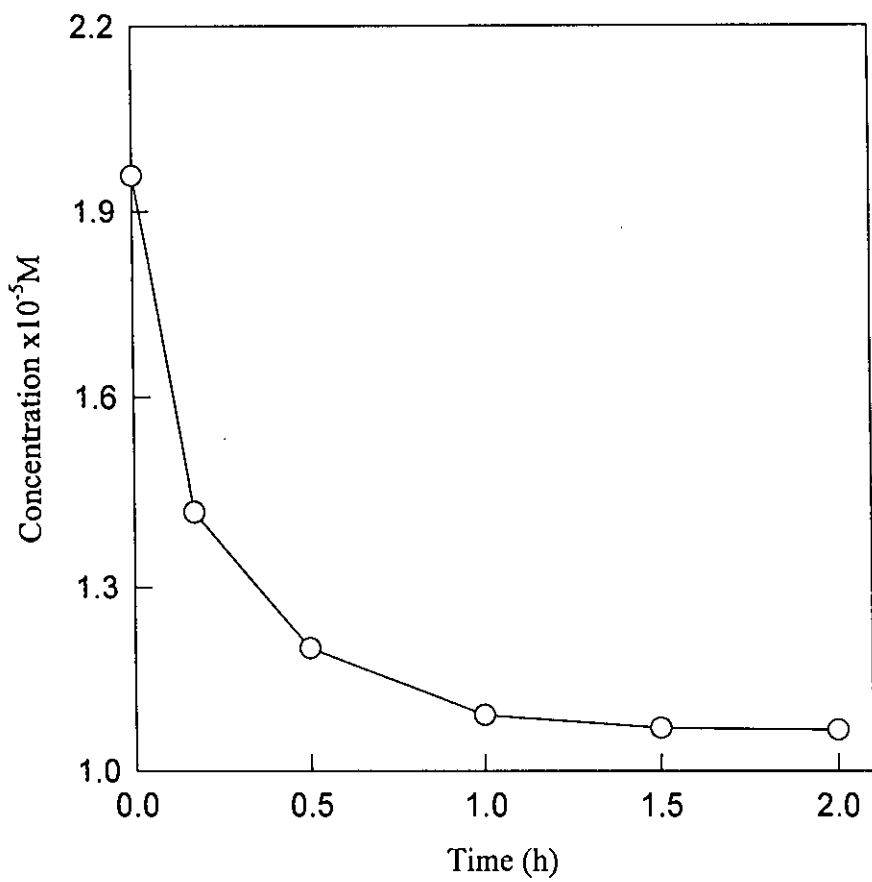


Fig. 26: Concentration vs time during PR adsorption on *n*-PANI.

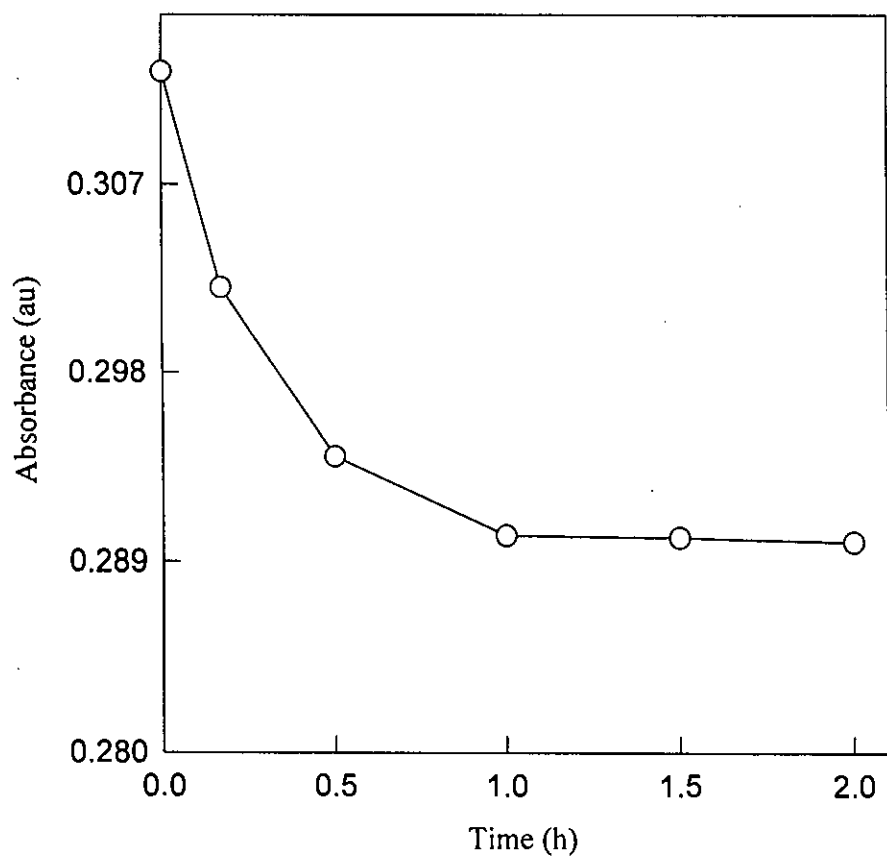


Fig. 27: Absorbance vs time during PR adsorption on *b*-PANI.

