MODIFICATION OF POLYANILINE SURFACE BY ELECTROCHEMICAL MEANS AND STUDY OF ADSORPTION ON THE MODIFIED SURFACE

BY

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Candidate's Declaration

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

15-04-08

Signature of the Candidate

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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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Certification of Thesis

A thesis on

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has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Philosophy (M. Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on April 12, 2008.

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Abstract

In the present work, a widely recognized electronic material, polyaniline (PANI) has been reported to be as an excellent surface matrix. The PANI matrix was prepared electrochemically from an electrolytic solution containing aniline and sulphuric acid. In order to make different surface activity of the PANI matrix, attempt was made to treat the PANI with aqueous solution of different pH *viz.*, 2.47, 7.35 and 10.01 to get the acidic-PANI, neutral-PANI and basic-PANI matrices respectively. The PANI that made in the presence of a dopant along with the electrolytic medium stated above, is referred as doped-PANI.

The treated PANI matrices were characterized using infra-red (IR) and UV-visible spectroscopy. The IR spectral analysis of the matrices clearly revealed that the presence of the PANI components. The UV-visible spectra of the matrices showed characteristics interband transition and mid-gap state as usually exhibited by PANI reported earlier. Though the spectral feature of IR and UV-Vis for the studied PANI matrices were found to be identical, the SEM analysis of the matrices yielded very significant differences in the surface morphologies of the matrices indicating that the surface activity of the matrices could be different.

In order to examine the surface properties of the PANI matrices, adsorption of a cationic dye, methylene blue (MB) onto the matrices was carried out. The adsorption study showed a higher adsorption capacity for the basic- and doped-PANI than the acidic- and neutral-PANI matrices. The adsorption of MB onto the PANI was recorder at different time intervals and monitored spectroscopically. The time to reach the

adsorption equilibrium was found to be within 150 min. in each matrices at 30 °C. The adsorption data suggested a Langmuir type adsorption. In addition, monolayer capacity and adsorption coefficients for different PANI matrices were derived also from the adsorption data. The results showed higher monolayer capacity and adsorption coefficients for the basic- and doped-PANI compared to acidic- and neutral-PANI. This result clearly suggests the superior surface activity of the basic- and doped-PANI matrice. Indeed, the SEM analysis of the matrices also predicted different surface morphologies of these matrices. The SEM images predicted higher porosity of the basic- and doped-PANI compared to that of acidic- and neutral-PANI matrices. On the other hand, the SEM images of acidic- and neutral-PANI showed compact and uniform morphology while those of basic- and doped-PANI matrices were seem to be loose, irregularly-shaped three-dimensional bodies with huge micro-pores available for adsorption sites which might allowed them to yield a higher adsorption. Furthermore, the superior adsorption capacity of basic-PANI for the MB adsorption may also result from the electrostatic interactions between the negatively charged basic-PANI matrix and positively charged MB.

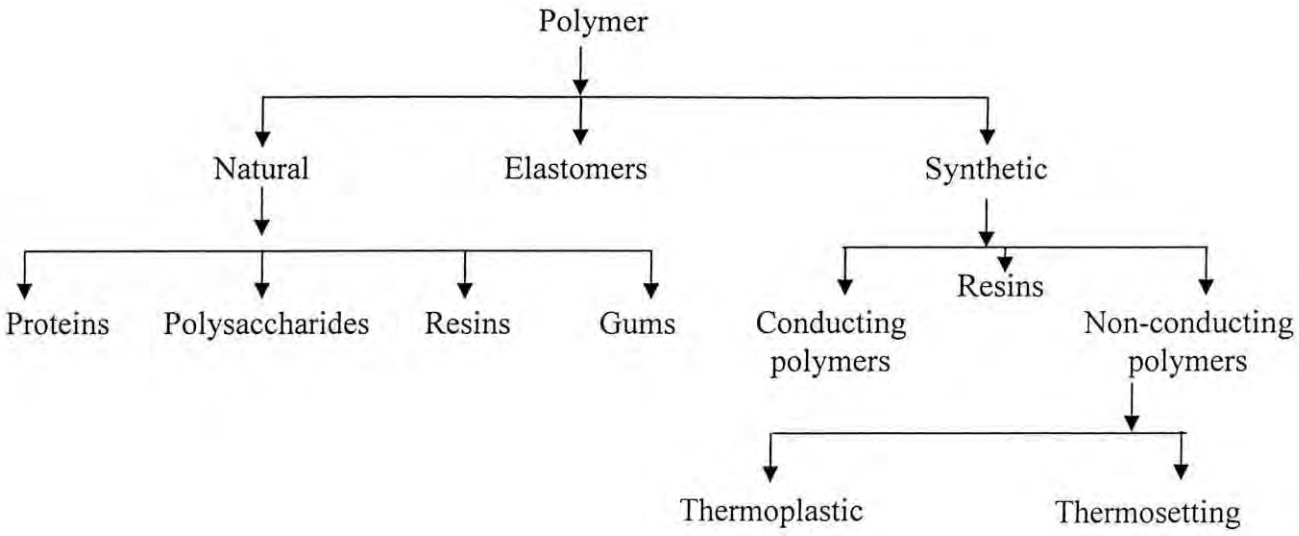
Chapter - 1

INTRODUCTION

1.1 Polymer Materials

Polymers are giant molecules composed of hundreds or thousands of the basic structural unit which is composed of a limited number of atoms strongly bonded together. This basic unit is called monomer. Polymers are chain like and macromolecules. The repeat unit (or basic unit) of the polymer is usually equivalent or nearly equivalent to the monomer. In some cases the repetition is linear, much as a chain is built up from its link. In other cases the chains are branched or interconnected to from three dimensional networks. The length of the polymer chain is specified by the number of repeat units in the chain. This is called the degree of polymerization. Starch, protein, lignin, cellulose, silk etc. are natural polymers and polyaniline (PANI), poly-*o*-toluidine (CH_3-PANI), polyaniline/poly-*o*-toluidine (PANI/CH_3-PANI), polyaniline/poly-*o*-toluidine/silica (PANI/CH_3-PANI/SiO_2), polypyrrole (PP), polyaniline/polypyrrole (PANI/PP), polyaniline/polypyrrole/silicondioxide (PANI/PP/SiO_2), Poly 2-amino benzoic acid (PABA), polyaniline/poly-2-amino benzoic acid (PANI/PABA), poly-*o*-toluidine / poly-2-amino benzoic acid (CH_3-PANI/PABA), polyethylene, nylon, synthetic rubber polypropylene etc. are the example of synthetic polymers. Some polymers are conductor of electricity although most of the polymers are non-conductor or insulator.

Polymers can be classified in different ways depending on their use, structure, origin and property. Depending on the nature of the polymers a broad classification is diagramically shown below:



(I) Natural polymers:

Natural polymers usually have more complex structure. They are classified as (a) proteins (b) polysaccharides (c) resins (d) gums.

(a) Proteins: Proteins are essential for life. All characteristics commonly attributed to living things such as reproduction, growth, movement, metabolism and sensory perception are entirely dependent on the function of proteins. Proteins are synthesized biologically as polymers of twenty amino acids.

(b) Polysaccharides: Polysaccharides are carbohydrate polymer in which monosaccharides (glucose, fructose etc.) residues are linked directly through glycosidic linkages. They are found in animal, plant and microbial kingdoms, where they may serve for energy storage, as structural materials.

(c) ***Resins:*** A neutral resin in any of various solid or semi-solid amorphous, fusible, flammable natural organic substances that are usually transparent or translucent and yellowish to brown, are formed especially in plan secretions, are electrical non-conductor and are used chiefly in medicine, varnishes, printing inks, plastics and sizes.

(d) ***Gums:*** Gums are very complex, amorphous substances of a polysaccharide nature. They contains very small amounts of Ca, Mg, K with the composition of C, H and O. They are used in pharmacy and industry.

(II) Elastomers:

Elastomers can either be natural or man made. Elastomers are considered different from other polymeric materials because of their special properties. Unlike fibres, elastomers do not in general lend themselves to uses. Elastomers must be amorphous when unstretched.

(III) Synthetic polymers:

Synthetic polymers are man made. They are synthesized in the laboratory by applying heat, pressure or catalyst (initiators). They are of two kinds, such as (a) conducting polymers and (b) non-conducting or insulator polymer.

(a) ***Conducting polymers:*** During the last two decades, a new class of organic polymer is synthesized which conduct electrical current. These polymers are called conducting polymers [1]. In general polymers are insulating materials having conductivities ranging from 10^{-10} Scm^{-1} for polyvinyl chloride to 10^{-18} Scm^{-1} for polytetrafluro-ethylene, which are many

orders of magnitude below compared to the conductivities associated with metals (>10^6 Scm^{-1}). As a result, polymers have found wide spread acceptance in a myriad of insulating and structural applications throughout electronic industries. One of the earliest approaches to make polymers conducting is to prepare a composite of polymers and a 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 present in such composites are non-conducting [2-5]. When anions like Cl^-, ClO_4^-, BF_4^- etc. are doped chemically to organic polymers, their electrical conductivity increases. Again when silicon dioxide is dopped in to these polymers, their mechanical stability is increased although its electrical conductivity may decrease.

(b) Non-conducting polymers: The polymers which cannot carry electricity are non-conducting polymers or insulation polymers, they are of two kinds, such as: (i) thermoplastic (ii) thermosetting.

(i) Thermoplastic: A thermoplastic polymer is one that is capable of being repeatedly soften by heating and hardening by cooling through a characteristic temperature range, and that in the softened state can be shaped by flow into articles by molding or extrusion. Thermoplastic applies to those materials which change upon heating is substantially physical.

(ii) Thermosetting: A thermosetting polymer is one that is capable of being changed into a substantially infusible or insoluble product when cured by heat or other means. The cured polymer may be termed thermoset.

1.2 Polymer Surface Modification

Researchers can alter the physical, electrical, and chemical properties of solids to create unique new materials which are not possible with conventional "equilibrium" processing techniques [6-12]. Surface modification is achieved using techniques such as ion implantation, doping, ion beam mixing, low energy ion deposition, ion beam annealing, chemical and electrochemical treatments [13-17]. These techniques are suitable for tailoring desired modifications in many different classes of materials, including metals, semiconductors, ceramics, insulators, polymers, and even biological samples [18-22].

Polymers are being used in an increasingly wider range of applications, particularly in the medical devices industry. It is vital to understand the surface characteristics of the polymer because many critical interactions between the polymer and its environment occur at the surface. For instance, the surface of a polymer used in a medical device is often the interface between the body and the device. By controlling the surface properties of the polymer, the medical device designer can enhance or inhibit various reactions of the body to the device. The interaction between the polymer and its environment depends largely on surface composition and structure. Treatments such as spraying, vacuum deposition, and chemical of plasma etching have been developed to produce other desired surface characteristics and topographies.

Since surface composition and topography play such an important role in the performance of the polymer, precise surface characterization can be an important part in the rapid development of new materials or understanding of problems and behavior in existing materials. Atomic Force Microscopy

(AFM), with its high -resolution surface mapping capabilities can be a key component of that characterization.

Surface Effects of Strain and Plasma Etching

The image presented here demonstrate the effect of strain and oxygen plasma etching on an ethylene vinyl acetate film used in medical device packaging. The first image, Figure 1.2.1 shows a 4-micron phase image of the as-received surface. To create a phase the cantilever is oscillated near its resonance frequency. The phase can be sensitive to physical property difference in the sample surface, as well as topography. The AFM phase image provides a detailed view of the polymer surface. The well-defined features in the phase image are probably the result of polymer lamellae that appear at the surface in slightly different orientations. The second image, Figure 1.2.2 is a 5- micron phase image of a different area of the same

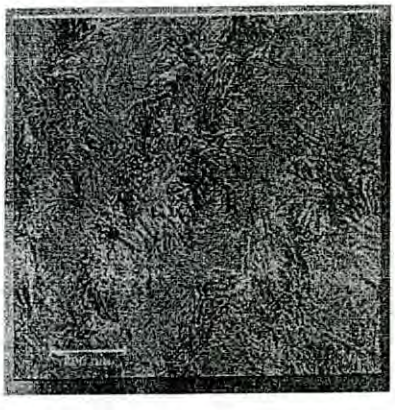


Fig. 1.2.1: Ethylene vinyl acetated film (as prepared).

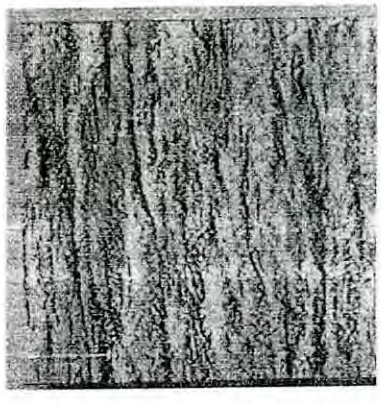


Fig. 1.2.2: Ethylene vinyl acetated film modification by applying strain.

sample after the sample had been strained to the breaking point and the stress then released. The strain direction runs from top to bottom in the image. Obviously, the surface has been modified by the applied stress. Combining this morphological information with detailed chemical analysis provides valuable information about the behavior of the sample. Since

neither of this images required any type of sample preparation, the results are not affected by artifacts that may be created during a preparation process.

Sample History

The history of a polymer sample can have an important effect on its behavior and performance. After the images shown in Figures 1.2.1 and 1.2.2 were acquired, the sample were etched in oxygen plasma for three different time intervals: 15 seconds, 1 minute and 3 minutes. It was observed that the strained surface structure was affected to a much larger degree than the unstrained surface.

While being able to visualize the surface of a polymer is useful in itself, the ability of actually quantify physical characteristics can be important in some cases. Surface roughness is an obvious parameter.

1.3 Aspects of Electrochemical Process

Electrochemistry involves the study of spontaneous oxidation-reduction that generates an electrical current and the study of non-spontaneous oxidation-reduction reactions that are forced to occur by the passage of an electrical current. In both cases, the conversion between chemical and electrical energy is carried out in an electrochemical cell. The arrangement of a complete electrochemical cell system is briefly discussed below:

Electrochemical cell

An electrochemical cell consists primarily of three electrodes and an electrolyte, together with a container. Commonly a glass frit, separator, or membrane may be incorporated to isolate the anolyte from the catholyte. Three electrodes are commonly employed: a working electrode that defines

the interface under study, a reference electrode which maintains a constant reference potential, and a counter (or secondary) electrode which supplies the current. The cell must be designed so that the experimental data are determined by the properties of the reaction at the working electrode.

Working electrode

Designs of working electrodes are diverse. Most commonly the working electrode is a small sphere, small disc, or a short wire, but it could also be metal foil, a single crystal of semiconductor or metal, an evaporated thin film, or a powder as pressed discs or pellets. An essential features is that the electrode should not react chemically with the solvent or solution components. In principle, the electrodes can be large or small, but there are commonly experimental reasons why the electrode area should be relatively small (<0.25 cm^2). Moreover, it should preferably be smooth, as the geometry and mass transport are then better defined. Wide ranges of solid materials are used as electrodes, but the most common 'inert' solid electrodes are lead, vitreous carbon, gold and platinum. In order to obtain consistent results with solid electrodes, it is important to establish a satisfactory electrode pretreatment procedure that ensures a reproducible state of oxidation, surface morphology and free from adsorbed impurities. Electrodes are polished on cloth pads impregnated with diamond particles down to 1 μm and then with alumina of fixed grain size down to 0.05 μm.

Counter electrode

The purpose of the counter electrode is to assist the flow of current required by the working electrode without in any way limiting the measured response of the cell. It is essential that the electrode process is

decomposition of the electrolyte medium or oxidation/reduction of a component of the electrolyte so that current flows readily without the need for a large overpotential.

The counter electrode should not impose any characteristics on the measured data, and in consequence it should have a large area compared to the working electrode. Moreover, as also noted above, its shape and position are important since these determine whether the working electrode is an equipotential surface, and consequently it is preferable to avoid a separator in the cell.

Reference electrodes

The role of the reference electrode is to provide a fixed potential which does not vary during the experiment (e.g. it should be independent of current density). In most cases, it will be necessary to relate the potential of the reference electrode to other scales, for example to the normal hydrogen electrode, the agreed standard for thermodynamic calculations.

In potentiostatic experiments, the potential between the working electrode and reference electrode is controlled by a potentiostat, and as the reference half cell maintains a fixed potential, any change in applied potential to the cell appears directly across the working electrode-solution interface. The reference electrode serves the dual purpose of providing a thermodynamic reference and also isolates the working electrode as the system under study. In practice, however, any measuring device must draw current to perform the measurement, so a good reference electrode should be able to maintain a constant potential even if a few microamperes are passed through its surface.

In practice the main requirement of a reference electrode is that it should have a stable potential and that it is not substantially polarized during the experiment. Hence, it is common to use the highly convenient aqueous saturated calomel electrode (SCE) in many experiments in all solvents. Even so, a very wide range of reference electrodes have been used in non-aqueous solvents.

A great deal of modern electrochemistry is carried out in non-aqueous solvent media, and often aqueous reference electrodes can be used at the expense of an unknown aqueous non-aqueous junction potential. In acetonitrile, the calomel electrode is unstable, and most frequently used reference electrodes are Ag/AgCl or Ag/Ag^{+}.

The electrolytic solution

The electrolytic solution is the medium between the electrodes in the cell, and it will consist of solvent and a high concentration of an ionised salt as well as the electroactive species; it may also contain other materials, complexing agents, buffers, etc. The supporting electrolyte is present (a) to increase the conductivity of the solution and hence to reduce the resistance between the working and counter electrodes (to avoid undue Joule heating, to help maintain a uniform current and potential distribution, and to reduce the power requirement on the potentiostat), and also to minimize the potential error due to the uncompensated solution resistance. With appropriate precautions, electrochemical experiments are possible in almost any medium. Table 1.3.1 lists some widely used media.

Table 1.3.1: Common solvents and media for electrochemical experiments.

1. Water

   Aqueous solutions of many salts and/or complexing agents at various pH. Buffered and unbuffered media.

2. Other protonic solvents

   e.g. acetic acid, ethanol, methanol, liquid HF.

3. Aprotic solvents e.g. acetonitrile, dimethylformamide, dimethylsulphoxide, sulphur dioxide, ammonia, propylene carbonate, tetrahydrofuran. Many studies use as electrolytes $R_4N^+ X^-$, R= CH_3, $C_2H_5^-$ or $C_4H_9^-$, X= ClO_4^-, BF_4^-, PF_6^-, or halide ion. Media difficult to buffer.

4. Mixed solvents

   Particularly mixtures of water with ethanol, acetronitrile, etc. Again, these media may be buffered or unbuffered, contain many electrolytes, etc.

5. Molten salts

   e.g. NaCl, KCl/NaCl/LiCl eutectics etc.

Electrode reactions can be extremely sensitive to impurities in the solution; for example, organic species are often strongly adsorbed even at 10^{-4} mol dm^{-3} bulk concentration from aqueous solutions. Hence salts should be of the highest available purity and/or recrystallised, solvents should be carefully purified, and solutions must be carefully deoxygenated. Purification and drying of non-aqueous solvents have been described elsewhere [23, 24] in some detail.

Instrumentation

The electrochemist's armoury is based on electronic apparatus designed to control/measure the charge passed (coulostat/integrator), current

(galvanostat/current follower) and potential (potentiostat/high impedance voltmeter) in an electrochemical cell.

Potentiostat: The potentiostat is a device for controlling the potential between the working electrode and the reference electrode at a fixed and selected potential (commonly we also wish to programme this potential with time).

Galvanostat: The simplest way to obtain a constant current is to apply a voltage from a low output impedance voltage sources across a large resistor in series with the cell. The current will be given by the ratio E_{in}/R (provided resistance R is very large compared with the impedance of the cell).

Processes at electrode surface

A solid conducting materials must be present to provide the site for each electrochemical reaction. These materials are called electrodes. The electrodes at which oxidation occurs is termed as the anode. The other electrode, the cathode, is the site of the reduction process.

i) Electrode reactions: An electrode reaction is a heterogeneous chemical process involving the transfer of electrons to or from a surface, generally a metal or a semiconductor. The electrode reaction may be an anodic process whereby a species is oxidized by the loss of electrons to the electrode, e.g.

$$2\,H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad 1.3.1$$

$$Ce^{3+} - e^- \rightarrow Ce^{4+} \qquad 1.3.2$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \qquad 1.3.3$$

$$Pb + SO_4^{2-} - 2e^- \rightarrow PbSO_4 \quad 1.3.4$$

$$2Al + 3H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+ \quad 1.3.5$$

By convention, the current density, *I*, for an anodic process is a positive quantity. Conversely, the charge transfer may be a cathodic reaction in which a species is reduced by the gain of electrons from the electrode, e.g.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad 1.3.6$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad 1.3.7$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad 1.3.8$$

$$PbO_2 + 4H^+ + SO_4^{--} + 2e^- \rightarrow PbSO_4 + 2H_2O \quad 1.3.9$$

$$2CH_2 = CHCN + 2H_2O + 2e^- \rightarrow (CH_2CH_2CN)_2 + 2OH^- \quad 1.3.10$$

and the current density for a cathodic process is a negative quantity. The diversity of electrode reactions can already be seen from Equation (1.3.1.–1.3.10): the electroactive species may be organic or inorganic, neutral or charged, a species dissolved in solution, the solvent itself, a film in the electrode surface, or indeed, the electrode materials itself. Moreover, the product may be dissolved in solution, in a gas, or a new phase on the electrode surface. Many types of electrodes reactions are also illustrated in Fig. 1.3.1.