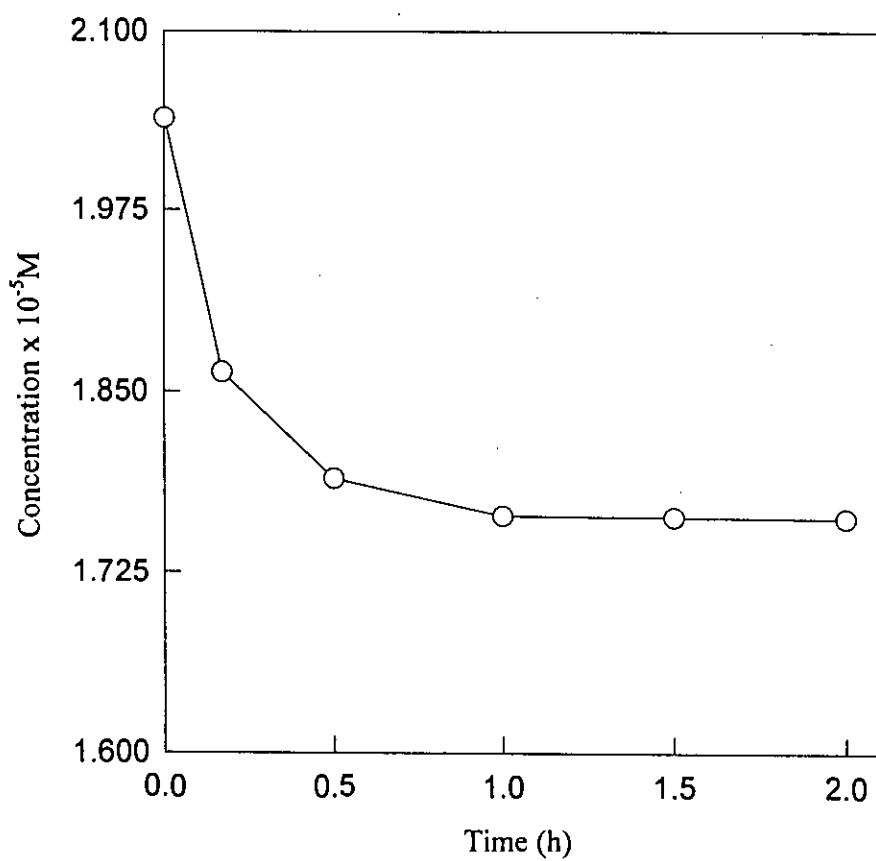


Fig. 28: Concentration vs time during PR adsorption on *b*-PANI.

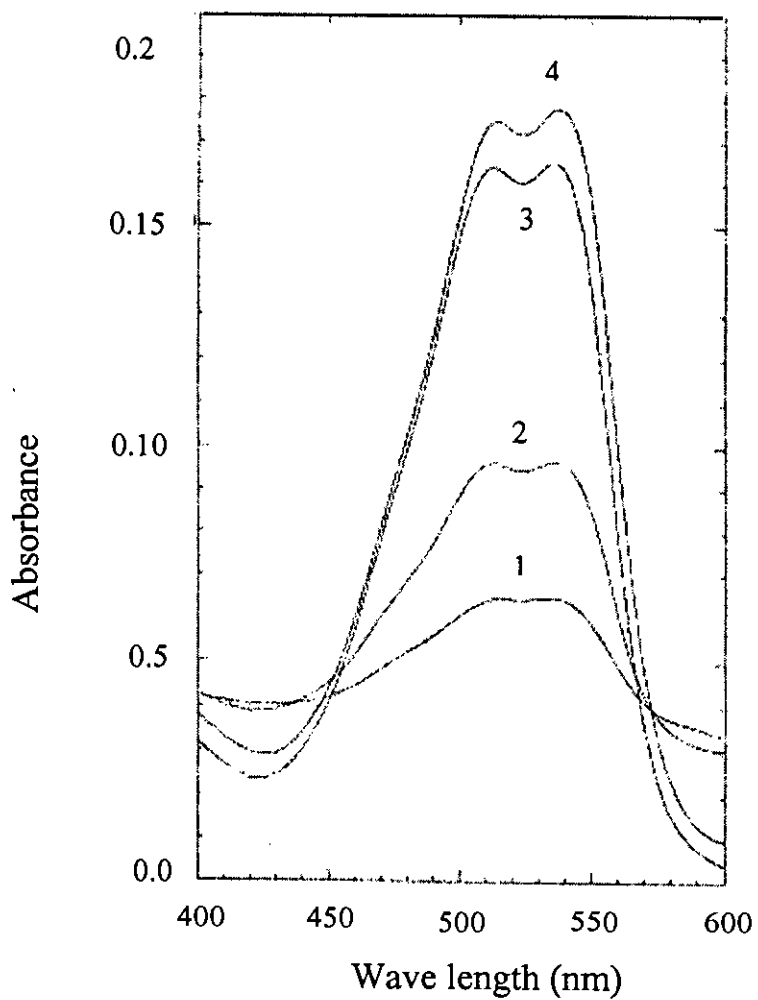


Fig. 29: Typical spectral feature after 2h of PR adsorption on (1) *a*-PANI, (2) *n*-PANI, (3) *b*-PANI and (4) stock solution of PR before adsorption.

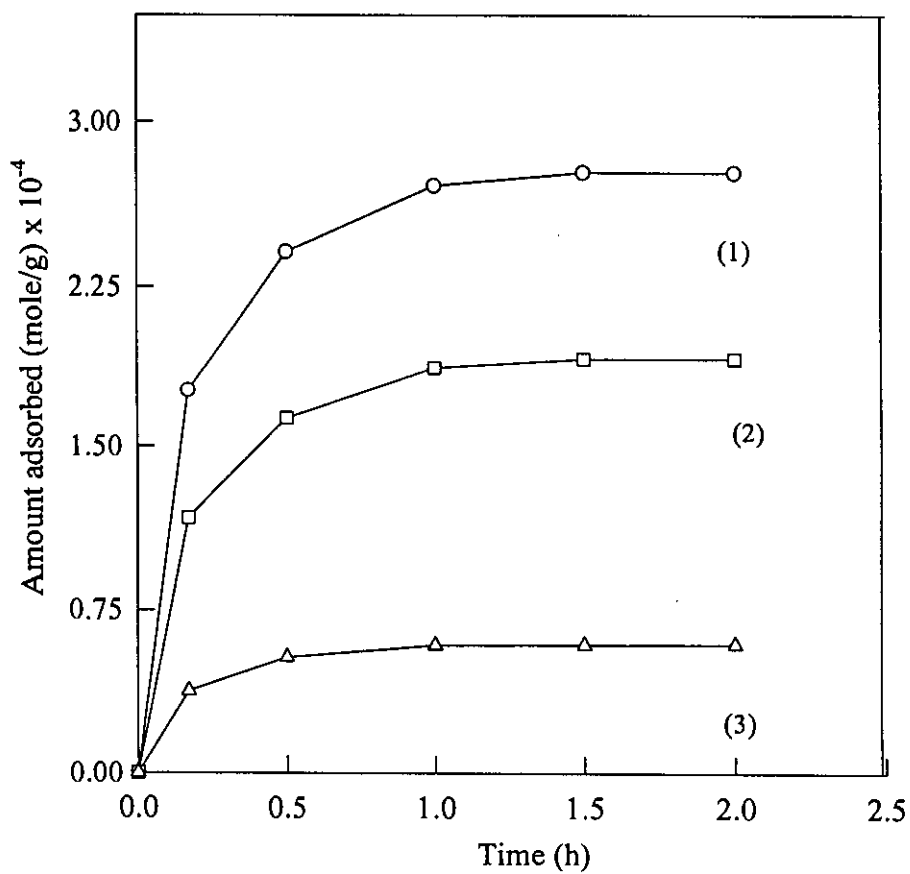


Fig. 30: Amount of PR absorbed with time on (1) *a*-PANI, (2) *n*-PANI and (3) *b*-PANI.

adsorbed on the *n*-PANI and *b*-PANI seems to be reasonable if one consider insignificant electrostatic attraction between PR and the PANI substrates.

Figure 31 shows the change of pH of the PR solutions at different time of adsorption. The magnitude of pH changes is also not very prominent however, careful observation reveals that the pH of the PR solutions turns to downward with the progress of adsorption. This means that the pH of the solution decline from its value that exists in the solution before adsorption. This can happen if anionic species are removed from the solution. Thus, the result again in agreement with the view that *a*-PANI is positively charged and preferentially removed the anionic PR from its solution by electrostatic nature of adsorption.