Electrolysis is only possible in a cell with both an anode and a cathode because of the need to maintain an overall charge balance, the amount of reduction at the cathode and oxidation at the anode must be equal.

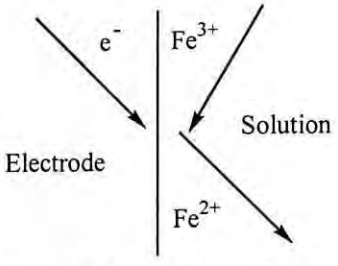
ii) Mass transport: In general, in electrochemical systems, it is necessary to consider three modes of mass transport; namely,

(a) Diffusion: Diffusion is the movement of a species down a concentration gradient, and it must occur whenever there is a chemical change at surface. An electrode reaction converts starting material to product (O→R), and hence close to the electrode surface there is always a boundary layer (up to 10^{-2} cm thick) in which the concentrations of O and R are a function of distance from the electrode surface. The concentration of O is lower at the surface than in the bulk, while opposite is the case for R, and hence O will diffuse towards and R away from the electrode.

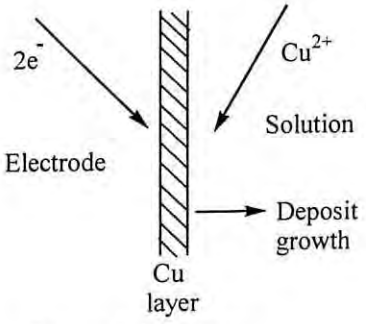
(b) Migration: Migration is the movement of charged species due to a potential gradient, and it is the mechanism by which charge passes through the electrolyte; the flow of electrons through the external circuit must be balanced by the passage of ions through the solution between the electrodes (both cations to the cathode and anions to the anode).

It is, however, not necessarily an important form of mass transport for the electroactive species even if it is charged. The forces leading to migration are purely electrostatic, and hence the charge can be carried by any ionic species in the solution. As a result, if the electrolysis is carried out with a large excess of an inert electrolyte in the solution, this carries most of the charge, and little of the electroactive species is transported by migration.

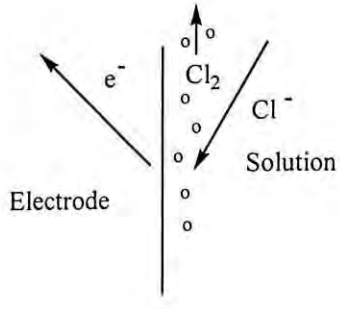
(c) Convection: Convection is the movement of a species due to mechanical forces. It can be eliminated, at least on a short timescale (it is difficult to eliminate natural convection arising from density difference on a longer time, i.e.> 10s) by carrying out electrolysis in a thermostat in the absence



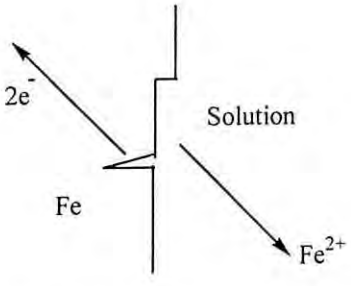
(a) simple electron transfer
$Fe^{3+} + e^- \rightarrow Fe^{2+}$



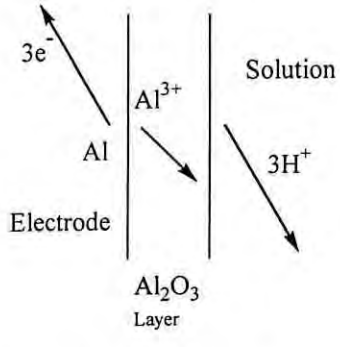
(b) metal deposition
e.g. $Cu^{2+} + 2e^- \rightarrow Cu$



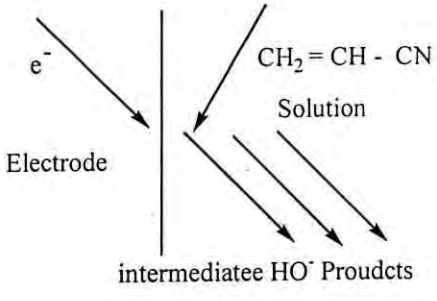
(c) gas evolution
e.g. $2Cl^- - 2e^- \rightarrow Cl_2$



(d) corrosion
e.g. $Fe - 2e^- \rightarrow Fe^{2+}$



(e) oxide film formation
$2Al + 3\,H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+$



(f) electron transfer with coupled chemistry
$2CH_2 = CH - CN + 2H_2O + 2e^-$
$\rightarrow (CH_2 - CH_2 - CN)_2 + 2OH^-$

Fig. 1.3.1: Schematic presentation of some electrode reactions.

of stirring or vibration. In industrial practice it is much more common to stir or agitate the electrolyte or to flow the electrolyte through the cell. These are all forms of forced convection when present, they have a very large influence on the current density.

1.4 Surface Characteristics

The surface phenomenon, adsorption, may be defined as a process in which the concentration of a chemical species is greater on the surface than 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 surface of an adsorption system 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 chemically inert two immiscible 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.

Adsorption isotherms

There are three adsorption isotherms known which are used most frequently:

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

$$X = \frac{X_m bp}{(1+bp)} \qquad (1.4.1)$$

or, $$\frac{1}{X} = \frac{1}{X_m bp} + \frac{1}{X_m} \qquad (1.4.2)$$

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, b = constant and p = pressure.

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

$$y = kC^{\frac{1}{n}} \qquad (1.4.3)$$

or, $$\log y = \log k + \frac{1}{n}\log C \qquad (1.4.4)$$

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:

$$\frac{P}{X(P_o - P)} = \frac{1}{X_m C} + \frac{C-1}{X_m C} \cdot \frac{P}{P_o} \qquad (1.4.5)$$

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

Factors Affecting Adsorption

i) Temperature: The level of adsorption at any particular concentration generally decreases with the increase in temperature; that is the adsorption process is exothermic. At higher temperature the adsorbed molecules have greater vibrational energies and therefore, more likely to desorb from the surface.

ii) Nature of the solvent: The solvent has an important effect, since it competes with the surface of the adsorbent in attracting the solute. There are three different ways to describe the influence of solvent on adsorption behavior of the solvent (a) its interaction with the solute in solution, (b) its interaction with the adsorbed layer, and (c) its interaction with the solute in the adsorbed layer. However, when the solvent is water, it is useless to consider the solvent effect.

iii) Particle and pore size: The adsorption efficiency increases as mean diameter of the particle decreases. Large surface area is available for adsorption with the small particles. Another reason is the reduced diffusive path length of the interior of small adsorbent particles and the adsorbate particles require less energy of jump from one active site to another, resulting in higher uptake by the adsorbent.

iv) pH of the solution: The effect of pH is extremely important when the adsorbing species is capable of ionizing in response to prevailing pH. It is well known that substances adsorb poorly when they are ionized. When the pH is such that an adsorbable compound exists in ionic form, adjacent molecules of the adsorbed species on the adsorbent surface will repel each other to a significant degree because they carry the same electrical charge. Thus the adsorbing species cannot be packed together very densely on the surface. This is the common observation that non-ionized forms of acidic and basic compounds adsorb much better than their ionized counterparts. The acidic species thus adsorb better at low pH and basic species adsorb better at high pH.

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 decrease of solution concentration is plotted against the equilibrium concentration. By analogy with gas adsorption, one might hope to calculate the monolayer capacity, the application of an equation of the individual isotherm has a pattern of a sharp knee followed by a clear plateau; the monolayer capacity is then given by the height of the plateau.

Specific Surface Area of the Adsorbent

The specific surface area refers to the area per unit weight of the material, usually expressed as m^2g^{-1}. This area depends on particle size, shape and on type of material present. Relative methods for measuring specific surface area are based on retention of a polar organic molecule such as ethylene glycol; these have been related to absolute values derived from statistical calculations of surface area. Another method for the estimation of surface area from adsorption measurements *viz.* those based on adsorption from solution, on heat of immersion, chemisorption, and on the application of Gibbs adsorption equation to gaseous adsorption. Amongst them adsorption from solution method is used in this purpose. This is particularly true of those solids that contain very fine pores and give rise to Langmuir-type isotherm.

The principle on which the determination of area is based required knowledge of the number of molecules in the unimolecular layer per gram of adsorbent and the average cross-sectional area of the molecule.

Monolayer Capacity

The monolayer capacity is defined as the quantity of the adsorbate, which can be accumulated in a completely filled, single layer of molecules (a monolayer) on the surface of the solid. The specific surface area, S (m^2g^{-1}) is directly proportional to the monolayer capacity. The relationship between the two is given by the following equation:

$$S = (\chi_m/M) \times N \times A_m \times 10^{-20} \qquad (1.4.6)$$

Here, χ_m = The monolayer capacity in grams adsorbate per gram of solid

M = Molecular mass of adsorbate

N = Avogadro's number

A_m = The area in $Å^2$ occupied per molecule of adsorbate in the completed Monolayer

S = The specific surface area of adsorbent in m^2g^{-1}.

To find the value of χ_m from the isotherm, it is necessary to interpret the isotherm in quantitative terms. In the calculation of χ_m, Langmuir-type isotherm is considered.

Solution pH

The pH concept was originated in 1909 by the Danish biochemist S. P. L. Sorensen. 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:

$$pH = \log_{10} 1/[H^+] \qquad (1.4.8)$$

or $$[H^+] = 10^{-pH} \qquad (1.4.9)$$

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 $[H^+] = 10^{-7}$ has a pH of 7; a solution with a hydrogen ion concentration of 1 mol L^{-1} has a pH of 0 ($[H^+] = 10^0$); and a solution with a hydroxide-ion concentration of 1 mol L-1 has $[H^+] = K_w/ [OH^-] = 10^{-14}/ 10^0 = 10^{-14}$, 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. Thus, pH refers to the protonation level of a solution. The extend of protonation, therefore can be controlled by controlling the pH of the solution.

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. 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.

1.5 The Adsorbent: Polyaniline

A key property of most polymers, which distinguish them from metals, is their inability to allow electricity pass through. During the past decades, however, a new class of organic polymers has been devised with the remarkable ability to conduct electrical current. The PANI refer to this class of organic conducting polymers. PANI and its derivatives have been studied extensively due to their good conductivity, electrochromic properties and environmental stability in air. Furthermore, the potential range needed to polymerize aniline and its derivatives is narrow when compared to other conducting polymers. Also, polymerization could be done in aqueous medium by avoiding the use of toxic organic solvents. Considering various structural, chemical and environmental merits of this new materials, in this work, the PANI material was used as adsorbent. Different aspects concerning its preparation, structure and other physico-chemical properties are cited below:

Conducting polymer, PANI, 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 [25] usually as ill-defined forms such as aniline black, emeraldine, nigraniline, *etc.* synthesized by the chemical or electrochemical oxidation of aniline. Fig. 1.5.1 shows the idealized oxidation state of PANI: leucoemeraldine, emeraldine, pernigraniline and emeraldine salt. Different structures result in different

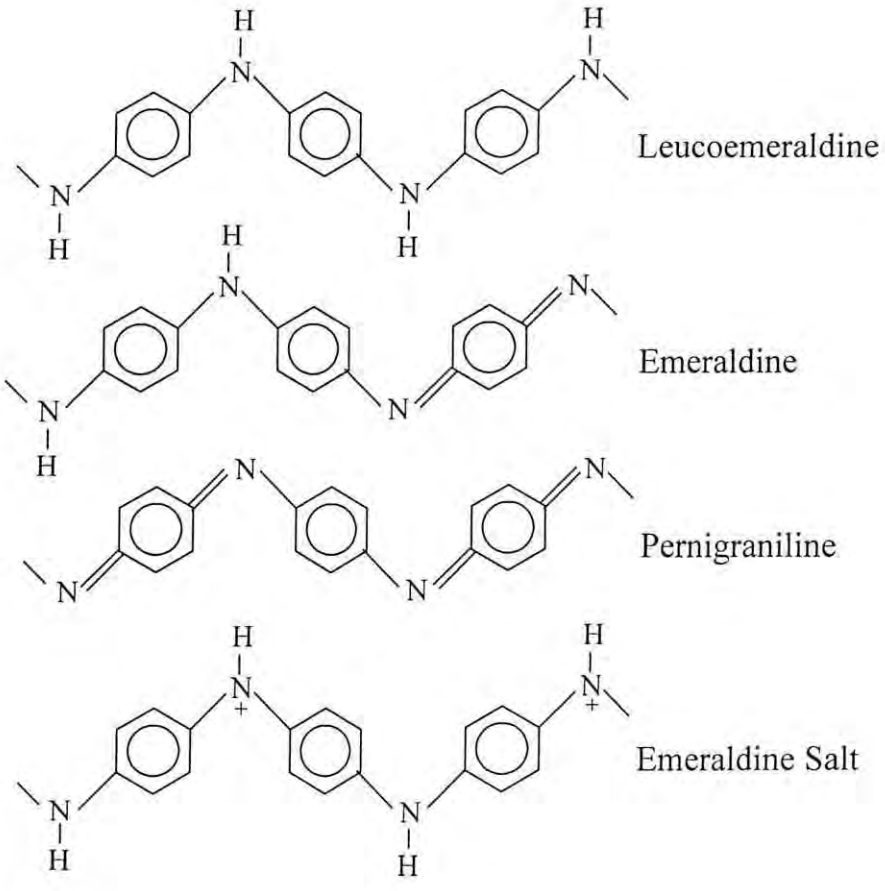
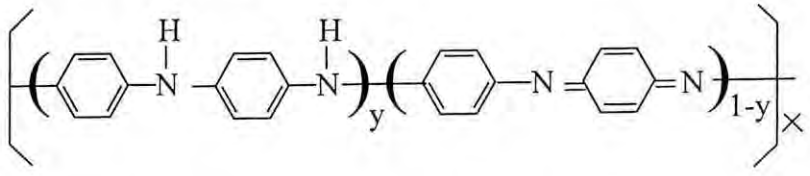


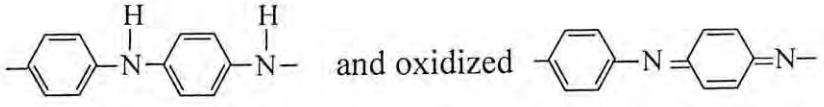
Fig. 1.5.1: Representation of idealized forms of PANI.

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

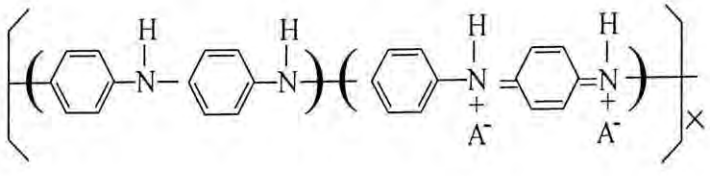
groups in the structure. The level of protonation in the structure causes dramatic changes in the conductivity. The base form of the polymer in the emeraldine oxidation state (y = 0.5)



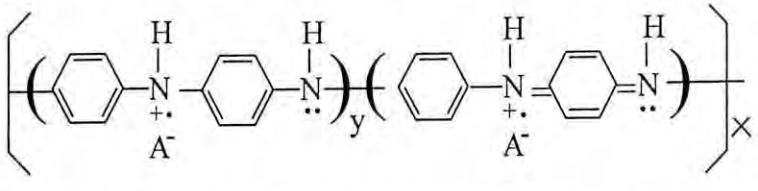
which contains equal number of alternating reduced,



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 [28-30].



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

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 dichromate [26, 27], ammonium persulfate or peroxydisulfate [28, 29], hydrogen peroxide, ceric nitrate and ceric sulfate [30, 31]. The reaction is mainly carried out in acid medium, in particular sulfuric acid, at a pH between 0 and 2 [26, 27]. However, MacDiarmid *et al.* [30, 31] used hydrochloric acid at pH 1. Genies *et al.* [37] used a eutectic mixture of hydrofluoric acid and ammonia, the general formula of which is NH_4F: 2.3 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 [33]. 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 [34, 35]. However, several studies have been carried out with other electrode materials: iron [36], copper [37], zinc and lead [38], chrome-gold [39], palladium [40] and different types of carbon vitreous, pyrolic or graphite [41] or on semiconductor [42, 43]. When

the polymerization is carried out at constant current, a maximum current density of 10 mA cm^{-2} is rarely exceeded.

Morphology and structure

The adherence and the homogeneity of a PANI film on an electrode varies according to the method of synthesis employed. Diaz [44] 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.* [45] 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.* [46] 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.

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 from optical data.

Conductivity

From conductivity measurements, Travers *et al.* [27] 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 ohm^{-1} cm^{-1} when the polymer is previously equilibrated at pH 6. MacDiarmid *et al.* [28, 29] 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 ohm^{-1} cm^{-1} when it is equilibrated at a pH between –1 and +1, and 10 ohm^{-1} cm^{-1} when it is equilibrated at a pH between 5 and 6. Elsewhere, they indicate that the conductivity of the polymer is a function of the level of doping, with a value of 1 ohm^{-1} cm^{-1} for 15% doping, and varying from 10^{-10} to 10^{-1} ohm^{-1} cm^{-1} for 0% to 10% doping. Measurements carried out by Brahma [47] revealed that PANI doped with iodine exhibits a conductivity four orders of magnitude greater than the undoped polymer.

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.* [34] 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.* [48] and involves proton acid dopants of large molecular size such as toluene-*p*-sulfonic acid, sulfanilic acid or polymeric electrolyte-polystyrene sulfonic acid.

Applications

PANI can be used as material for modified electrodes [41, 44], as a corrosion inhibitors for semiconductors in photoelectrochemical assemblies [49], in microelectronics [50] and as electrochromic material [51]. 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 [52].

More recent systematic studies have been undertaken by numerous groups [28, 29, 49] on the possible use of PANI as an active electrode material. These investigations deal with the behavior of PANI in aqueous and organic media as a function of the mode of synthesis.

1.6 The adsorbate: Methylene Blue Dye

A dye must be colored, but it must also be able to impart color to something else on reasonably permanent basis before it can be considered as a dye.

A dye consists of a color producing structure, the chromogen (electron acceptor), and a part to regulate the solubility and dying properties, the auxochrom (electron donor). Without both parts, the material is simply a colored body.

The Chromogen is an aromatic body containing a color-giving group, called the chromophore. Chromophore groups cause color by altering absorption bands in the visible spectrum. Common chromophores are: nitroso group (- NO), nitro group ($-NO_2$), azo group (- N=N -), ethylene group (>C = C <), carbonyl group (>C = O), carbon nitrogen groups (>C = NH and – CH =N-), carbon sulphur groups (> C = S and →C– S-S-C←) etc.

Theses groups add color to aromatic bodies by causing displacement of, or an appearance of absorption bands in the visible spectrum. In modern point of views, these groups place the ground and excited state in the range that corresponds to the visible range of the spectrum.

The auxochrome, an essential part of a dye molecule, cause the dye to adhere to the material which it colors, enhance the color of dye, improve solubility in the solvent which is important for application on the materials.

Common auxochrome are: - NH_2, - OH, -NR_2, -COOH, - SO_3H etc.

Methylene blue (MB) is a typical organic ionic dye. MB is cationic in nature. The chemical structure of MB is shown in Fig. 1.6.1

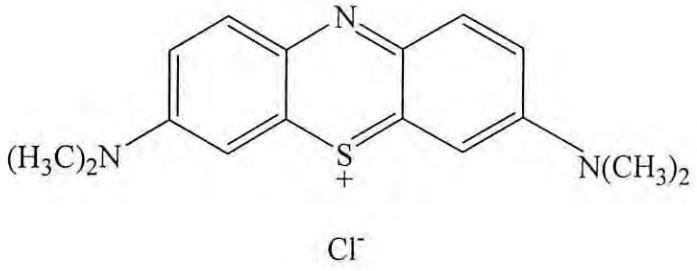


Fig. 1.6.1: Chemical structure of MB.

1.7 Theories of Experimental Techniques

Cyclic voltammetry

Electrochemical process is widely used in the polymerization of organic polymer. Most of the system for electrochemical polymerization consists of compartment where three electrodes are dipped into the solution containing monomer and electrolyte solution. Appropriate potential is applied to the working electrode for polymerization of the monomers. The potential of the working electrode, where deposition of the polymer film takes place, is controlled versus the reference electrode using a feed-back circuit or a potentiostat. Feed-back circuit drives the circuit between the working and counter electrode while ensuring that none passed through the reference electrode circuit.

The nature of the working electrode is a critical consideration for the preparation of these films. Since the films are produced by an oxidative process, it is important that the electrode is not oxidized concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a platinum or a gold electrode.