Figure 32 shows the change of molar conductance of PR solution with time during its removal process employing *a*-PANI, *n*-PANI and *b*-PANI substrates. A significant increase in the molar conductance of the PR solution is observed with *a*-PANI and *b*-PANI substrates while considerably small increment of molar conductance can be seen if *a*-PANI employed. Since higher molar conductance results from the decrease of concentration of a solution, the present results suggests further that anionic PR is preferentially adsorbed on the positively charged *a*-PANI substrate by electrostatic nature of adsorption. It is interesting to note here that only a little or insignificant amount of PR is found to be adsorbed on the anionic substrate, *b*-PANI. However, adsorption of PR on *n*-PANI is seen to be occurred to some extent, although much less than that observed on *a*-PANI. This may be due to the complete physical force operating between PR and *n*-PANI.

Figure 33 shows the isotherm during the adsorption of PR on *a*-PANI. This isotherm also seems to follow Langmuir type as found for MB.

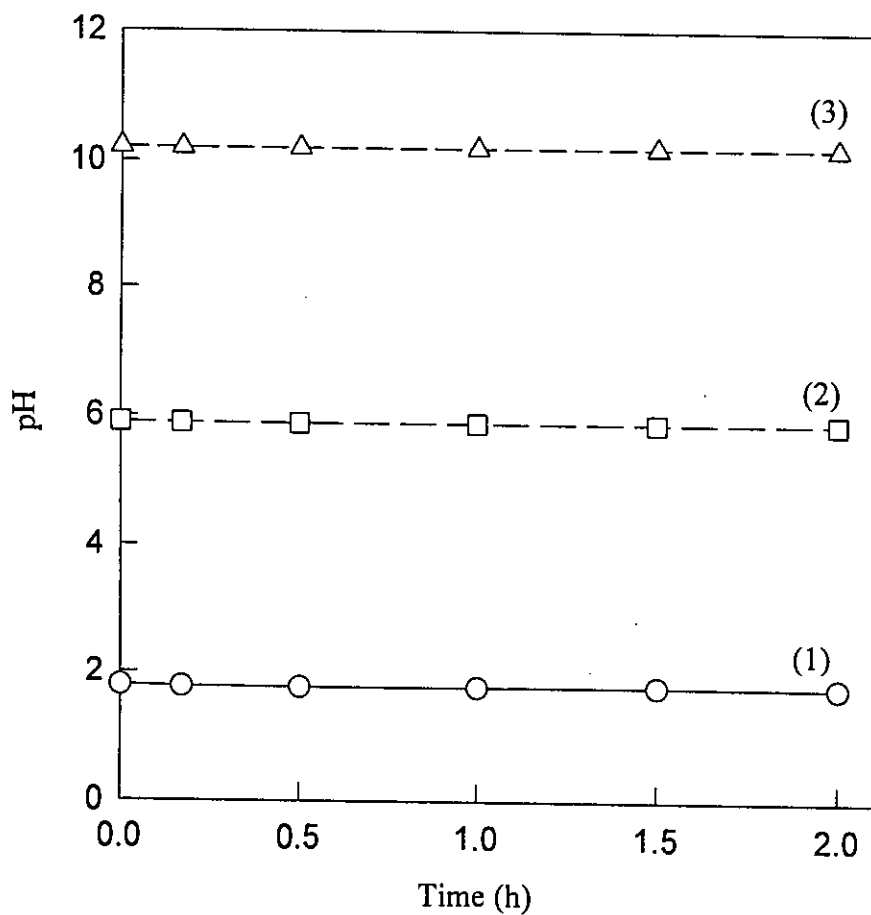


Fig. 31: Change of pH during PR adsorption on (1) *a*-PANI, (2) *n*-PANI and (3) *b*-PANI.