Potentiostatic, galvanostatic and potential sweep techniques such as cyclic voltammetry are widely used for electrochemical polymerization of aromatic compounds. In potentiostatic technique, a constant potential is applied to the working electrode which is sufficient to oxidize the monomers to be polymerized on the electrode. In galvanostatic process, a constant current density is maintained to polymerize the monomers while film thickness can be monitored in the similar way as described for potentiostatic technique. On the other hand, cyclic voltammetry involves sweeping the potential between potential limits at a known sweep rate. On reaching the final potential limit, the sweep is reversed at the same scan rate to the initial potential and the sweep may be halted, again reversed, or alternatively continued further. In such experiments, cell current is recorded as a function of the applied potential.

Infra-red (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 absorption by the quantum relation

$$\Delta E = h\nu \qquad 1.7.1$$

where $h \rightarrow$ Planck's constant, $\nu \rightarrow$ frequency. Infrared frequencies have the wave length range from 1 μm to 50 μm and 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 number 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 tried to observe the change in IR frequency of different samples. IR spectrum of all the compounds were recorded on IR spectrophotometer in the region of 4000-400 cm^{-1}. Samples were introduced as KBr pellets. A block diagram of an IR spectrophotometer is shown in Fig. 1.7.1.

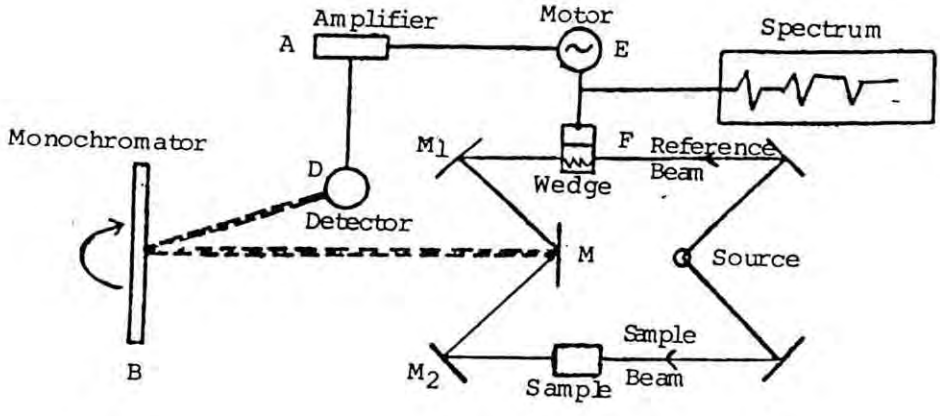


Fig. 1.7.1: A block diagram of an IR spectrophotometer.

Ultraviolet-visible (UV-Vis) spectroscopy

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

$$-\frac{dI}{dx} = \alpha I \qquad 1.7.2$$

where, $I \rightarrow$ intensity of photon beam

$dI \rightarrow$ reduction of intensity

$dx \rightarrow$ rate of photon absorption with distance (x) travel

$\alpha \rightarrow$ absorption co-efficient of the material

Now if I_0 is the initial intensity at thickness 1 = 0 and I is the transmitted radiation at x = 1, then by integration, we can write

$$ln\frac{I_0}{I} = \alpha l \qquad 1.7.3$$

For polymer, UV-Vis spectrum is taken to measure the impurity level, band gap energy etc. The spectra of the prepared compounds were recorded on a UV-Vis recording spectrophotometer in the wave length range 300-800 nm. A schematic diagram of UV-Vis spectrophotometer is shown in Fig. 1.7.2.

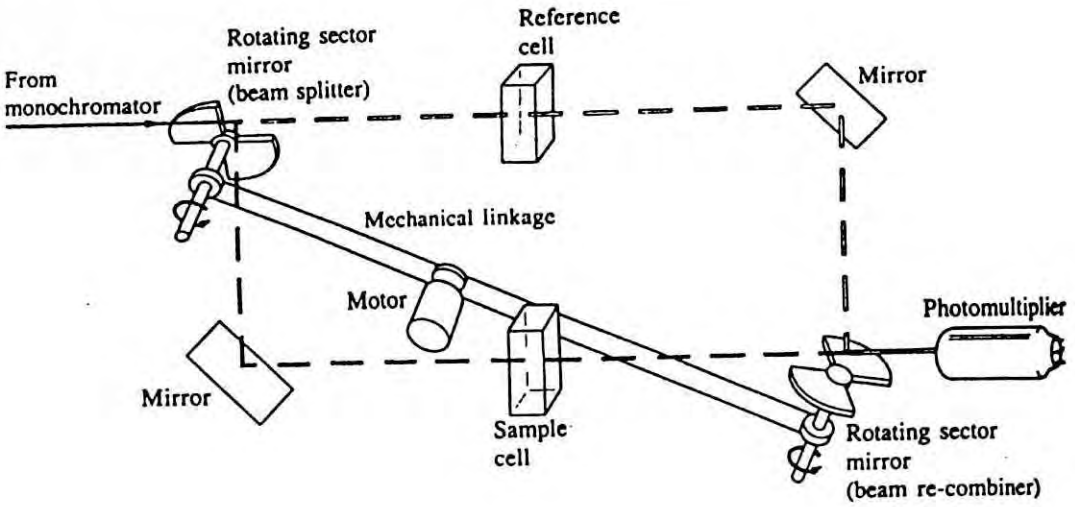


Fig. 1.7.2: A block diagram of an UV-Vis spectrophotometer.

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 has a specific structure, different image will be collected from different samples, even if they have the same geometric appearance.

The specimen stage of SEM allows movement of the specimen along 5 axis. 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 over ride.

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.

1.8 Review of Literature and Aim of the Present Work

Many investigation concerning polymers, *viz.* PANI and its derivatives have been reported with interesting results and attractive applications such as light weight batteries, electrochromic displays, MOSFECT-like devices, schottky diode, sensor, anticorrosion and electrocatalysis [53]. The application of electrochemical method for the generation and modification of conducting polymer is now well-established [54]. The quality and physical properties of electrochemically deposited polymers are strongly affected by the deposition condition, substrate, solvent and the nature of the electrolyte species. More importantly, a wide choice of solvent and counter ions available from different electrolytes allows facile variation of polymer properties and surface morphology [55-57]. However, majority of the studies with conducting polymers concern their ability to be switched between an insulating and a conducting state [58, 59] whereas the surface phenomena of these system is less developed. In some previous work [60, 61], chemically prepared PANI matrices were found to exhibit an appreciable surface area with surface binding capacity in removing organic pollutants. In the present work, electrochemical mode of synthesis has been employed to generate and modify PANI surface which was then examined further for its surface adsorption characteristics. In other words, the main objective of the present study is to explore a surface active new polymeric system that would be generated and modified by electrochemical means. In this context, surface characterization by adsorption processes onto the polymeric matrix are planned to be examined in this thesis.

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Chapter - 2

EXPERIMENTAL

2.1 Materials and Devices

A. Chemicals

Analytical grade chemicals and solvents were used throughout the work and were used as received unless stated otherwise. The monomer aniline was distilled prior to its use in polymerization reactions. Doubly distilled water (H_2O) was used as solvent to prepare most of the solutions utilized in this work except for UV-Vis analysis where N, N–dimethyl formamide (DMF) was employed as solvent. The important chemicals and solvents utilized throughout the experiments are listed below:

i) Aniline [E. Merck, Germany]
ii) *p*-toluene sulfonic acid sodium salt ($C_7H_7NaO_3S$)
iii) Sulphuric acid (98%) [E. Merck, Germany]
iv) N, N-dimethyl formamide [E. Merck, Germany]
v) Ammonium hydroxide (25%) [E. Merck, India]

B. Instruments

Analysis of the samples performed in this work employed the following devices:

i) Potentiostat / Galvanostat / Coulombmeter [HABF 501, Hokuto Denko, Japan]
ii) X-Y recorder [F–5C, Riken Denshi Co. Ltd, Japan]
iii) Infra red spectrophotometer [IR–470, Shimadzu, Japan]
iv) UV-visible spectrophotometer [UV-1601 PC, Shimadzu, Japan]
v) Scanning electron microscope [Philips XL 30, Holland]
vi) pH meter [HM-16s, TOA, Japan]
vii) Digital balance [FR-200, Japan]
viii) Centifuge machine [Universal 16A, Hettich, Germany]
ix) 100 mesh sieve [Endecotls test sieves limited, England]

2.2 Electrochemical preparation of Polyaniline

The electrochemical synthesis of PANI were carried out at room temperature in a standard three-electrode one-compartment electrolysis cell. A schematic representation of the electrochemical cell employed in this work is illustrated in Fig. 2.2.1. The cell consisted of a 0.50 cm^2 working electrode (WE) made of platinum (Pt), a 0.50 cm^2 Pt foil counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode (RE). Prior to each experiment, the working Pt electrode was carefully polished with fine–grained abrasive paper, followed by rinses in distilled water and 5 min immersion in concentrated nitric acid (HNO_3), before it was finally dried on clean laboratory tissues. The reproducibility of experimental results was greatly improved with this pretreatment of the working electrode. The films were grafted onto the working Pt electrode either by sweeping the potential or constant potential mode. Voltammetric sweeps were always started in the anodic direction from 0.0V at 100 mV/s, unless stated otherwise. A Hokuto Denko electrochemical measurement system provided necessary potential and current control.

PANI was prepared on the Pt working electrode by the ordinary anodic polarization method as described by the early workers [1-6]. The working Pt was the anode and counter Pt foil was used as the cathode. A 0.8M sulphuric acid (H_2SO_4) in distilled H_2O containing (i) 0.5 M aniline (ii) 0.5M aniline + 0.1 M *p*-toluene sulfonic acid sodium salt were used as the electrolytic solutions. Electrolysis was carried out either by sweeping the potential between –0.2 V and +1.0 V *vs* SCE at a scan rate of 100 mV/sec or at a constant potential of +1.0 V *vs* SCE. After polymerization, the potential

of the PANI film coated Pt electrode was held at 0.0V until the cathodic current disappeared to dedope the PANI deposit. The PANI as grown and dedoped, was washed several times in distilled water to remove any traces of monomer or any other reactants or by–products that might be produced during electrolysis.

The obtained PANI was then treated with aqueous solutions of different pH to make four different types of PANI adsorbents. The PANI adsorbents are:

i) acidic-PANI: The electrochemically prepared PANI was kept in contact with 0.8 M H_2SO_4 solution (pH =2.47) for over night.

ii) neutral-PANI: The PANI mass after getting electrochemically was kept in contact with double distilled water (pH = 7.35) for over night.

iii) basic-PANI: As grown by chemical means, the PANI was kept in contact with 0.1 M NH_4OH solution (pH = 10.01) for over night.

iv) doped-PANI: The electrochemically prepared PANI (from the electrolytic solution containing *p*-toluene sulfonic acid sodium salt) was kept in contact with 0.1 M NH_4OH solution (pH = 10.01) for over night.

After treatment, all the PANI samples were dried initially in air followed by vacuum for several hours.

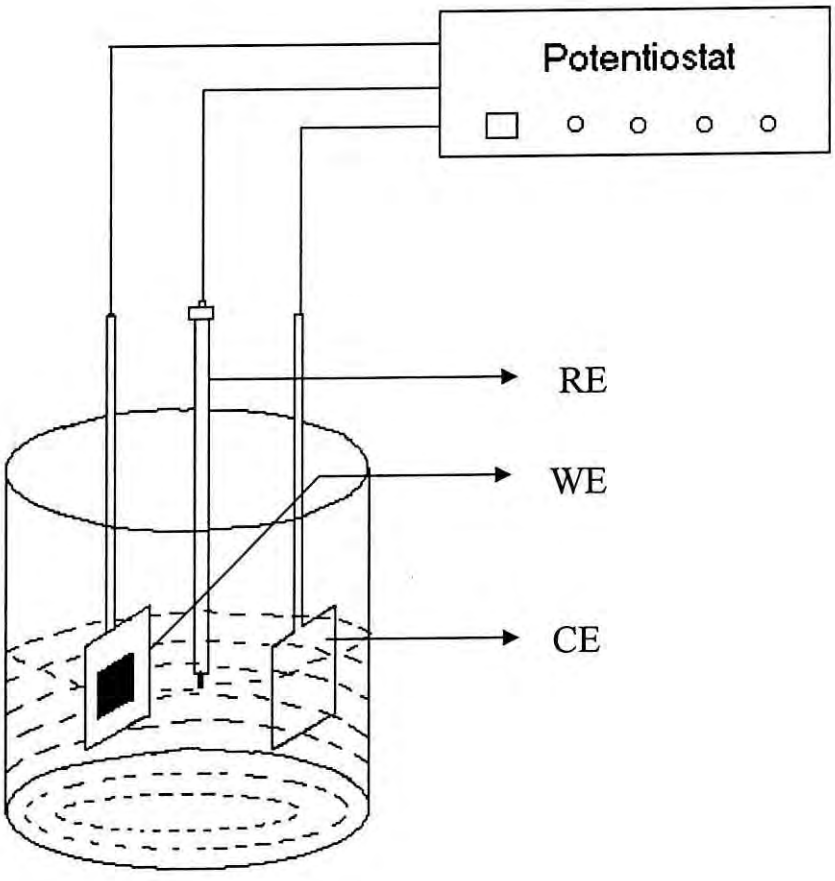

Fig. 2.2.1: Three electrodes for electrochemical cell.

2.3 Preparation of Methylene Blue Dye Solution

Stock methylene blue (MB) solution

A stock solution of MB was prepared by dissolving its 0.036 g in 500 mL solvent. The resultant MB stock solution gave a concentration of 2.02×10^{-4} M. Three different solvents were employed in the preparation of stock; these includes, i) double distilled water (pH= 7.35), ii) aqueous acidic solution of 0.8 M H_2SO_4 (pH = 2.47) and iii) aqueous basic 0.1 M NH_4OH solution (pH =10.01).

During experiments, the MB solutions of other concentration were also employed. These intermediate solutions were prepared by appropriate dilution of the MB stock. The intermediate 0.5×10^{-5} M, 1.0×10^{-5} M, 1.5×10^{-5} M, 2.0×10^{-5} M, 2.5×10^{-5} M and 3.0×10^{-5} M MB solutions were prepared by diluting 1.25 mL, 2.5 mL, 3.7 mL, 5.0 mL, 6.2 mL and 7.5 mL of stock solution respectively to 50 mL with the solvent.

The characteristics feature of MB was found to be quite sustainable in the solution of pH ranging from 2.47 to 10.01 employed. The spectral feature of MB in the different solution are depicted in Figs. 2.3.1, 2.3.2 and 2.3.3. Moreover, the characteristics UV-Vis spectra of MB in these solutions were also found to be stable at least for 3 hrs after their preparation.

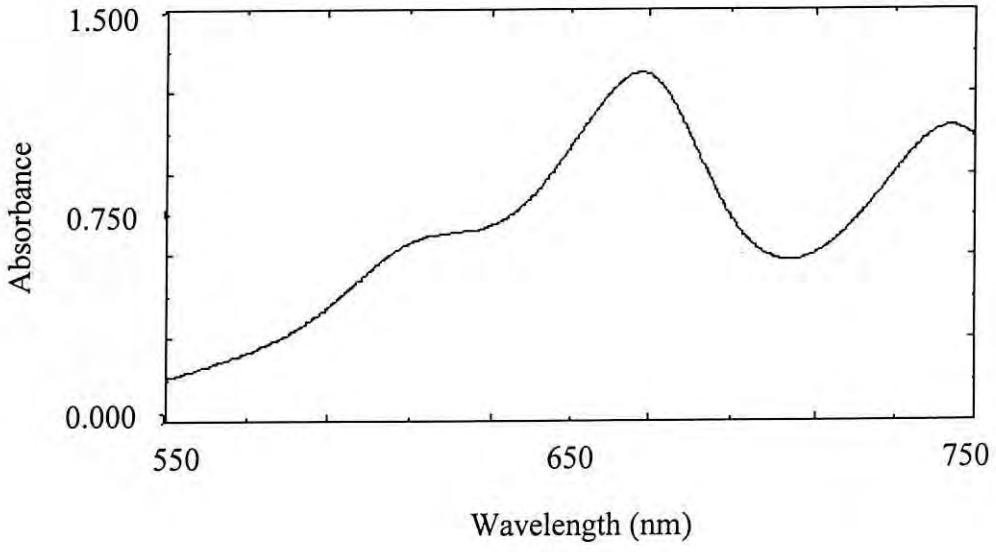

Fig. 2.3.1: Absorption spectra of MB in 0.8 M H_2SO_4 solution (pH = 2.47).

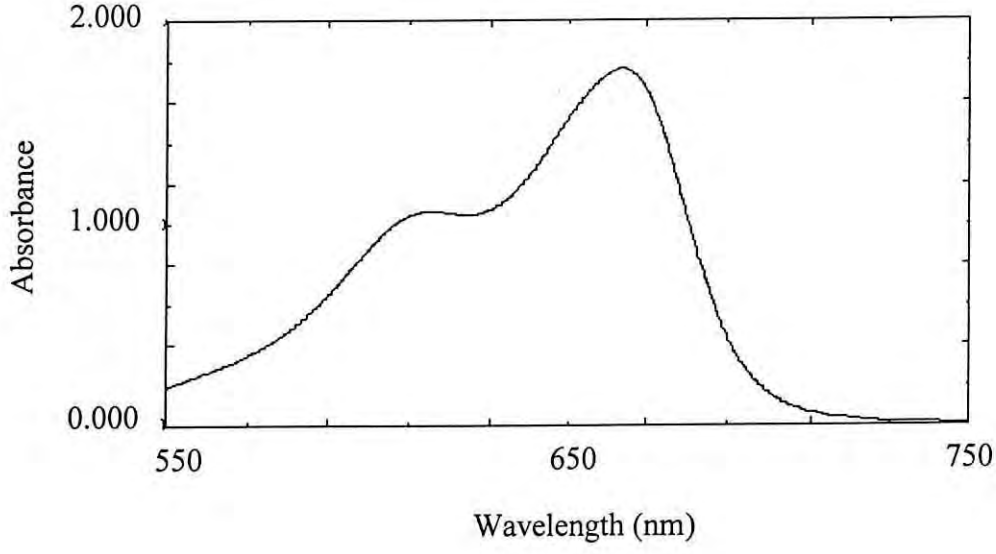

Fig. **2.3.2:** Absorption spectra of MB in double distilled water (pH = 7.35).

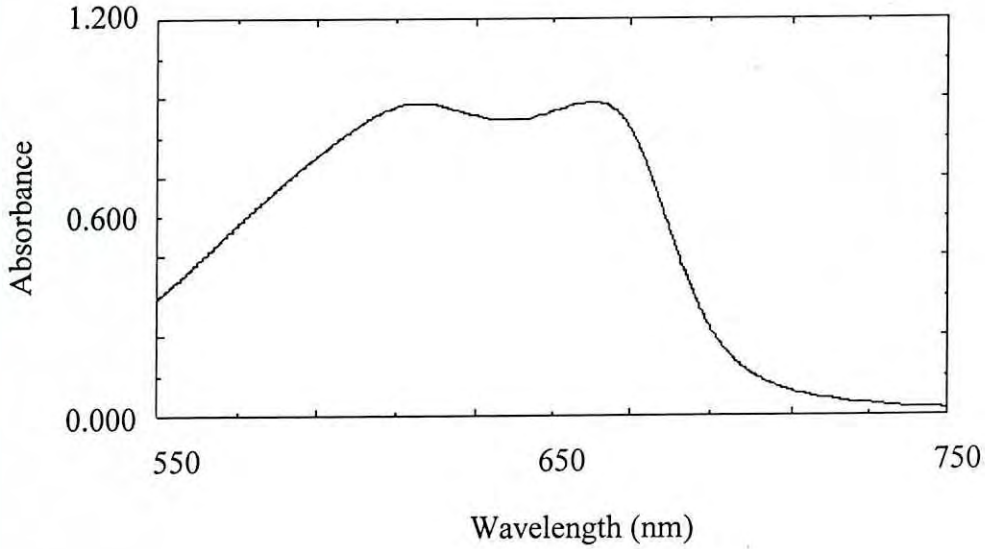

Fig. 2.3.3: Absorption spectra of MB in aqueous NH_3 solution (pH = 10.01).

2.4 Spectral Analysis

A. Infra-red Spectra

The PANI samples were obtained electrochemically, as described in section 2.2, either as thin films grafted on the Pt electrode or as thick deposits, which can be scratched off the Pt electrode, rinsed and dried. They were crushed to powder and used for IR measurements. IR spectra of the studied solids were frequently obtained by mixing and grinding a small portion of the materials with dry and pure KBr crystals. Thorough mixing and grinding were carried out in a mortar by a pestle. The powder 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. IR spectra of all the studied samples were recorded by an IR spectrophotometer in the region of 4000–400 cm^{-1}.

B. Ultra Violet–Visible Spectra

Optical spectra of the solid samples were recorded in their solution states. The solutions of MB and PANI samples were made by dissolving small amount of each solid in 50 mL of either aqueous of DMF solvents. The dissolution employed 30 min, sonication in an ultrasonic bath to allow appreciable extent of dissolution. The sample solutions exhibited deep color in some cases. Thus, to ensure preferred dilution of the sample solutions for this spectral measurement, the solutions were diluted with the solvent to a visible extent in such a way that the optical density remains within the range 0.1 to 2.0. The sample solution was placed in the sample holder while the reference holder was filled with the corresponding solvent. The UV-Vis

spectral analysis of the samples employed a double beam spectrophotometer attached with a synchronized personal computer (PC) for recording the spectral data. All the optical analysis were performed at room temperature to within 30^{o} ($\pm 2^{o}$)C.

2.5 Surface Analysis by SEM

Scanning electron microscopic technique was adapted to analyze the surface morphology of the samples. The PANI, samples as prepared onto the Pt electrode as films were utilized for SEM analysis. The films thus grown were rinsed and dried under vacuum before subjected to their surface analysis. The samples were loaded to the SEM chamber where these were kept under evacuation of 10^{-3} to 10^{-4} torr for ~ 30 min. Then a very thin layer of gold, ~ few nanometers thick, was sputtered onto the sample surface to ensure electrical conductivity of the sample surface under studied. The sample was then placed in the main chamber to view its surface image. A Philips XL 30 SEM arrangement was employed for this analysis. The image of the surface morphology is recorded in a PC that interfaced with the main SEM system. The operation system performed all the analysis under in situ vacuum conditions.

2.6 Adsorption Study

In this work, adsorption of MB dye was carried out onto the polymeric matrices, viz., neutral-PANI, acidic-PANI, basic -PANI and doped -PANI. The progress of adsorption was followed spectroscopically. The procedure of the adsorption study described below: Adsorption of MB on neutral -PANI, acidic-PANI and basic-PANI and doped PANI matrices

were performed from the aqueous solutions of pH 7.35, 2.47 10.01 and 10.01, respectively.

A fixed amount, either 0.050 g or 0.020 g of adsorbent sample was taken to each of the seven reaction vessels. Each vessel was charged with 50 mL MB solution of desired concentration. Immediately after the addition of MB solution to the container, the shaking device was allowed to function. The bottles were put down from the shaker by turn after 15 min, 30 min, 45 min, 60 min, 90 min, 120 min and 150 min respectively. After shaking, the solutions were filtered with cotton and pipette until clear solution was appeared. Finally, the absorbance of the remaining unadsorbed clear solution was taken by the UV-vis spectrophotometer.

In this way, the MB solute was allowed to adsorb from its solution on the surface of adsorbents employed. To a series of MB solutions of 0.5×10^{-5} M, 1.0×10^{-5} M, 1.5×10^{-5} M, 2.0×10^{-5} M, 2.5×10^{-5} M and 3.0×10^{-5} M, the same procedure for adsorption was adopted for a particular sample. The adsorption on the other samples were studied under an identical set of experimental conditions mentioned above.

2.7 Determination of Surface Area

Adsorption of MB dyes onto the PANI matrices allow to predict the specific surface area of the polymeric matrices employed.

The amount of MB solute adsorbed from the original solution was found from the absorbance of the remaining solution. In all the case, equilibrium time of adsorption was seen to be reached within ~2h. The equilibrium amount adsorbed (mg g^{-1}) from different concentrations of MB

dyestuff was calculated from the original concentration (M) of MB solution and the corresponding concentration for the observed absorbance of the remaining solution. The equilibrium concentration was obtained from the absorbance at equilibrium time with the help of a calibration curve. Calibration curve represents absorbance of stock solution at its different concentrations. Figures 2.7.1-2.7.3 show the calibration curves of MB solution prepared in aqueous H_2SO_4 (pH = 2.047), distilled water (pH = 7.35) and aqueous NH_4OH (pH = 10.01) solutions respectively. In fine, a plot of adsorption (mg g^{-1}) vs equilibrium concentration (M) was used to find out the monolayer capacity (mg g^{-1}) from the steady point of the curve. This value of monolayer capacity was put in the equation. In the equation the values of other parameters like molecular mass, M, of MB (i.e. $C_{16}H_{18}ClN_3S.\ 2H_2O$ = 355.89 g mol^{-1}); Avogadro constant, N = 6.023×10^{23} and the cross-sectional surface area of MB, A_m= 130×10^{-20} $Å^2$ BET with N_2, and A_m = 78×10^{-20} $Å^2$ BET with Ar were put and the specific surface area, S ($m^2\ g^{-1}$) of the six different samples were calculated.

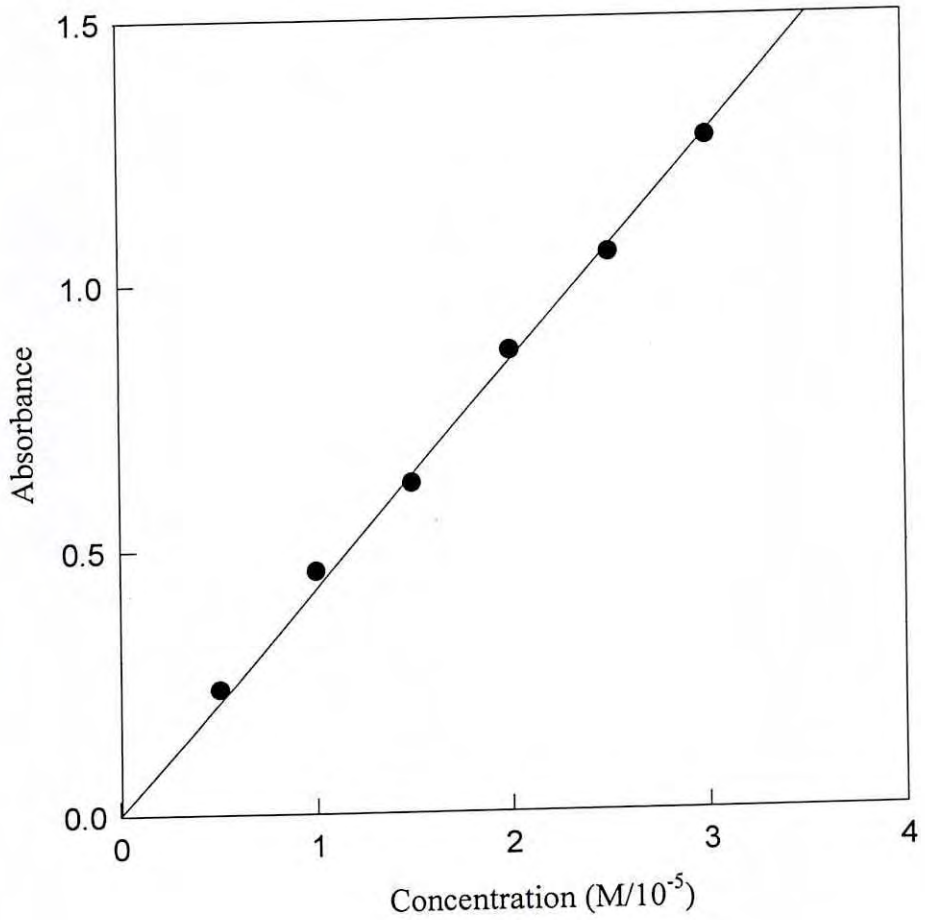

Fig. 2.7.1: Calibration curve of MB in aqueous H_2SO_4 solution (pH = 2.47).

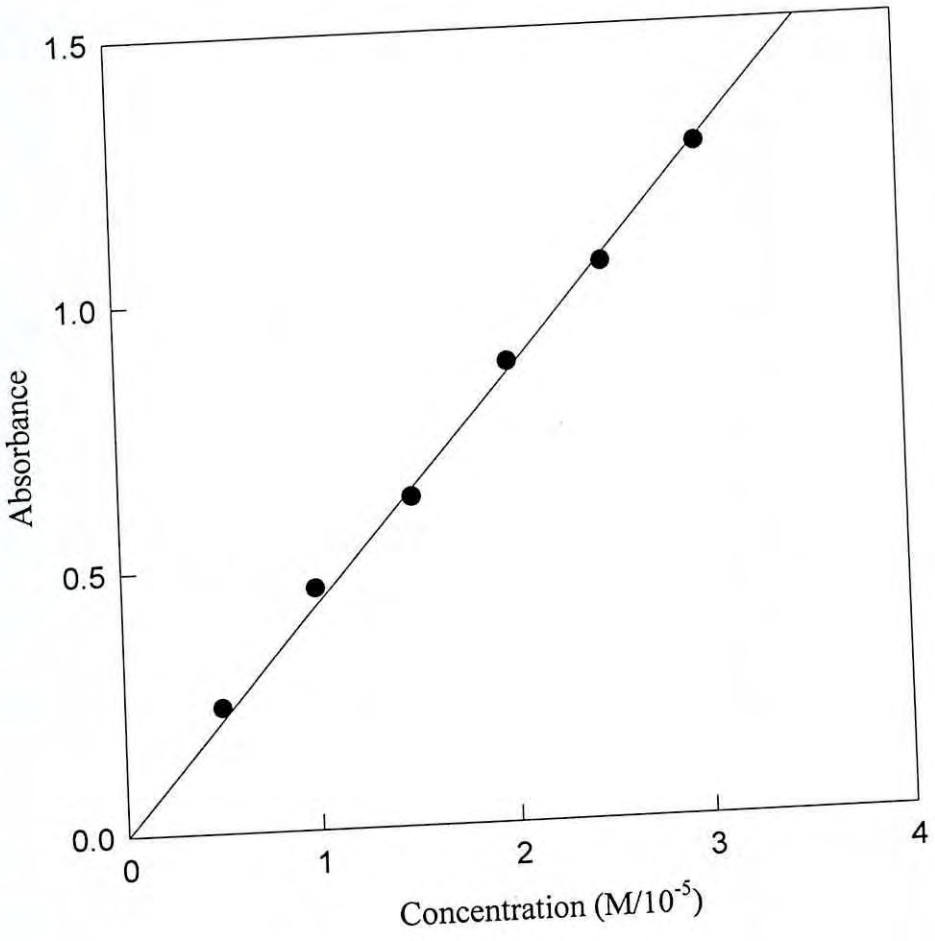

Fig. 2.7.2: Calibration curve of MB in double distilled water (pH = 7.35).

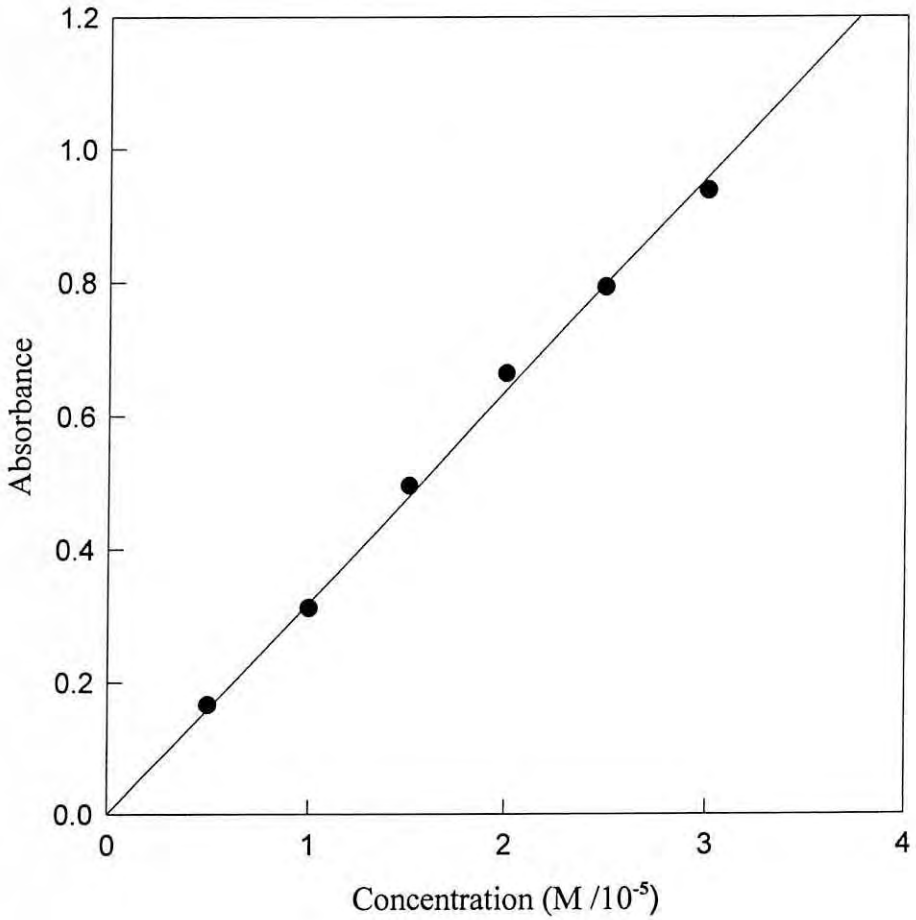

Fig. 2.7.3: Calibration curve of MB in aqueous ammonia solution (pH = 10.01).

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Chapter - 3

RESULTS & DISCUSSION

3.1 Electrochemically Modified Polyaniline Adsorbent

Many novel approaches to control the surface structure of several kinds of materials have been proposed. Recently, some interests have been focused on the potential application of polymer surface as adsorbents for separation and purification problems [1-3]. One clear advantage of polymers is the ability to control their pore structure and internal surface area by varying the polymerization conditions [4-6]. Such uniformity of physical properties has adsorption homogeneity and often allows regeneration under milder conditions. The feasible applications of polymeric adsorbents are to remove hydrophobic components from dilute solutions and air streams.

PANI is one of the most potentially useful conducting polymers and has received considerable attention in recent years by many workers. PANI has a reactive NH group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which having a lone pair of electrons, is responsible for the technologically interesting chemistry and physics. Protonation of PANI does not only involve the ingress of protons, but also accompanied by ingress of anions, to maintain charge neutrality. This suggests that the behavior of PANI depends on the pH and on the counter ion of the Brönsted acid used for doping. The insulator state of PANI can be protonated (doped) with non-oxidizing protonic acid such as HCl, H_2SO_4 or organic acids e.g. *p*-toluene sulfonic acid. In view of the above facts, it is expected that surface modification of PANI may take place by controlling its mode of preparation and doping processes. In this work, PANI is synthesized electrochemically and protonated under different pH condition with a view to modify the surface of PANI. The electrochemical synthesis and its doping characteristics are discussed below.

Anodic oxidation of the monomers on the inert metallic electrodes to yield polymer is the most current electrochemical method for the synthesis of conductive polymer films, such as, PANI, polypyrrole (PP), polythiophene (PT) etc. The anodic oxidation of aniline is generally effected on an inert material which is generally Pt [7-13]. In the present work, electrochemical synthesis of PANI was carried out by anodic oxidation of aniline onto a Pt electrode. Typical CV of electrochemical polymerization of aniline is given in Fig. 3.1.1. On sweeping the potential from –0.2 to +1.0 V *vs* SCE, a sharp rise in current is seen at a potential *ca.* +0.8 V indicating the oxidation of aniline to yield PANI [14, 15]. A thin deep blue film is seen on the Pt surface. As the sweeping repeated, i.e., in the second and subsequent cycles, the peak current increases further indicating the formation of more deposits of PANI on the substrate. Potential cycling was repeated upto 5 cycles for the deposition of PANI film. The anodic peak at *ca.* + 0.20 V is observed from the second scan. This peak can be assigned to the oxidation of PANI film that deposited on the electrode corresponding to the conversion of amine units to radical cations in the polymer chain [16-17]. The deep blue color of the film turned to greenish-yellow when potential sweep approached to the cathodic direction at *ca.* +0.0 V or lower. Figure 3.1.2 also represents the CV of electrochemical polymerization of aniline from an electrolytic solution containing 0.8 M H_2SO_4 + 0.1 M *p*-toluene sulfonic sodium salt. Here polymerization was also allowed to grow on the Pt upto 5 cycles. The CV of PANI film shows characteristic peaks as also observed in Fig. 3.1.1. It is interesting to note here that the polymerization current for the later case is much higher then the first one. The higher current indicates the formation of a greater amount of PANI in the later case (Fig. 3.1.2) suggesting a greater influence of electrolytic media on the polymer formation.

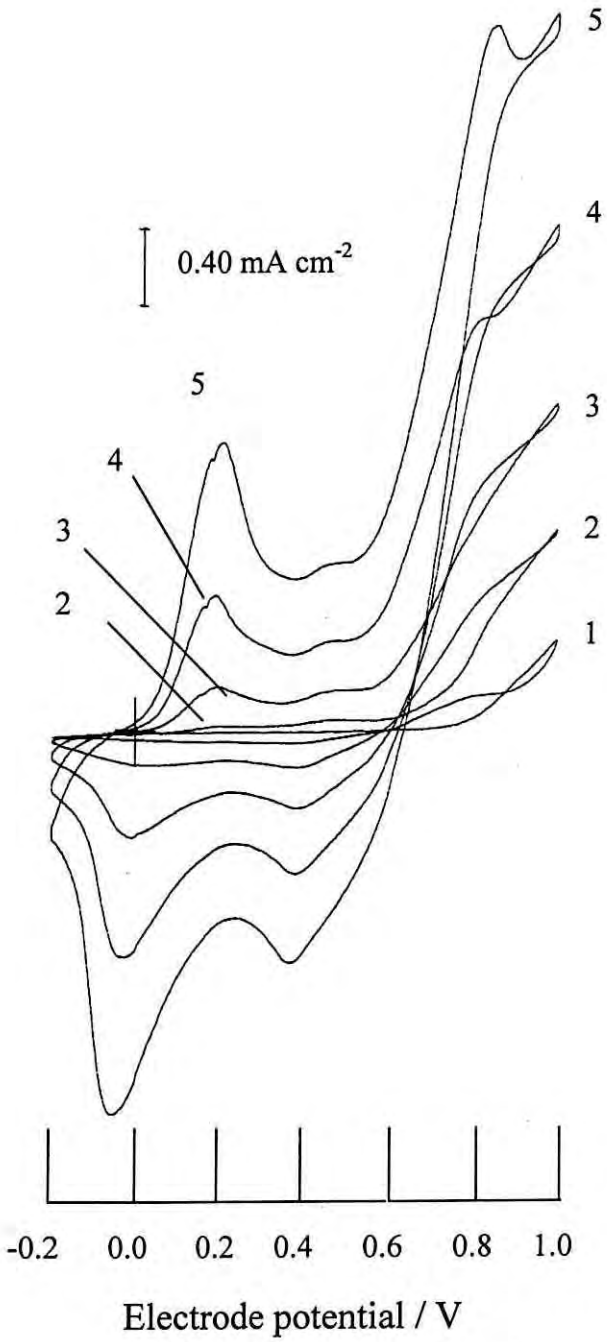


Fig. 3.1.1: CV during electrochemical synthesis of PANI from 0.5 M aniline + 0.8 M H_2SO_4