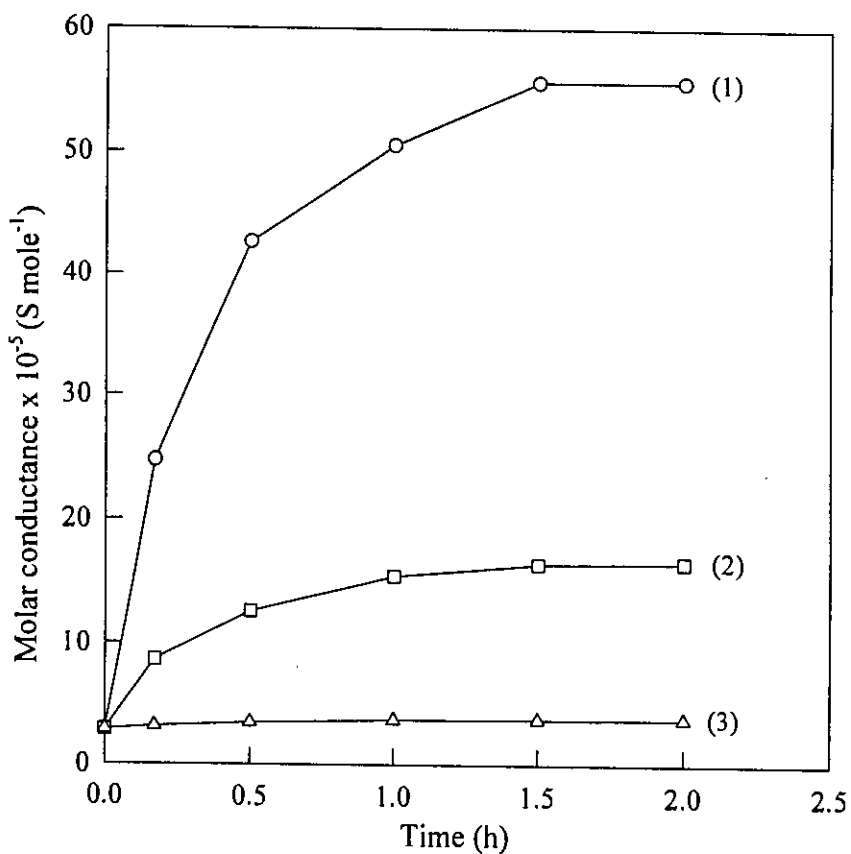


Fig. 32: Change of molar conductance during PR adsorption on (1) α -PANI, (2) n -PANI and (3) b -PANI. The quantity 1093.44 and 31.76 are subtracted from the original molar conductance data of curve (1) and (3), respectively.

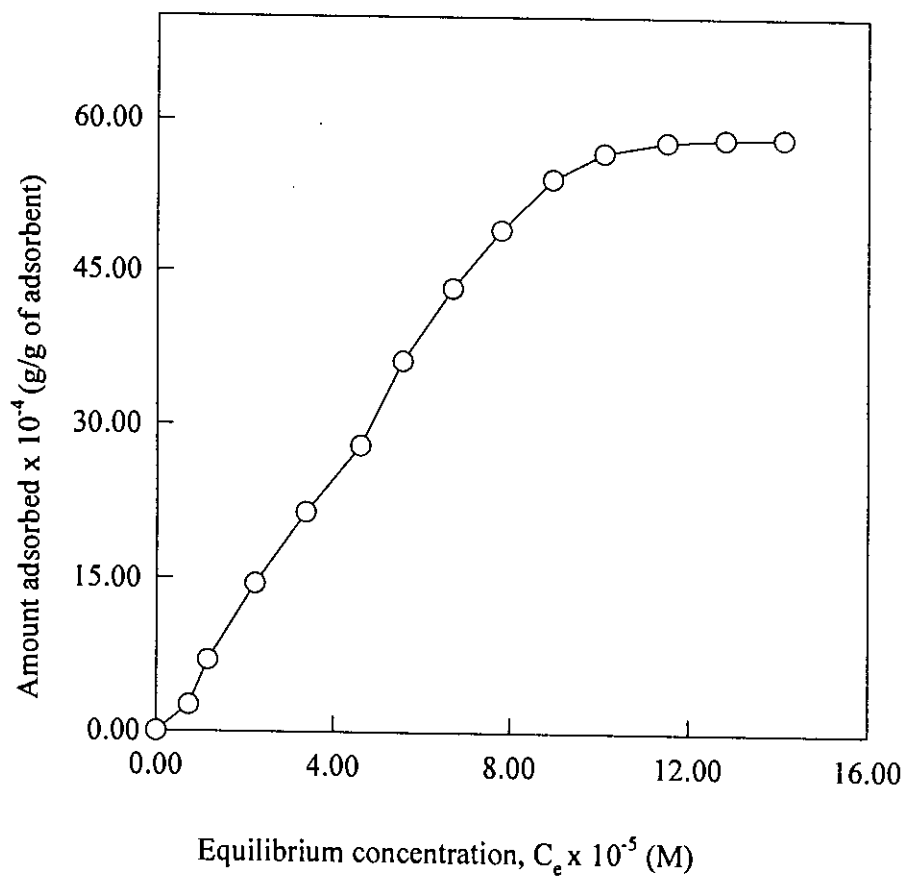


Fig. 33: PR adsorption isotherm on α -PANI substrate at 30°C.