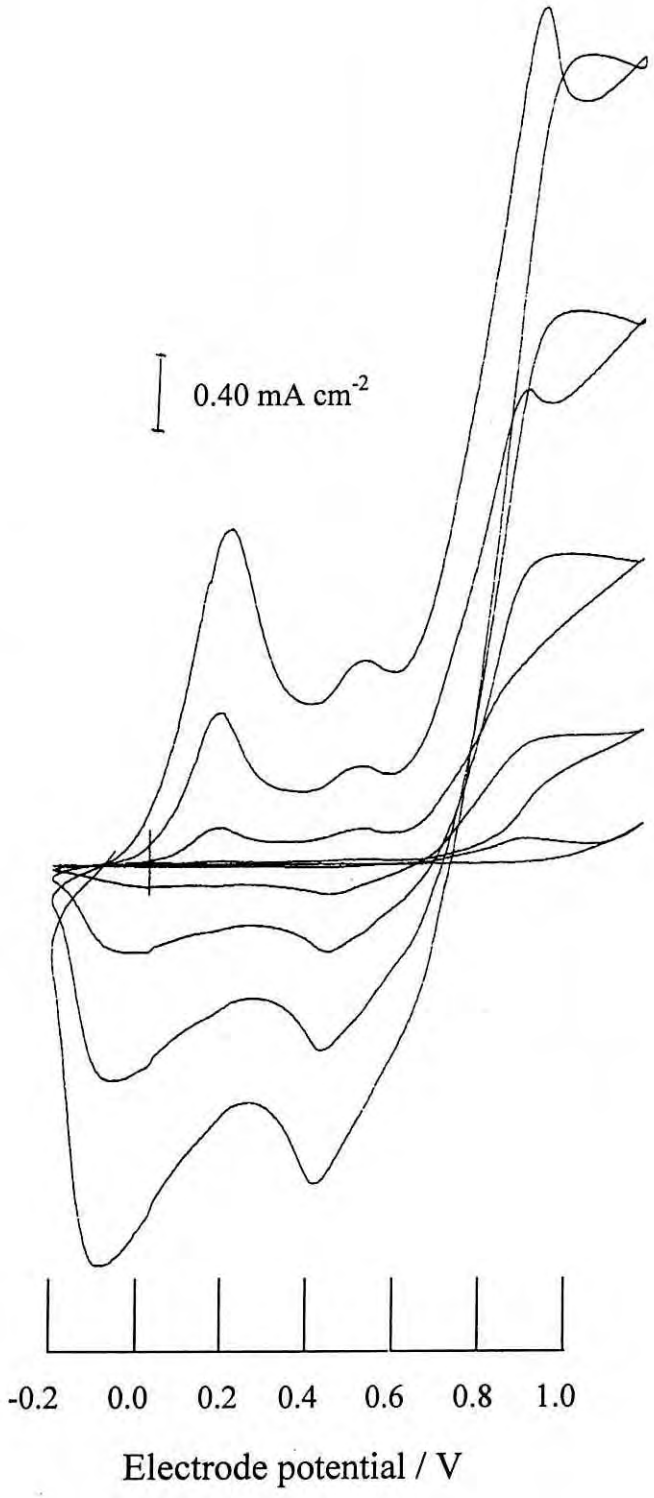
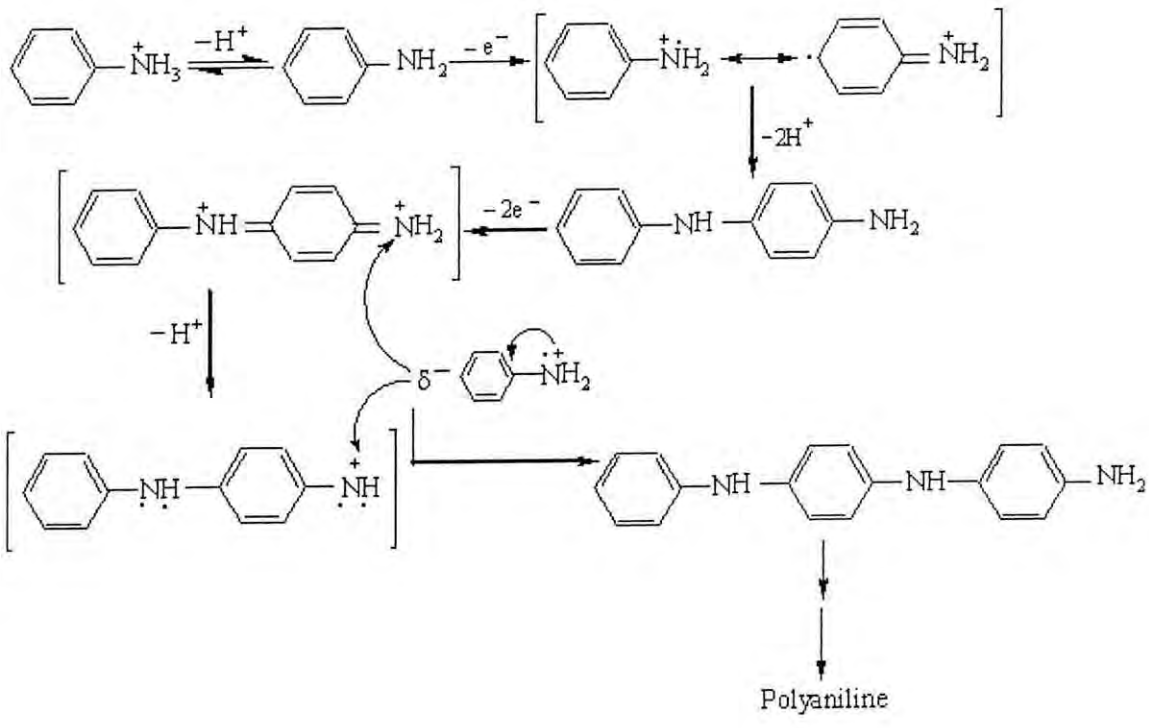


Fig. 3.1.2: CV during electrochemical synthesis of PANI from 0.5 M aniline + 0.8 M H_2SO_4 + 0.1 M *p*-$C_6H_4CH_3SO_3Na$.

The mechanism for the electrochemical formation of PANI as proposed by Y. Wei *et. al.* [18], is presented in Scheme –1. The oxidation of aniline to form the diamer is a slow reaction [18, 19]. Since the diamer has a lower oxidation potential than does aniline [7, 20], it will undergo oxidation immediately after its formation to yield a diimminium ion [19]. An electrophillic attack of aniline monomer by the diiminium or by a nitrenium ion [21], which could be generated from a deprotonation of the diiminium ion [19], would accomplish a growth step and lead eventually to the final polymer.

Scheme- 1: *Mechanism for the electrochemical formation of PANI.*



Electrochemical doping – dedoping process

The electrochemical behavior, i.e. doping–dedoping processes, of the PANI film electrode was examined by cyclic voltametry in the aqueous

electrolytic media. The typical CV are shown in Fig. 3.1.3 and 3.1.4 the PANI film that are deposited previously on the Pt electrodes were used for this purpose. The film coated Pt electrode was washed several times with distilled water and then immersed in an aniline free aqueous solution of H_2SO_4 (0.8M). The CV of the Pt coated PANI (Fig. 3.1.3) shows clearly one defined peak at +0.2 V in the anodic sweeping while in its cathodic scan the peak appears at *ca.* +0.02 V while the other CV (Fig. 3.1.4) shows identical peaks at 0.26 and 0.0 V *vs* SEC, suggesting the presence of electroactive regions in both the PANI films [22, 23]. The peaks at +0.2 and +0.26 V indicate the oxidation of the PANI films at which electrolyte anion is doped into the polymer film. The PANI film reduced at +0.02 and 0.0 V where dedoping of the electrolyte anion occurs. The oxidation and reduction waves are not symmetrical as can be seen in the CV (Fig. 3.1.3, 3.1.4). The shape of the redox peaks and the difference in the peak potentials suggest that the electrochemical reaction is quasi-reversible and that there are differences between the reduction and oxidation kinetics [24]. The redox process of PANI in aqueous electrolytic media thus employed in the present work may be interpreted as follows:

$$(\text{Polymer}^{+}\,X^{-}) + e^{-} \leftrightarrows \text{Polymer}^{\circ} + X^{-}$$

($\text{Polymer}^{+}\,X^{-}$) is the oxidized polymer obtained through electro-polymerization and/or doping, polymer $^{\circ}$ is the reduced polymer and X^{-} is the electrolyte anion (SO_4^{2-}, $C_6H_5CH_3SO_3^{-}$).

The redox reaction of the PANI films are accompanied by the color changes. The films appears as a deep blue color when the electrode potential in the anodic direction is positive by +0.2 V + 0.26 V and turns to a transparent

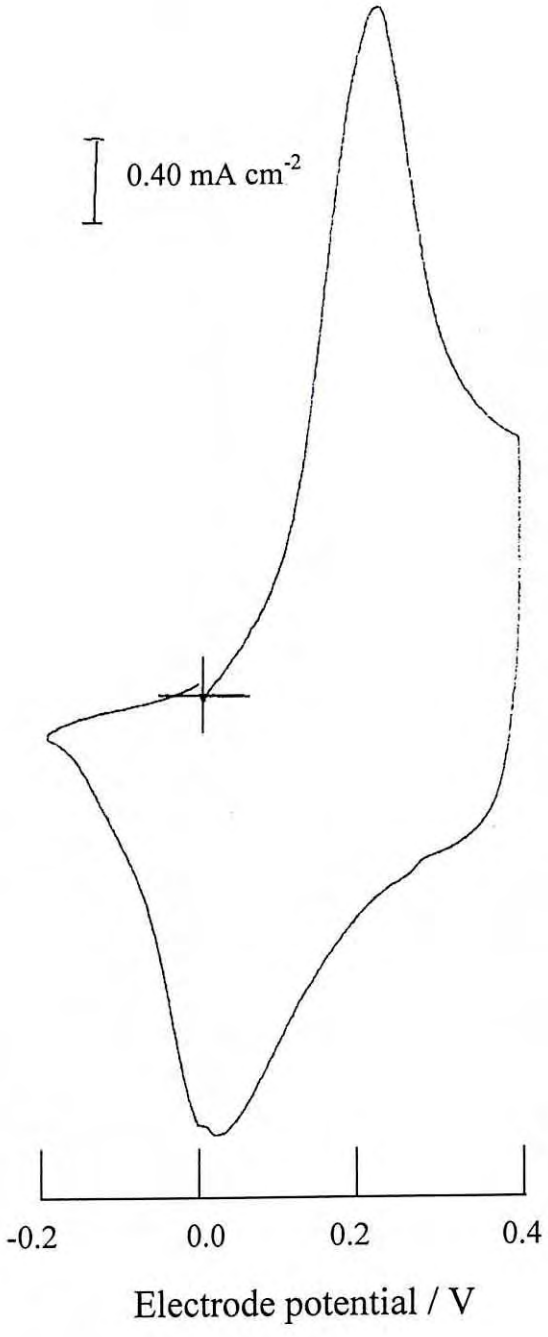


Fig. 3.1.3: CV for the doping -dedoping of PANI in 0.8 M H_2SO_4 solution.

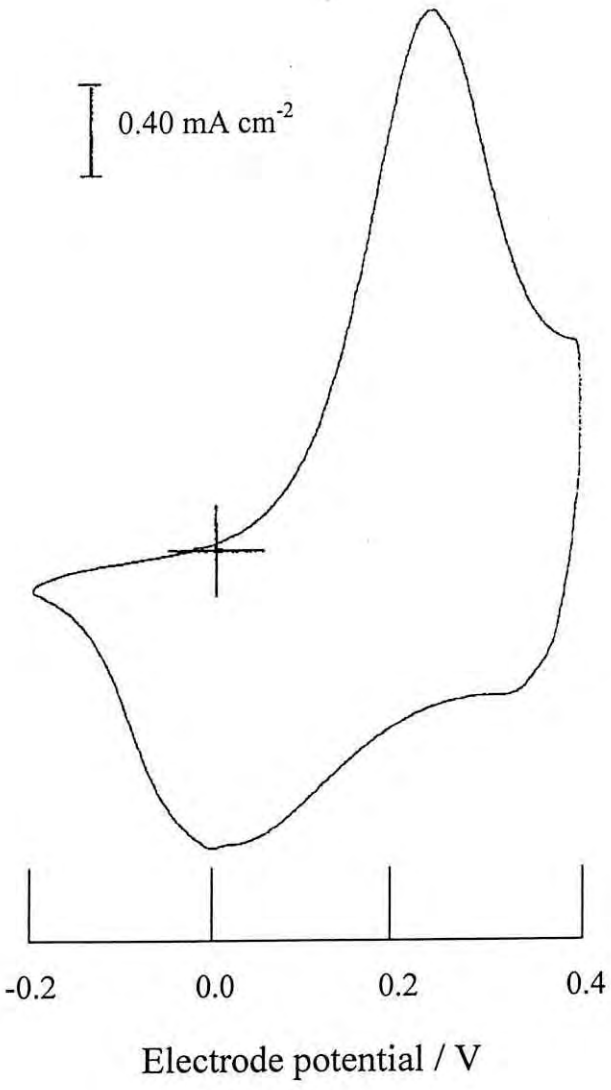


Fig. 3.1.4: CV for the doping -dedoping of PANI in 0.8 M H_2SO_4 + 0.1 M *p*-$C_6H_5CH_3SO_3Na$.

greenish-yellow when it is switched to the cathodic direction at *ca.* +0.2 and 0.0 V. The color changes occur evenly throughout the film with no evidence of region with different reactivity. Similar observation for color change with PANI in its redox process has also been reported previously [25, 26].

3.2 Characterization of Polyaniline Adsorbent

A. Infra red spectral analysis:

Compounds, particularly organics absorb in the IR region. Although the IR spectrum is characteristic of the entire molecule, it is true that certain groups of atoms give rise to bonds at or near the same frequency regardless of the structure of the rest of the molecule. Since identification of a compound is not solely depended on IR spectra, a detail analysis of the spectrum usually not be required. In this present work, IR spectral analysis were performed in order to get some insight about the structure of the synthesized matrices and the results are described below:

The IR spectra of the PANI matrices that prepared electrochemically are presented in Fig. 3.2.1 - Fig. 3.2.4. It is worthwhile to mention that the observed IR spectra are consistent with the previous studies [27-33] and discussed below according to the frequency region:

N-H stretching region lies in between 3500-3100 cm^{-1}. 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}.

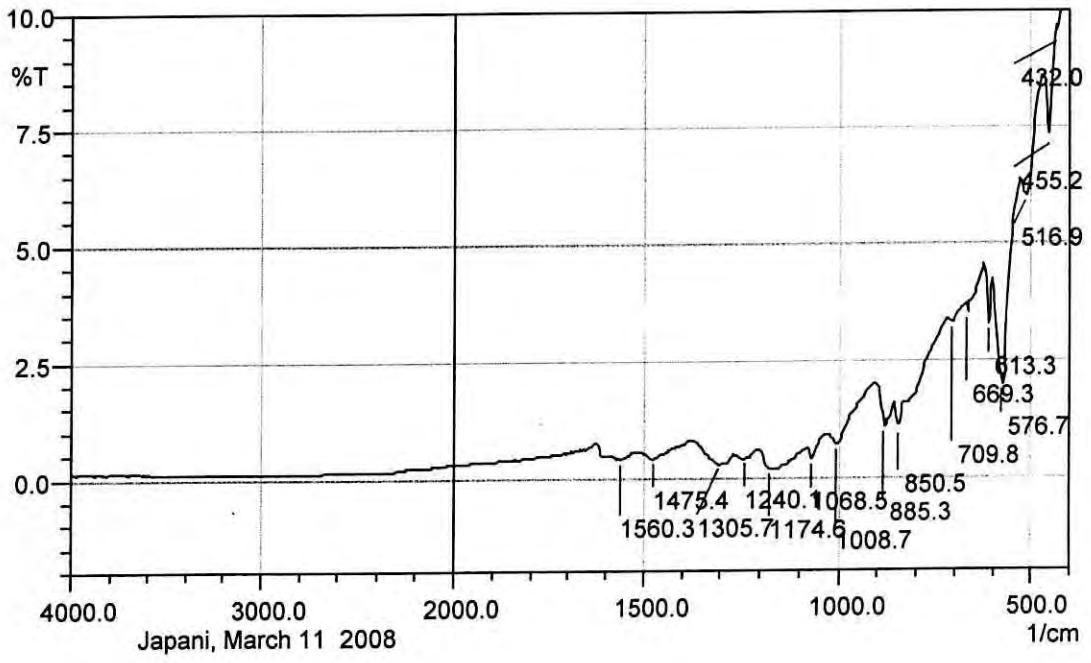


Fig. 3.2.1: IR spectra of acidic-PANI.

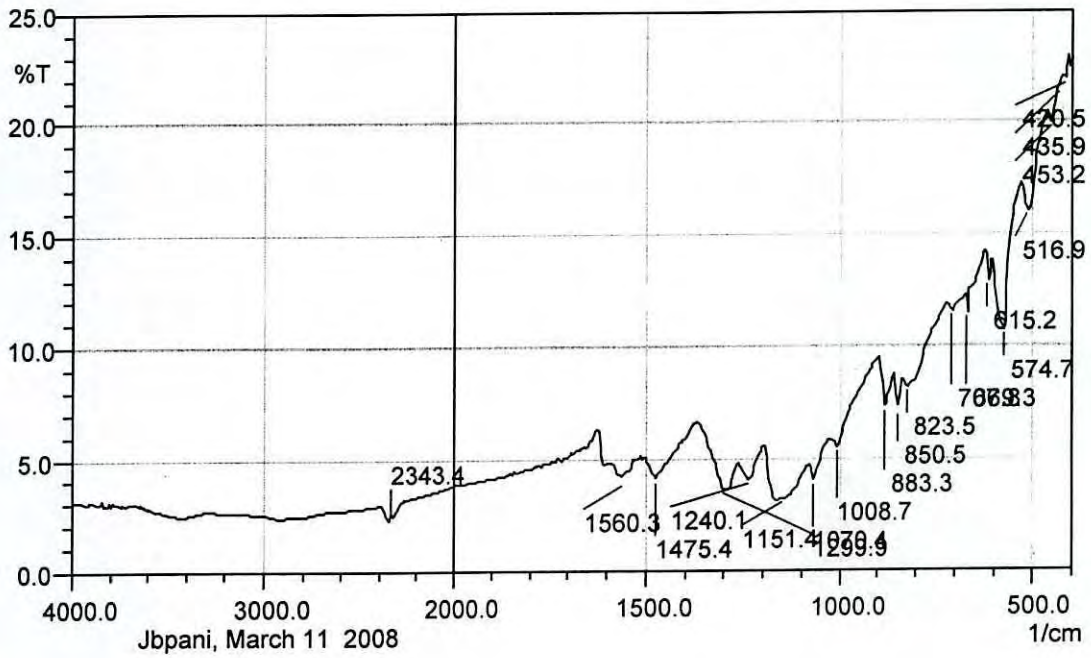


Fig. 3.2.2: IR spectra of neutral-PANI.

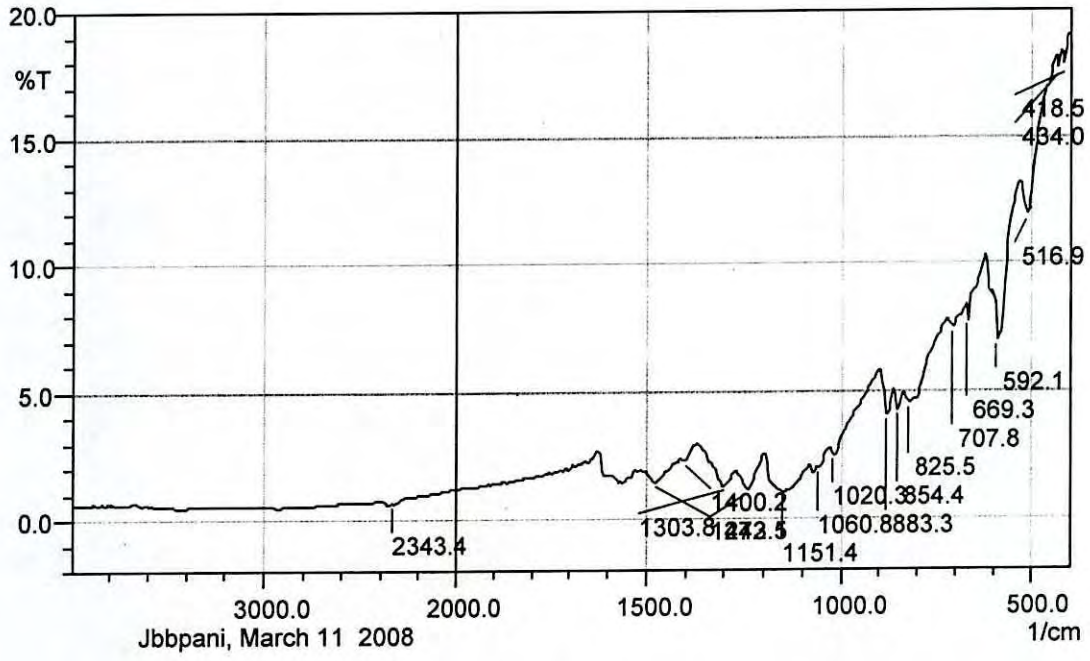


Fig. 3.2.3: IR spectra of basic-PANI.

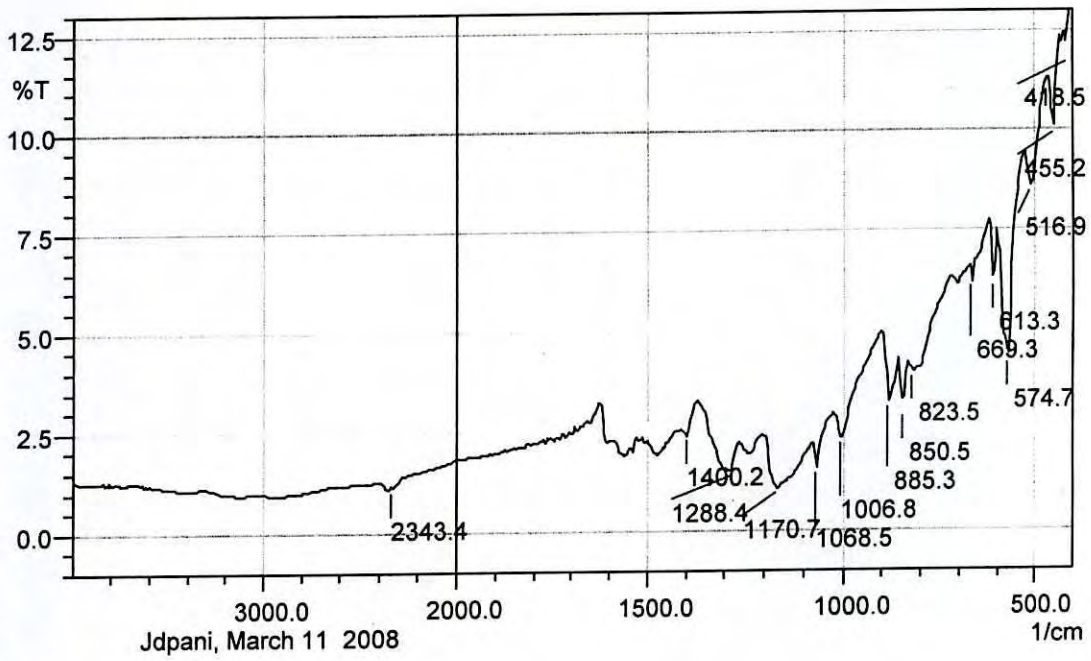


Fig. 3.2.4: IR spectra of doped -PANI.

The C-H stretching region is 3100- 2800 cm^{-1}. The absorption of PANI in this region is even weaker but it is observable at 3050 – 3030 and 2960 – 2850 cm^{-1}.

Aromatic ring breathing, N-H deformation and C=N stretching all give absorption in the 1600-1450 cm^{-1} 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 this range.

1400-1240 cm^{-1} 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 band at 1160 and 1140 cm^{-1} 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 structure. The 1140 cm^{-1} band is a vibrational mode of $B\text{-}\overset{+}{N}H{=}Q$ or $B{-}\overset{\bullet+}{N}H{-}B$ 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].

The *in-plane* and *out-of-plane* bending of C-H bonds on aromatic rings appears at 1220-500 cm^{-1}. 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.

Absorption at 1120 and 625 cm^{-1} are also observed in the spectra of the PANI film and correspond to the presence of HSO_3^{-2} ions, which were used as an electrolytic anion in the film [37].

The IR results are summerized further in Table 3.2.1.

Table-3.2.1: Tentative assignment of the IR spectra of acidic-PANI sample.

Frequency (cm^{-1})	Assignment*
3590-3710	presence of H_2O
3300-3500	NH_2 asym. str.
1560	str. of N=Q=N
1475	str. of benzene ring
1240	C-N str. in BBB
1151	a mode of N=Q=N
1008	C-H *ip* on 1,2,4-ring
883	C-H *op* on 1,2,4-ring
850	
823	C-H *ip* on 1,4-ring
706	C-H *ip* on 1,2-ring
615	aromatic ring deformation
516	

* Abbreviations: asym = asymmetric, str = stretching, *ip* = in-plane bending, *op* = out-of-plane bending, Q = quinoid unit.

B. Ultra violet- visible spectroscopy

UV- Vis spectra of the PANI recorded in DMF solutions / suspension at room temperature are given in Fig. 3.2.5. The possible electronic processes that can take place under the electromagnetic UV-Vis irradiation

on the present samples have been reflected on the spectra. In principle, every electronic transition is manifested as a peak in the optical spectrum.

Optical spectra of all the PANI samples, shows strong absorptions at 360 nm and a week shoulders at *ca.* 560 nm and 630 nm. The result is similar to the studies reported by the early workers [38, 39] and suggests that the peak observed at 335 nm corresponds to the interband $\pi - \pi^*$ (valence band to conduction band) transition while the other two transitions observed in the spectra at around 450 and 660 nm may be responsible for PANI conductivity by forming polaron and bipolaron as mid-gap state. Similar phenomenon has also been observed with other conducting polymers such as PP [40, 41]. In fact, polaron state is a radical cation, i.e. contains one electron whereas bipolaron is a dication, *i.e.* electronless. At low doping level, polaron formation takes while at highly doped states, bipolaron formation predominates. However, because of the greater stability, a bipolaron is favored over polaron.

The absorption intensities at 360 nm seems to different for different PANI samples. This may be due to the differences of solubility of the PANI in DMF. The PANI samples were indeed treated at different solution pH. However, it is important to note that the absorption show the same wave length and thus the band gap of the different treated PANI should be the same. The bipolaron states, thus the electrical conductance of the PANI samples could not be quantify as the responses appeared as dull shoulder through it expected that the PANI samples should exhibit non-identical electrical property. However, the optical spectrum as obtained in the present study clearly demonstrated the characteristic features of PANI [38, 39].

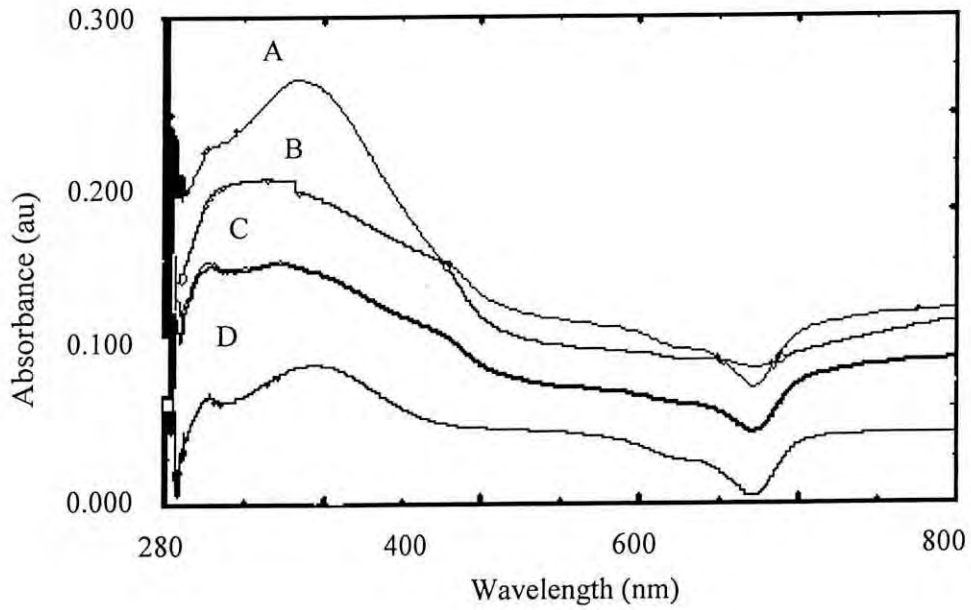


Fig. 3.2.5: UV-visible absorption spectrum of PANI in DMF solution. A= acidic-PANI, B= basic-PANI, C= neutral-PANI and D= doped-PANI.

C. *Scanning electron microscopy*

Scanning electron microscopy appears to be the best choice for the determination of surface morphology because of its potential for precise analysis of a solid surface. Chemical composition and morphological structure of a material strongly depends on the mode of synthesis, be it chemical or electrochemical, on the synthetic conditions such as pH, concentration of reactants and products, chemical nature of oxidant, oxidation potential etc. Thus, a variety of chemical structure and morphology of a material is possible. In the present work, PANI samples were synthesized electrochemically and the samples thus prepared were treated with different solution pH. The treated samples are then examined by SEM to predict their surface morphologies. Figure 3.2.6 shows the SEM images of (A) acidic-PANI (B) neutral-PANI (C) basic-PANI and (D) doped-PANI surfaces. It can be seen that a grain-like morphology appears when PANI is prepared electrochemically from electrolytic solution containing H_2SO_4 and the surface is not uniformly covered with the PANI grain is all the cases. The granular morphology changes when PANI is treated with distilled water having pH=7.35 as depicted in B. The grains seems to be aggregated to a bigger deposit and randomly pilled on the substrate. In both the acid- and neutral-PANI, the morphologies seem to be continuous and thus compact suggesting less in their structures. The basic- and doped-PANI shows quite a dissimilar morphologies than those of acidic- and neutral-PANI. The particulates form rigid deposits, distributed randomly on the substrate. The deposit are seem to be three dimensional structure with plenty of pores in it. The pores and the dimensionality obviously provide greater surface area and thus surface activity. The size of the particle deposits in the basic-PANI and doped-PANI are seen to be ranging from 5-50 μm.

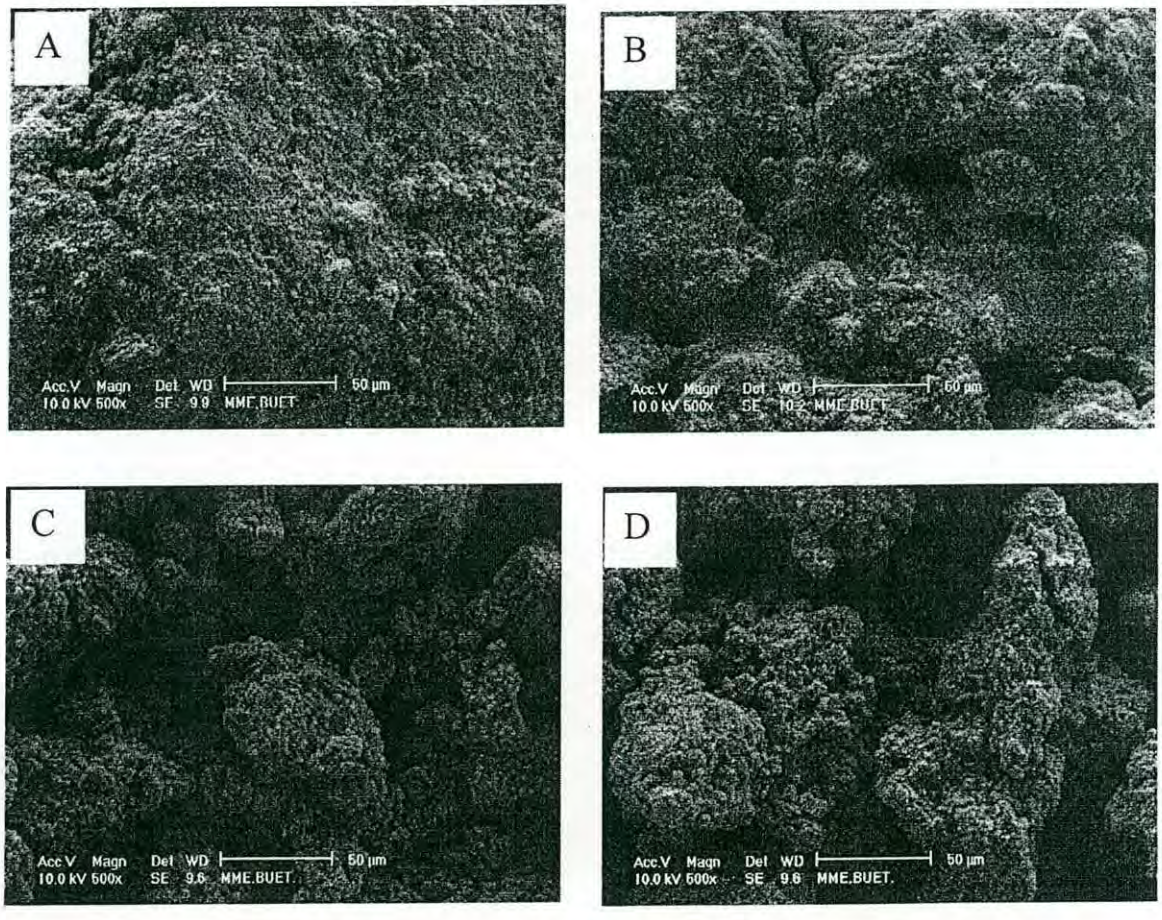


Fig. 3.2.6: SEM micrographs of (A) acidic-PANI, (B) neutral-PANI, (C) basic-PANI and (D) doped-PANI.

The present SEM observation clearly suggests that the PANI surface is modified by treatment with solution of different pH. Besides, the present PANI prepared electrochemically is clearly different than the PANI when prepared chemically. Modification of the PANI surface is also reported by the previous workers [42-44]. From the observed dissimilar morphological features of the PANI samples, it is expected that their surface activity i.e. surface area, could be different. The surface capacity of the PANI matrices will be discussed in the following sections.

D. Moisture absorption Capacity

Hydrophobicity and hydrophilicity are the very important properties of a materials. Based on these two properties, the materials are design for their appropriate technological application. Because of hydrophilic nature, many intelligent materials fail to be commercialized. As for example conductive PANI is an extremely important organic semiconductor and proved to be utilized in many technological application, but because of its high hydrophilic nature, their stability is reduced by absorbing water from atmosphere. In the present work, three different types of PANI were prepared. The PANI samples were thus investigated for their moisture absorption tendency simply by exposing a definite amount of the sample in open air. The result is shown in 3.2.7. Of the three samples, the acidic-PANI seems to absorp higher amount of than those of neutral- and basic PANI. The basic-PANI shows the least tendency to absorp water suggesting a hydrophobic nature of the materials. It is interesting to not that, electronic characteristics of the PANI is obtained in its acid treated form, i.e. in acidic-PANI. But acidic-PANI is highly hygroscopic. On the other hand, on treating with base, the PANI lost its electronic properties, but a tremendously interesting superior surface activity is seen to be generated in the basic-PANI. The surface activity of the basic PANI is discussed in section 3.3 and 3.4.

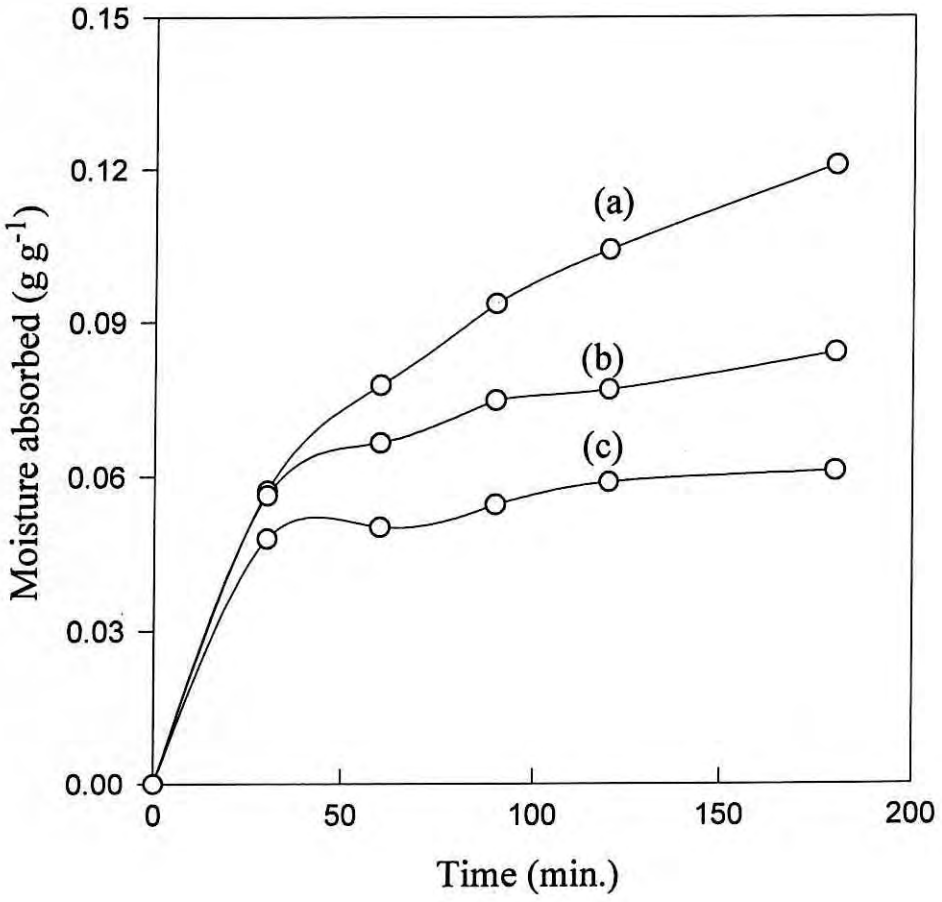


Fig. 3.2.7: Moisture absorption capacity of (a) acidic-PANI, (b) neutral- PANI and (c) basic-PANI.

3.3 Analysis of Monolayer Capacity and Surface Area

In monolayer adsorption all the adsorbed molecules are in contact with the surface layer of the adsorbent. The monolayer capacity is defined as the amount of adsorbate which is needed to occupy all adsorption sites as determined by the structure of the adsorbent and by the chemical nature of the adsorbate and for physical adsorption, as the amount needed to cover the surface with a single monolayer of molecules in close-packed array.

Monolayer capacity can be predicted from an isotherm from an experimental isotherm obtained by adopting adsorption process. In the present study, the adsorbate MB was allowed to be adsorbed on the adsorbent *viz.* acidic-PANI, neutral-PANI, basic-PANI and doped-PANI. The progress of MB adsorption with time on the above mentioned adsorbents were monitored spectrophotometrically. Typical adsorption spectra during the course of adsorption are given in Figs. 3.3.1(i)-3.3.1(iv). In each adsorbent, MB adsorption was carried out for its different initial concentrations, *viz* 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0×10^{-5}M. The spectral data at different time of adsorption for each concentration are then converted into amount adsorbed at each case. The data of spectral change and the corresponding amount adsorbed are presented elsewhere in this section.

The surface area of an adsorbent can be determined by adsorption method. In this case, it is necessary to know the monolayer capacity and the cross sectional area of the adsorbed molecule. Lamgmuir equation is applied to the experimental adsorption data to estimate the monolayer capacity. In the present work, MB solution was allowed to be adsorbed onto four different PANI matrices at room temperature. In order to evaluate the monolayer capacity and surface area of the PANI matrice, the results of the MB adsorption are presented in the Table 3.3.1- 3.3.52 and Figs. 3.3.1-3.3.52.

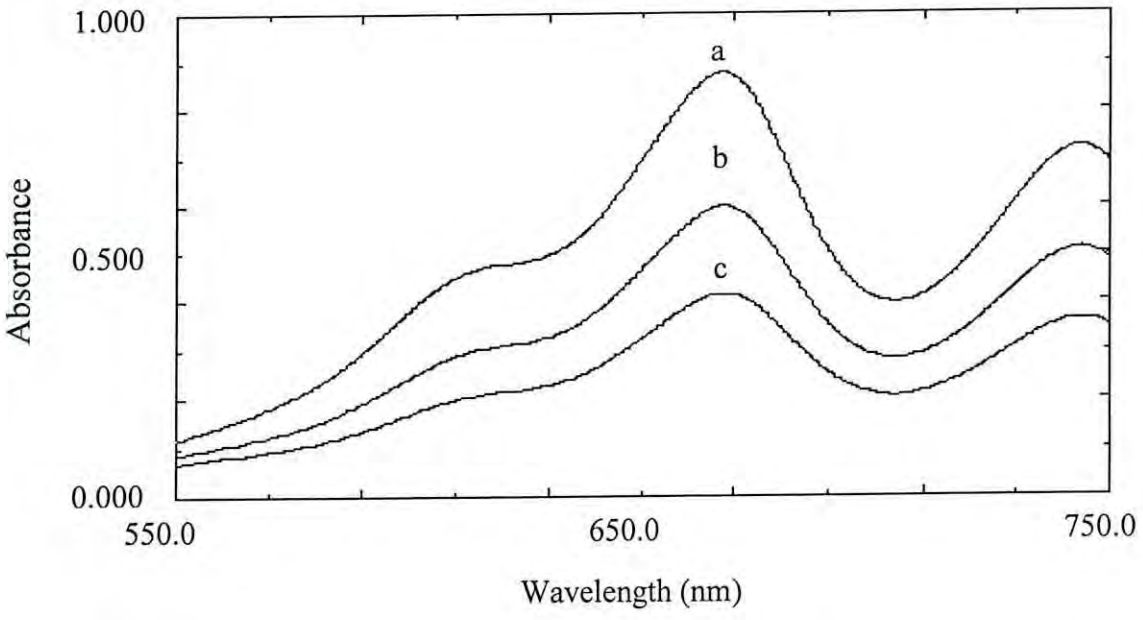


Fig. 3.3.1(i): Absorption spectra of 2.5×10^{-5} M MB on acidic-PANI at (a) 0 min, (b) 15 min and (c) 120 min.

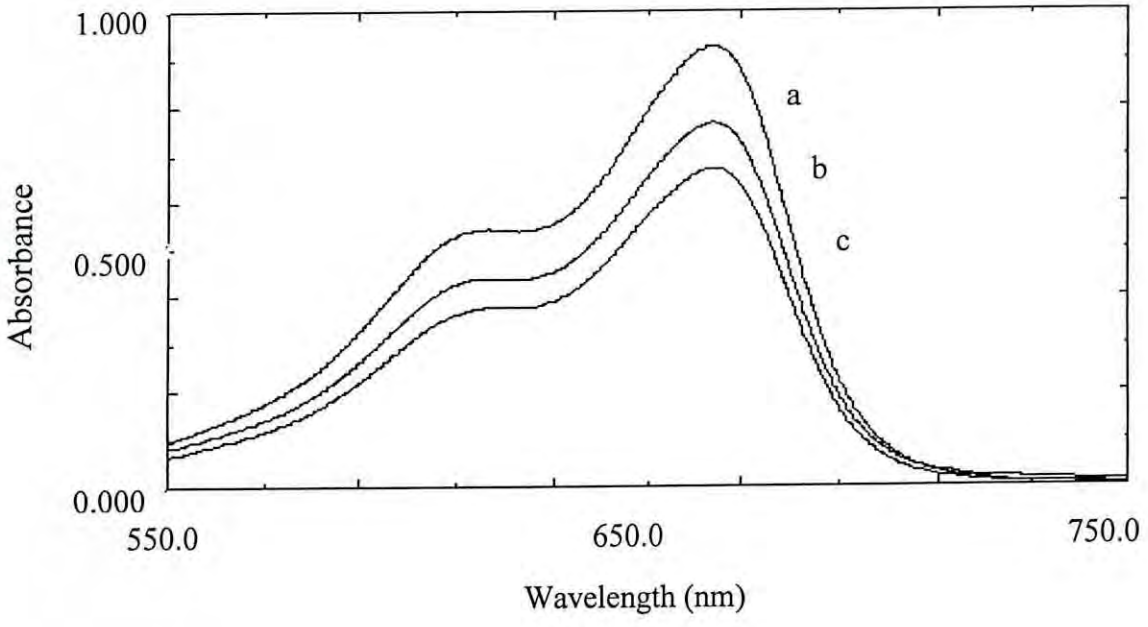


Fig. 3.3.1(ii): Absorption spectra of 2.5×10^{-5} M MB on neutral-PANI at (a) 0 min, (b) 15 min and (c) 120 min.