C. Removal of NiCl_2 from its aqueous solution

In the present study, attempt was also made to determine the uptake of inorganic adsorbate uptake by the PANI matrices. For this purpose, an inorganic salt, *viz.*, NiCl_2 was employed. The aqueous solution of NiCl_2 both in acid (pH=1.71) and distilled water (pH=6.86) were prepared. In order to effect its removal, a definite concentration of NiCl_2 solution was exposed to a known mass of PANI ($\sim 0.464\text{g}$). The nickel solution was withdrawn occasionally for spectroscopic measurement as before. Figure 34 and 35 show the spectral feature of NiCl_2 solutions during the course of its removal from the solutions. The result shows that the decline of absorbance with time is significantly less. Even after 2h, only a slight decrease in the absorbance of the solution was observed. The capacity of the PANI for the removal of inorganic salt seems to be very low compared to that of organic dye. However, the spectral data was converted to the corresponding amount of the salt absorbed. This is shown in Fig. 36. The result shows that the state of equilibrium is not probably attained even after 2h adsorption. The amount adsorbed after 2h by the PANI seems to be very low. Both the adsorbents, *a*-PANI and *n*-PANI show hardly any differences in the adsorption capacity and kinetics. The selectivity of the adsorbent as observed for the removal of organic dyes, could not be examined fully in this case, since in the removal of dye, *b*-PANI was employed as adsorbate to allow absorption from a basic solution. The basic solution of NiCl_2 , however, was found to be quite unstable. The insignificant adsorption of inorganics by the PANI adsorbent is not clear at this stage. The longer adsorption time could be effective to get appreciable adsorption of the inorganics. In a previous study [47], uptake of some metal salts by polymeric materials show time to reach equilibrium adsorption is as long as 48 h. In an another report [48], an ion interchange

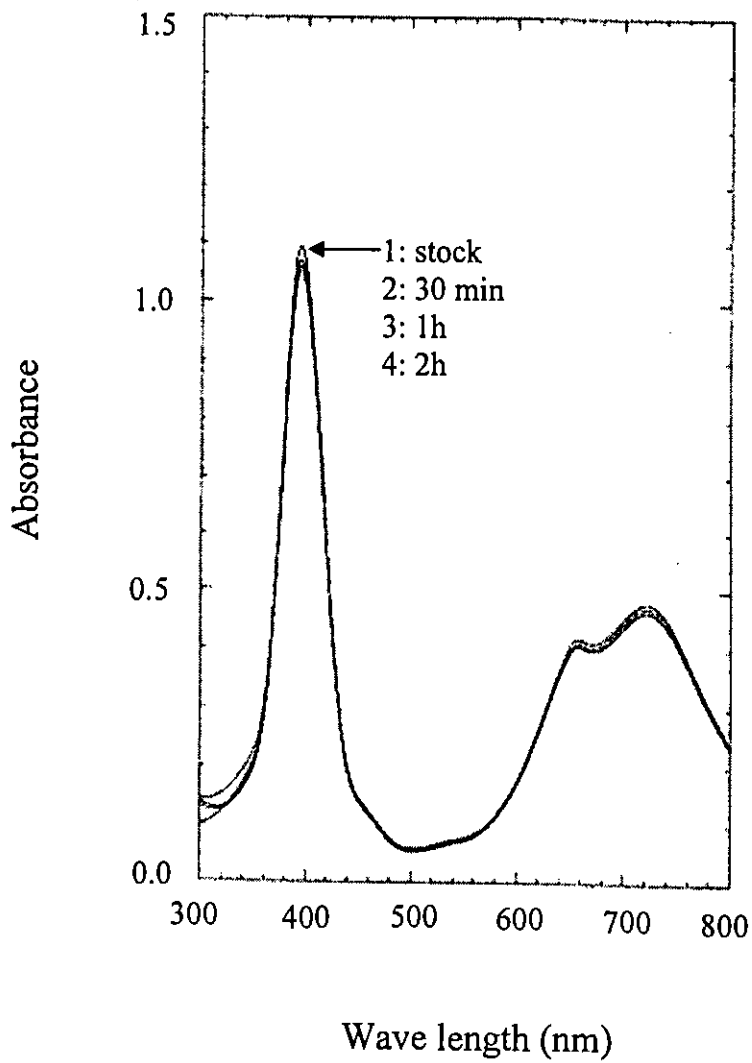


Fig. 34: Typical spectral feature of NiCl₂ solution (1) for stock and (2, 3, 4) are for after adsorption on α - PANI at different time.