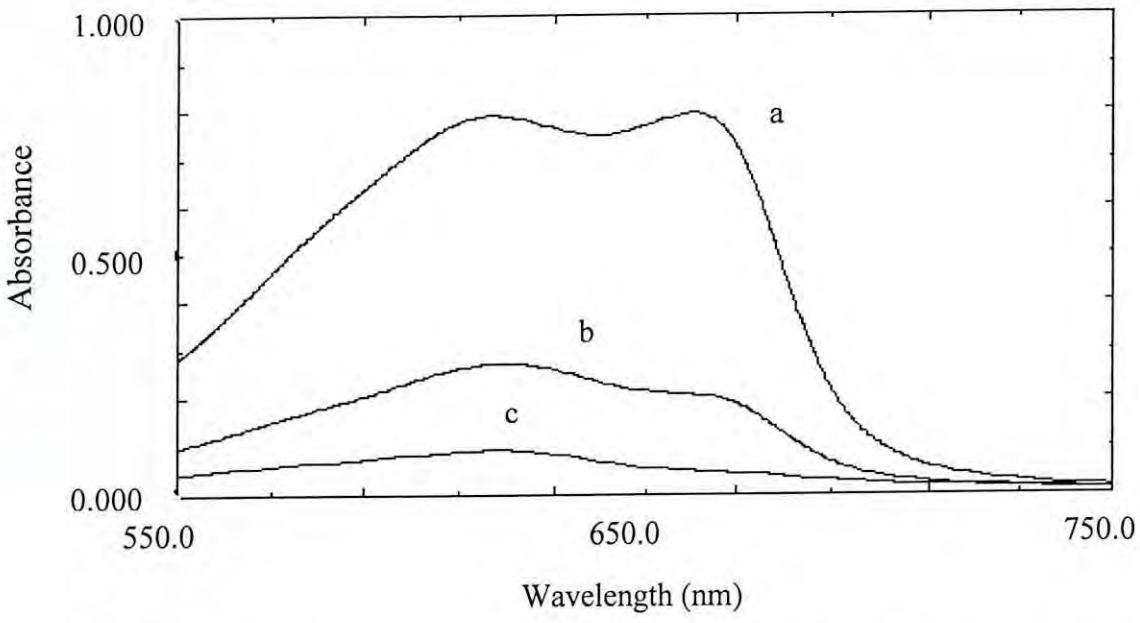


Fig. 3.3.1(iii): Absorption spectra of 2.5 $\times 10^{-5}$ M MB on basic-PANI at (a) 0 min, (b) 15 min and (c) 120 min.

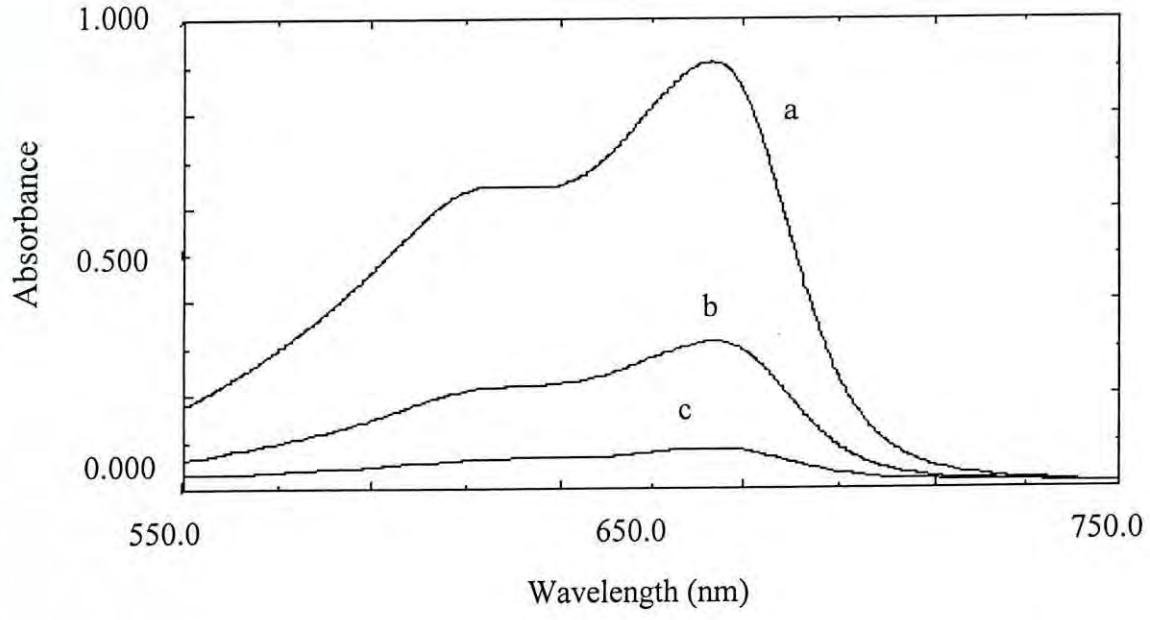


Fig. 3.3.2 (iv): Absorption spectra of 2.5 $\times 10^{-5}$ M MB on doped-PANI at (a) 0 min, (b) 15 min and (c) 120 min.

Table 3.3.1: Adsorption of MB dyestuff on acidic-PANI from 0.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
0.5×10^{-5}	0.050	15	0.1567	0.2384
		30	0.1227	
		45	0.1184	
		60	0.1025	
		90	0.0905	
		120	0.0905	
		150	0.0904	

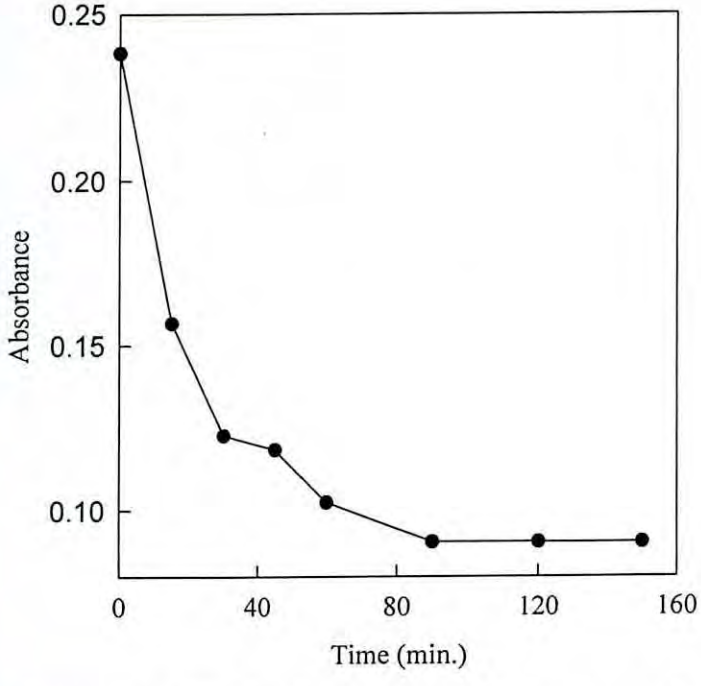


Fig. 3.3.1: Progress of MB adsorption with time on acidic-PANI (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.2: Amount of MB dyestuff adsorbed by acidic -PANI from 0.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 0.5×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.1567	0.0817	0.6821
30	0.1227	0.1157	0.9659
45	0.1184	0.1200	1.0018
60	0.1025	0.1359	1.1345
90	0.0905	0.1479	1.2347
120	0.0905	0.1479	1.2347
150	0.0904	0.1480	1.2331

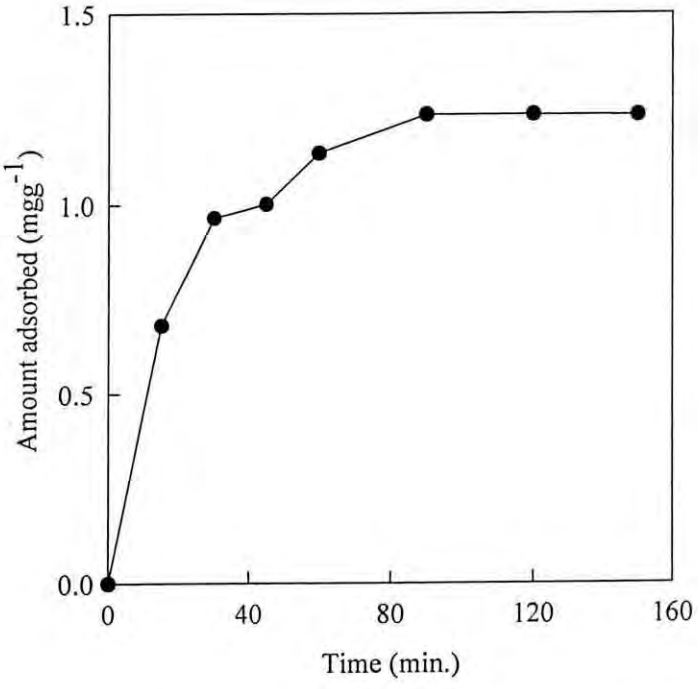


Fig. 3.3.2: Amount of MB adsorbed by acidic-PANI at different time of adsorption (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.3: Adsorption of MB dyestuff on acidic-PANI from 1.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.0×10^{-5}	0.050	15	0.3079	0.4600
		30	0.2808	
		45	0.2395	
		60	0.2251	
		90	0.2012	
		120	0.1918	
		150	0.1918	

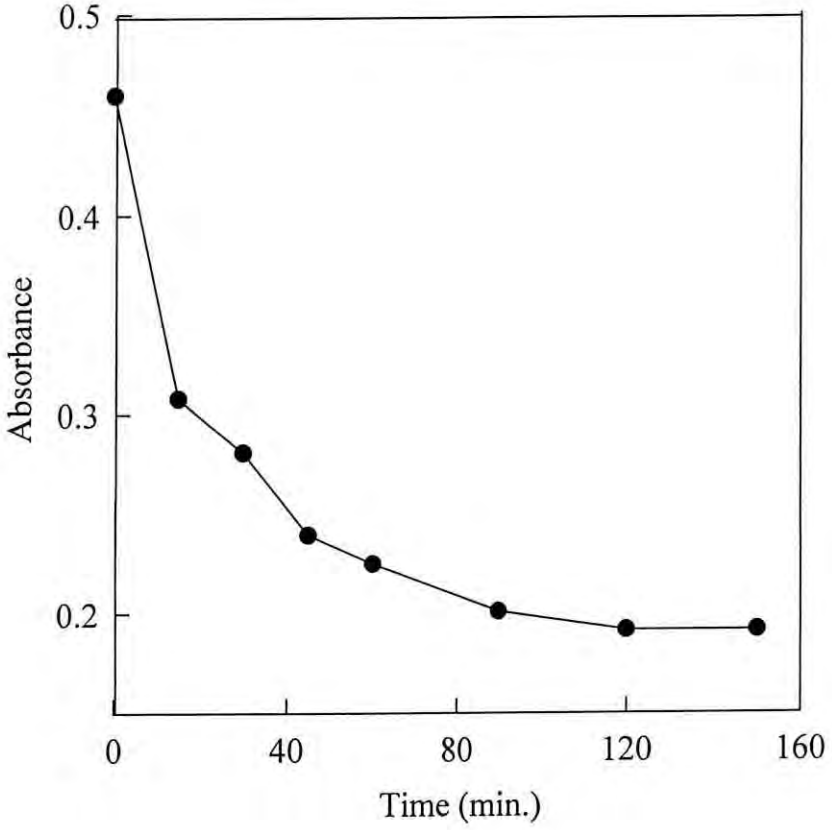


Fig. 3.3.3: Progress of MB adsorption with time on acidic-PANI (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.4 : Amount of MB dyestuff adsorbed by acidic -PANI from 1.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.0×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.3079	0.1521	1.2698
30	0.2808	0.1792	1.4960
45	0.2395	0.2205	1.8408
60	0.2251	0.2349	1.9610
90	0.2012	0.2588	2.1606
120	0.1918	0.2682	2.2390
150	0.1918	0.2682	2.2390

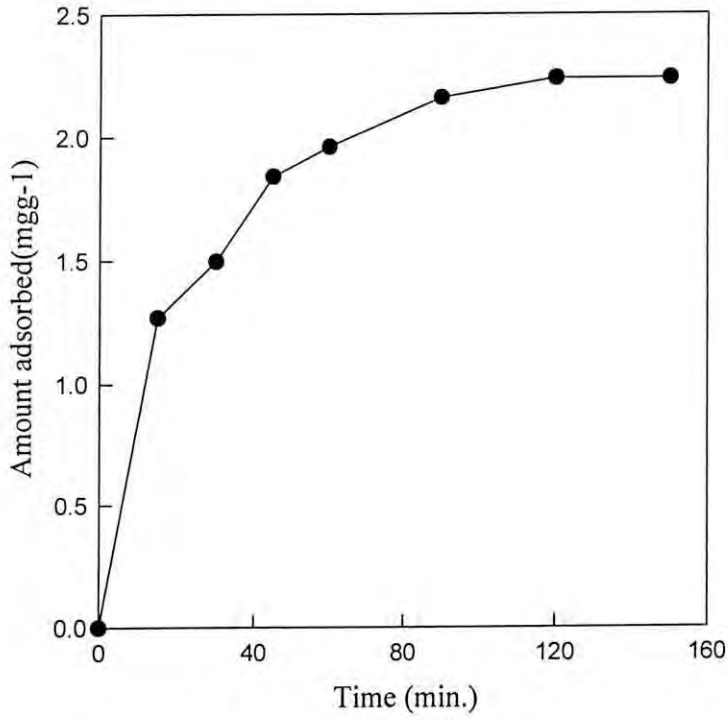


Fig. 3.3.4: Amount of MB adsorbed by acidic-PANI at different time of adsorption (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.5: Adsorption of MB dyestuff on acidic-PANI from 1.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.5×10^{-5}	0.050	15 30 45 60 90 120 150	0.4213 0.3625 0.3451 0.3367 0.2843 0.2656 0.2655	0.6245

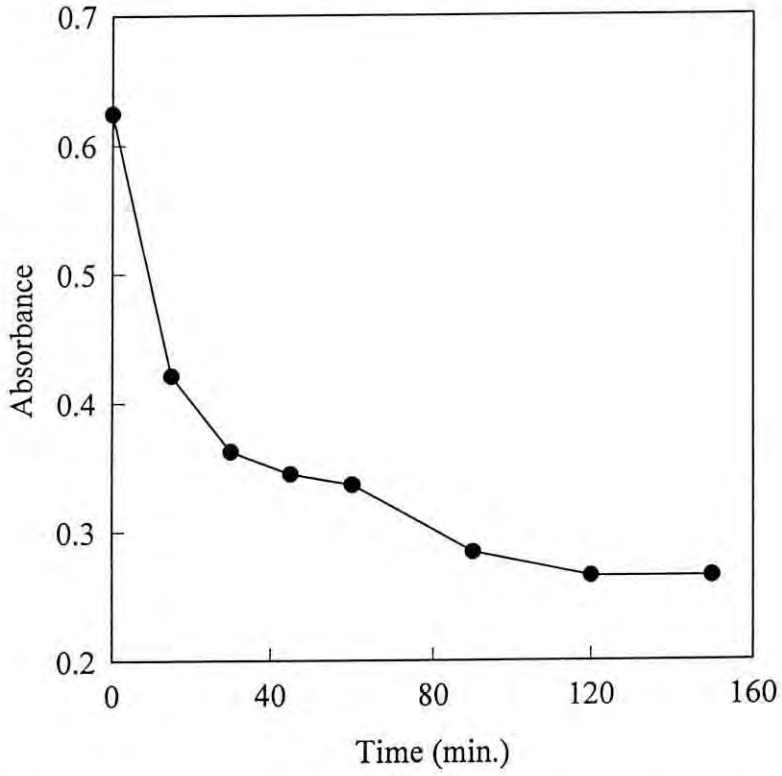


Fig. 3.3.5: Progress of MB adsorption with time on acidic-PANI (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.6 : Amount of MB dyestuff adsorbed by acidic -PANI from 1.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.5×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.4213	0.2032	1.6964
30	0.3625	0.2620	2.1873
45	0.3451	0.2794	2.3325
60	0.3367	0.2878	2.4027
90	0.2843	0.3402	2.8401
120	0.2656	0.3589	2.9962
150	0.2655	0.3590	2.9971

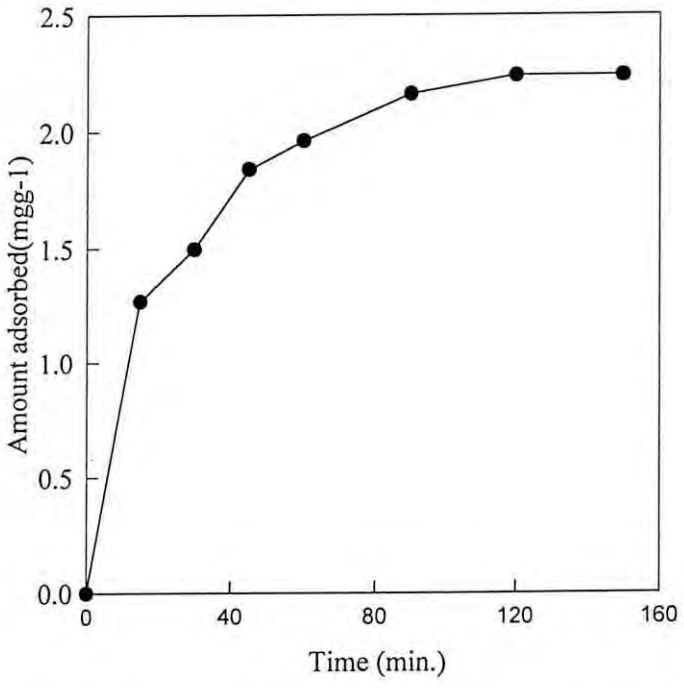


Fig. 3.3.6: Amount of MB adsorbed by acidic-PANI at different time of adsorption (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.7: Adsorption of MB dyestuff on acidic-PANI from 2.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.0×10^{-5}	0.050	15 30 45 60 90 120 150	0.6200 0.5714 0.5499 0.5060 0.4463 0.4188 0.4188	0.8708

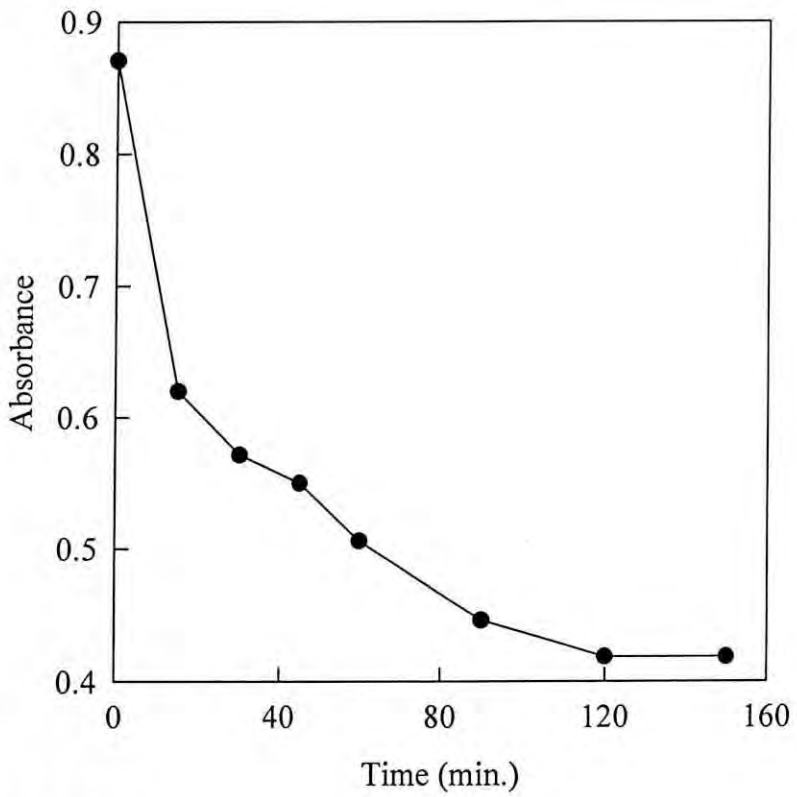


Fig. 3.3.7: Progress of MB adsorption with time on acidic-PANI (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.8 : Amount of MB dyestuff adsorbed by acidic -PANI from 2.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.0×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.6200	0.2508	2.0938
30	0.5714	0.2994	2.4995
45	0.5499	0.3209	2.6790
60	0.5060	0.3648	3.0455
90	0.4463	0.4245	3.5439
120	0.4188	0.4520	3.7735
150	0.4188	0.4520	3.7735