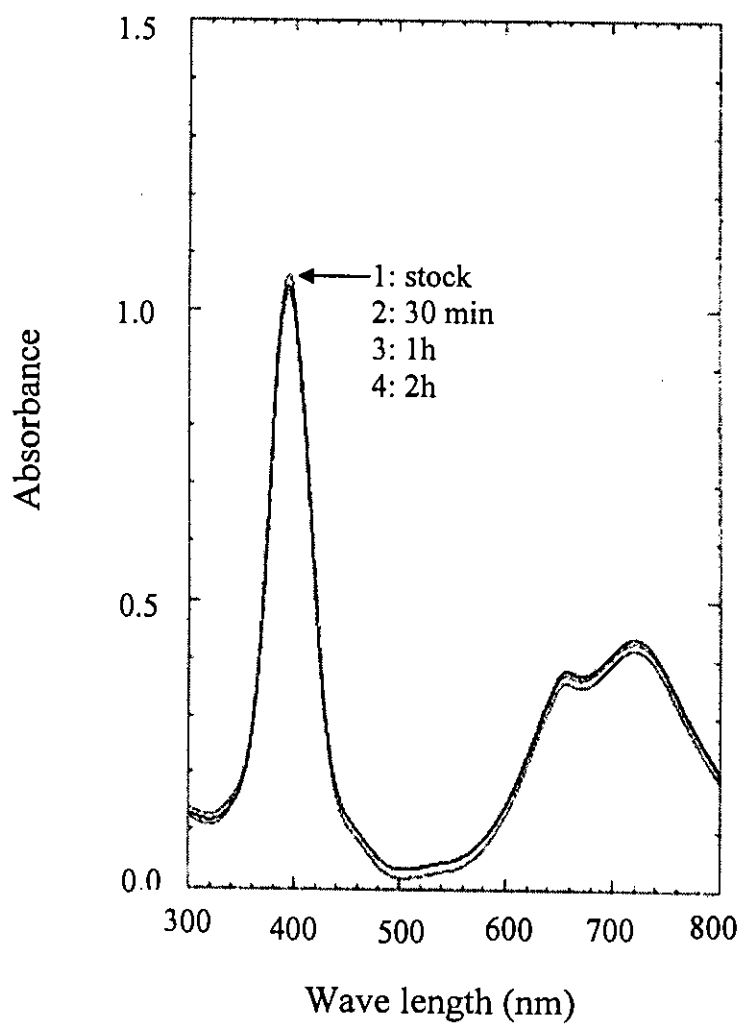


Fig. 35: Typical spectral feature of NiCl₂ solution (1) for stock and (2, 3, 4) are for after adsorption on *n*-PANI at different time.

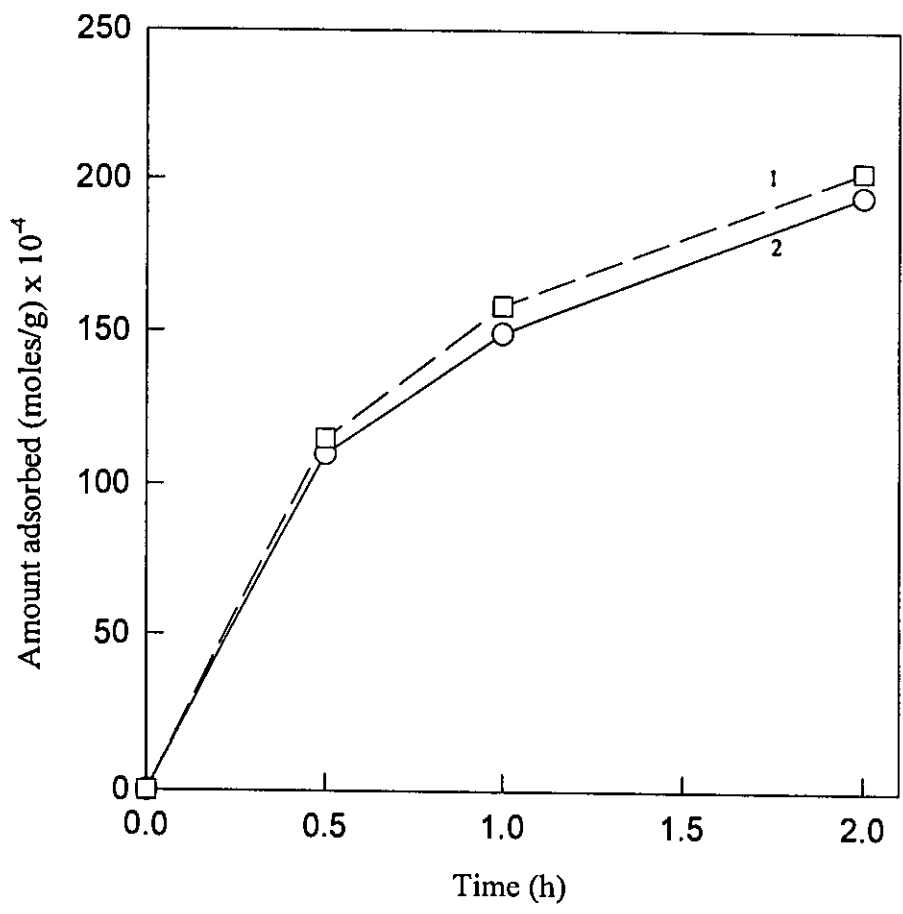


Fig. 36: Amount of NiCl₂ adsorbed with time on (1) α-PANI and (2) n-PANI.

mechanism is proposed for the removal of small ions such as Cu, Ni, Pb, Co etc. while the bigger ions tend to deposit on the surface of the adsorbent. In the present adsorbent, the interchange of Ni^{+2} with the longer chain of cationic PANI, perhaps not feasible and thus leads to an insignificant adsorption. Furthermore, the solubility of NiCl_2 in aqueous solution is very high and thus the degree of attraction between NiCl_2 and water could be much higher than the electrostatic force of attraction between the Ni-salt and the PANI substrate that requires for its adsorption. Therefore, naturally the salt remains in the solution rather than adsorbed on the PANI matrices. However, the observed smaller adsorption of the Ni-salt may arise due to just trapping of the salt entity in molecular skeleton of the PANI chain or held together with the adsorbent simply by some physical force [49].

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Conclusion

The post-synthesis treatment of chemically prepared PANI provides a novel and facile pathway for modifying physico-chemical properties of the organic polymer. Morphology and surface properties of conducting PANI can be modified by controlling the pH of the solution medium with which the PANI is treated.

On treatment with distilled water (pH=6.86), aqueous hydrochloric acid (pH=1.71) and aqueous ammonium hydroxide (pH = 10.01), the PANI matrices appear to be neutral and charged. The acid and the base treatments make the PANI matrices charged positively and negatively, respectively while it is neutral if treated with distilled water.

The solid-state pellet conductivities of matrices are significantly affected by the acid and base treatments. The conductivity of the base-treated PANI lowers by several orders of magnitude than that treated with acid. The change of such electrical property becomes further evident in the spectral properties. The mid-gap state transition appeared in the visible region, as observed for acid treated PANI, found to vanish for the distilled water and base treated PANI sample. This transition is, indeed, responsible for polymer conductivity. IR spectra also confirmed the conducting and insulating structures for the acid and base treated PANI, respectively. However, the XRD studies of the treated polymers indicate that, on treatment, the molecular arrangement, i.e. crystallinity of the PANI matrices remains unaffected and exists in the amorphous state.

Surface morphology of the PANI is significantly affected by the post-synthesized acid and base treatments. On acid treatment, a deposit of PANI agglomerates forms while treating it with distilled water or aqueous ammonium hydroxide solution, a granular morphology of the matrices results.

The structurally and morphologically modified PANI can be used efficiently as adsorbents for the removal of organic pollutants, such as anionic and cation dyestuff from their aqueous solutions. The adsorbent thus treated show a high selectivity for the removal of dyes. The removal as a consequence of adsorption of the dyes appears to be significant when the adsorbent and adsorbates are of opposite charges. On the other hand, the inorganics, such as nickel chloride, seems to have a little affinity to be adsorbed either on the neutral or charged PANI matrices, suggesting a different nature of adsorption phenomena to be adopted for its removal and would need further investigation. The present study, however, provides a new concept for the application of these electronic PANI materials to surface processes.

List of abbreviations

<i>Abbreviation</i>	<i>Explanation</i>
PAT	<i>Polyacetylene</i>
PANI	<i>Polyaniline</i>
PP	<i>Polypyrrole</i>
PT	<i>Polythiophene</i>
S	<i>Siemen</i>
cm	<i>Centimeter</i>
(SN) _x	<i>Polysulfur nitride</i>
Pt	<i>Platinum</i>
d.c.	<i>Direct current</i>
XRD	<i>X-ray diffraction</i>
IR	<i>Infrared</i>
SEM	<i>Scanning electron microscopy</i>
BET	<i>Brunauer, Emmett and Teller</i>
UV-Vis	<i>Ultraviolet- visible</i>
DMF	<i>Dimethyl formamide</i>
HCl	<i>Hydrochloric acid</i>
(NH ₄) ₂ S ₂ O ₈	<i>Ammonium peroxydisulfate</i>
<i>a</i> - PANI	<i>Acidic PANI</i>
<i>n</i> -PANI	<i>Neutral PANI</i>
<i>b</i> -PANI	<i>Basic PANI.</i>

<i>Abbreviation</i>	<i>Explanation</i>
NH_4OH	<i>Ammonium hydroxide</i>
MB	<i>Methylene blue</i>
PR	<i>Procion red</i>
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	<i>Hydrated nickel chloride</i>
h	<i>Hour</i>
min	<i>Minute</i>
L	<i>Liter</i>
Mol	<i>Mole</i>
g	<i>Gram</i>
au	<i>Arbitrary unit</i>