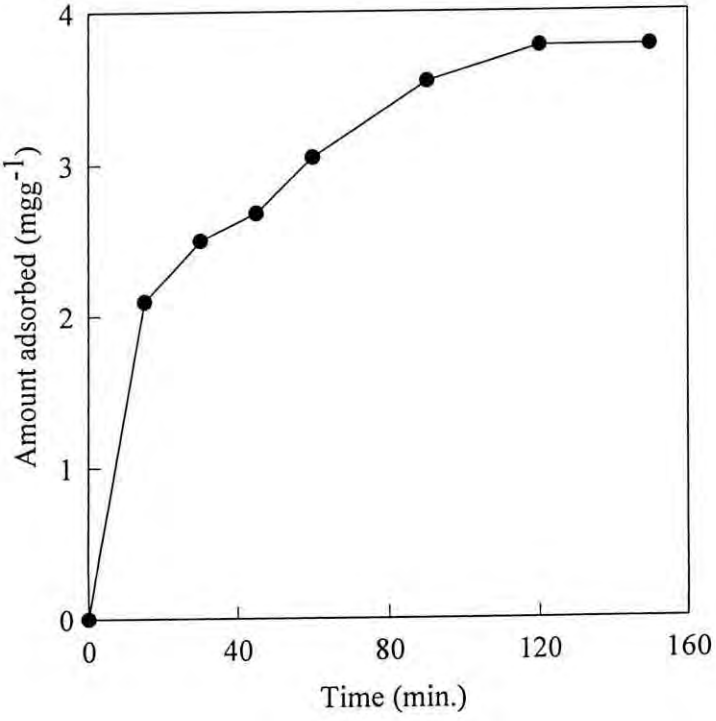


Fig. 3.3.8: Amount of MB adsorbed by acidic-PANI at different time of adsorption (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.9: Adsorption of MB dyestuff on acidic-PANI from 2.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.5×10^{-5}	0.050	15	0.7162	1.0520
		30	0.6587	
		45	0.6329	
		60	0.5999	
		90	0.5535	
		120	0.4991	
		150	0.4990	

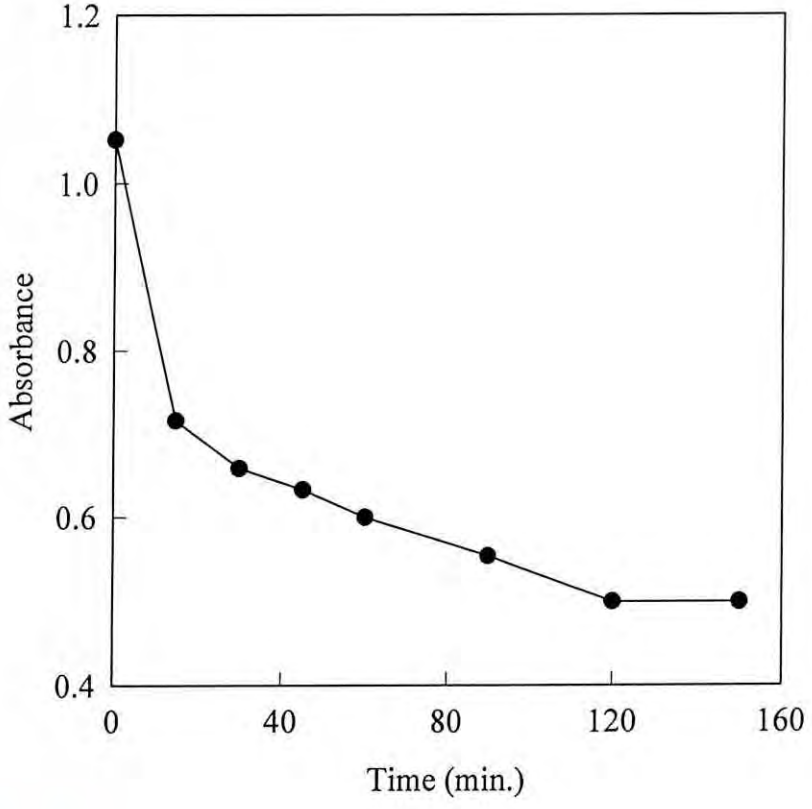


Fig. 3.3.9: Progress of MB adsorption with time on acidic-PANI (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.10 : Amount of MB dyestuff adsorbed by acidic -PANI from 2.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.7162	0.3358	2.8034
30	0.6587	0.3933	3.2834
45	0.6329	0.4191	3.4988
60	0.5999	0.4521	3.7743
90	0.5535	0.4985	4.1617
120	0.4991	0.5529	4.6158
150	0.4990	0.5530	4.6166

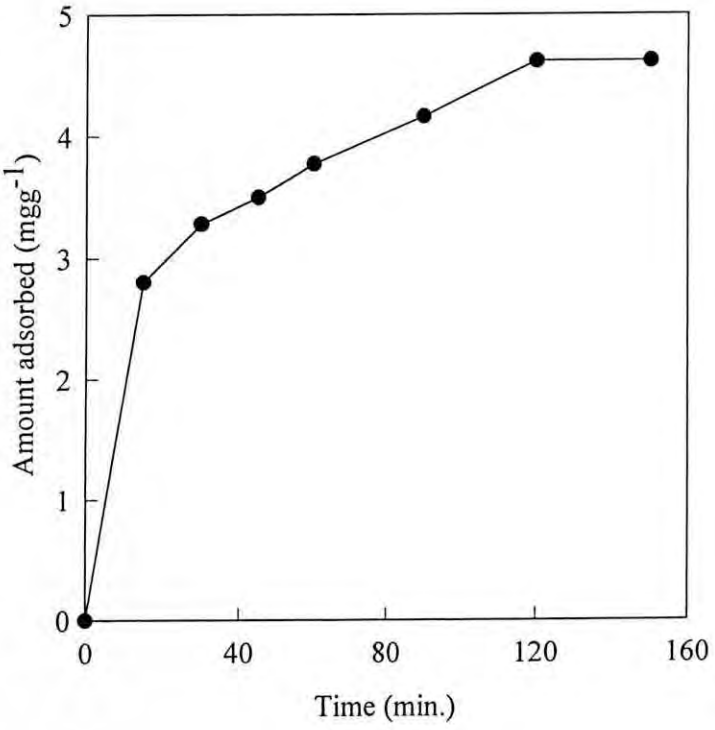


Fig. 3.3.10: Amount of MB adsorbed by acidic-PANI at different time of adsorption (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.11: Adsorption of MB dyestuff on acidic-PANI from 3.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
3.0×10^{-5}	0.050	15 30 45 60 90 120 150	0.7162 0.6587 0.6329 0.5999 0.5535 0.4991 0.4990	1.0520

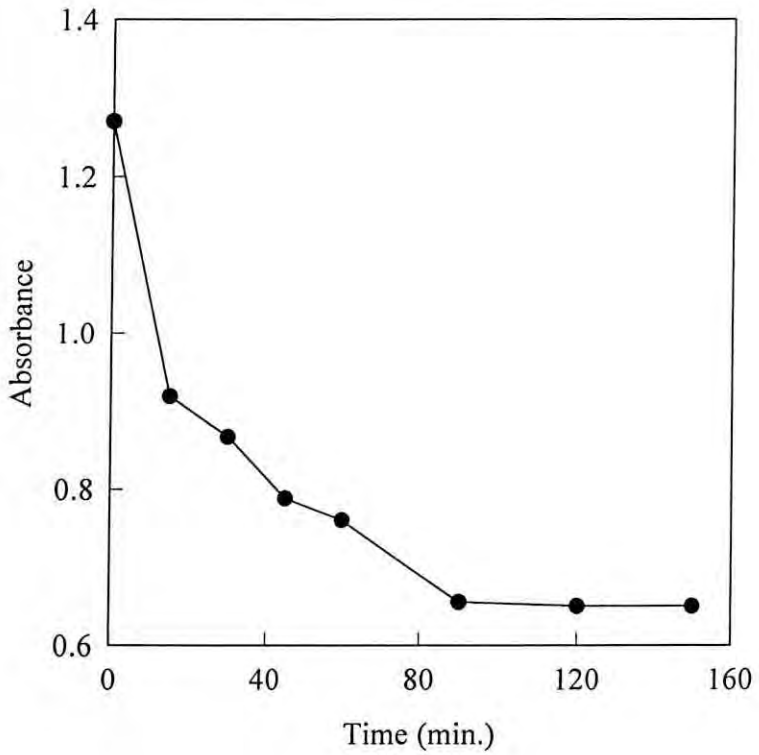


Fig. 3.3.11: Progress of MB adsorption with time on acidic-PANI (Initial concentration of MB = 3.0×10^{-5} M).

Table 3.3.12 : Amount of MB dyestuff adsorbed by acidic -PANI from 3.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 3.0×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.7162	0.3358	2.8034
30	0.6587	0.3933	3.2834
45	0.6329	0.4191	3.4988
60	0.5999	0.4521	3.7743
90	0.5535	0.4985	4.1617
120	0.4991	0.5529	4.6158
150	0.4990	0.5530	4.6166

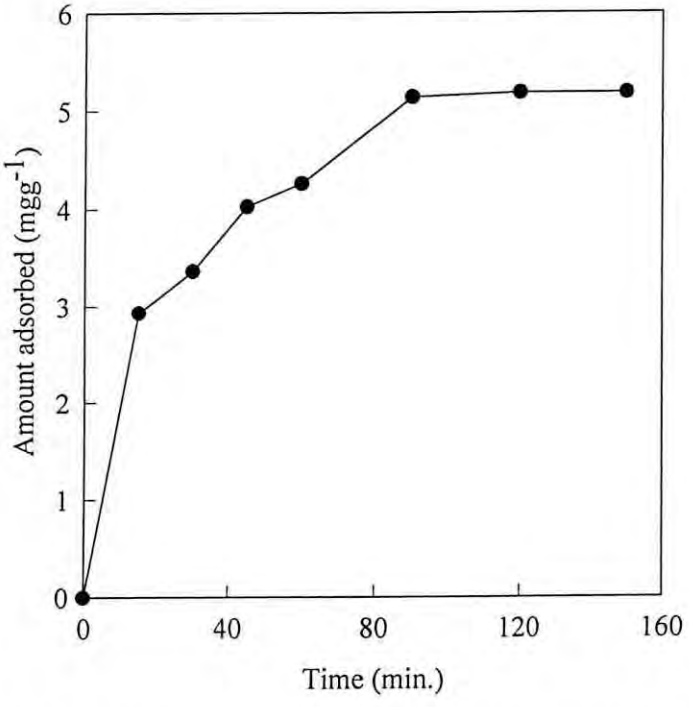


Fig. 3.3.12: Amount of MB adsorbed by acidic-PANI at different time of adsorption (Initial concentration of MB = 3.0×10^{-5} M).

Determination of monolayer capacity (χ_m) for acidic- PANI

Table 3.3.13: The amount of MB adsorbed on acidic-PANI at different equilibrium concentration of MB solution.

Initial concentration ($M/10^{-5}$)	Equilibrium time (min.)	Absorbance of the remaining MB solution at equilibrium time	Amount adsorbed at equilibrium time (mgg^{-1})	Equilibrium concentration ($M/10^{-5}$)
0.5	150	0.0904	1.2331	0.2121
1.0		0.1918	2.2390	0.4499
1.5		0.2655	2.9971	0.6228
2.0		0.4188	3.7735	0.9824
2.5		0.4990	4.6166	1.1705
3.0		0.6504	5.1768	1.5257

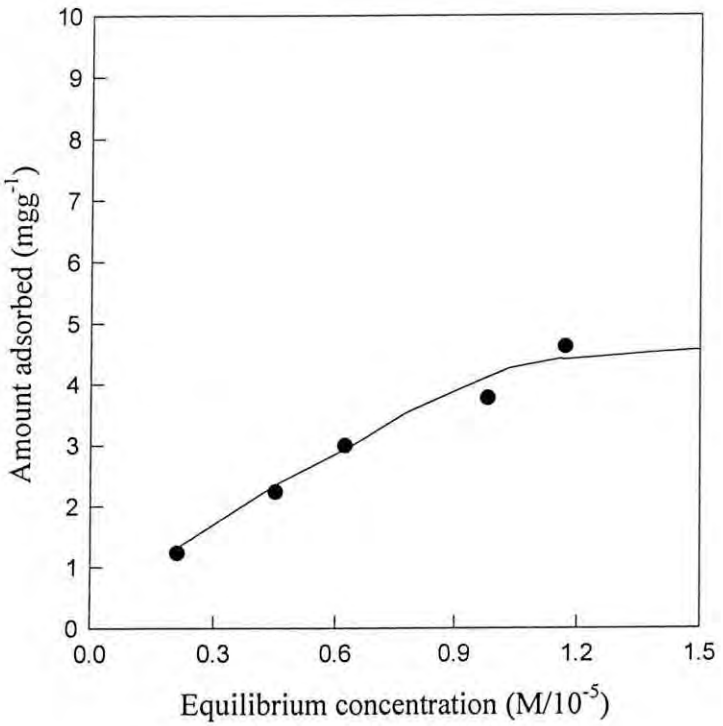


Fig. 3.3.13: Isotherm for the determination of monolayer capacity of MB at acidic-PANI.

Calculation of Specific Surface Area of acidic-PANI Substrate

The specific surface area of the acidic–PANI substrate can be calculated using the following equation,

$$\mathbf{S = (\chi_m / M) \times N \times A_m \times 10^{-20}}$$

Here,

Monolayer capacity $(\chi_m) = 4.17\ mgg^{-1} = 4.17 \times 10^{-3}\ g\ g^{-1}$

Molecular mass of MB (M) = 355.89 g mol^{-1}

Avogadro constant (N) = 6.023×10^{23}

(i) Cross-sectional area of MB ($\mathbf{A_m}$) = 130×10^{-20} $Å^2$ BET with N_2

(ii) Cross-sectional area of MB ($\mathbf{A_m}$) = 78×10^{-20} $Å^2$ BET with Ar

Specific surface area = $\mathbf{S}\ (m^2 g^{-1})$ = **?**

(i) $S = (4.17 \times 10^{-3} / 355.89) \times 6.023 \times 10^{23} \times 130 \times 10^{-20}$

$= 9.174\ (m^2 g^{-1})$

(ii) $S = (4.17 \times 10^{-3} / 355.89) \times 6.023 \times 10^{23} \times 78 \times 10^{-20}$

$= 5.504\ (m^2 g^{-1})$

Table 3.3.14: Adsorption of MB dyestuff on neutral-PANI from 0.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 25 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
0.5×10^{-5}	0.02	15	0.1954	0.3016
		30	0.1843	
		45	0.1800	
		60	0.1746	
		90	0.1713	
		120	0.1691	
		150	0.1690	

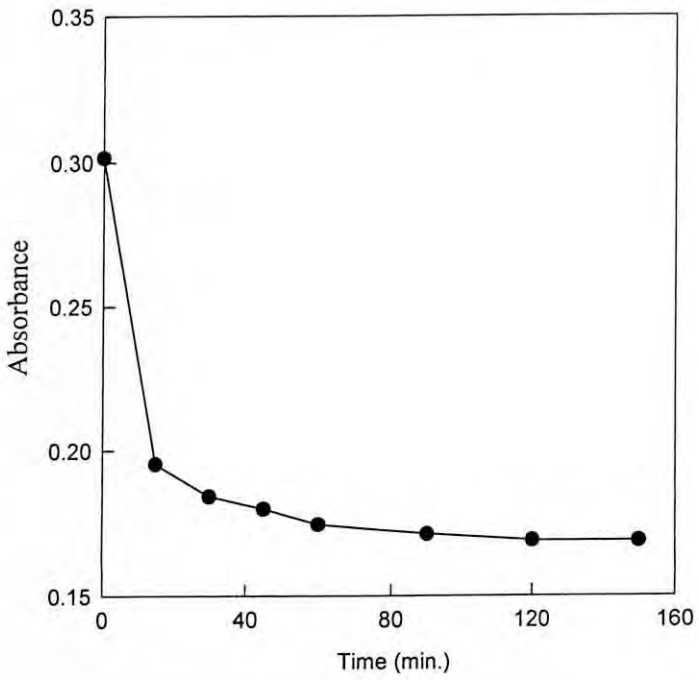


Fig. 3.3.14: Progress of MB adsorption with time on neutral-PANI (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.15 : Amount of MB dyestuff adsorbed by neutral -PANI from 0.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 0.5×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.1954	0.1062	0.7942
30	0.1843	0.1173	0.8772
45	0.1800	0.1216	0.9093
60	0.1746	0.1270	0.9497
90	0.1713	0.1303	0.9744
120	0.1691	0.1325	0.9908
150	0.1690	0.1326	0.9916

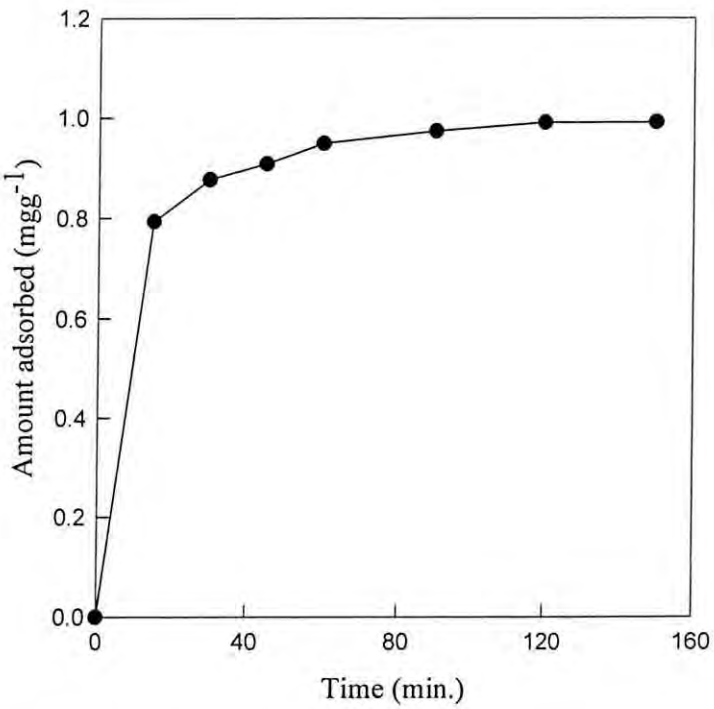


Fig. 3.3.15: Amount of MB adsorbed by neutral-PANI at different time of adsorption (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.16: Adsorption of MB dyestuff on neutral-PANI from 1.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 25 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.0×10^{-5}	0.02	15 30 45 60 90 120 150	0.4424 0.3899 0.3519 0.3387 0.3315 0.3269 0.3269	0.5957

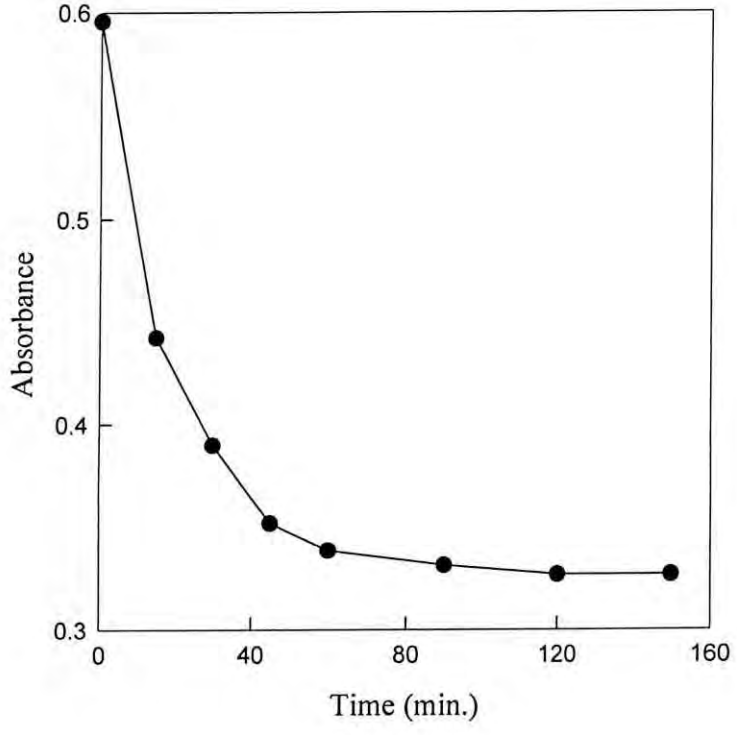


Fig. 3.3.16: Progress of MB adsorption with time on neutral-PANI (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.17 : Amount of MB dyestuff adsorbed by neutral -PANI from 1.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.0×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.4424	0.1533	1.1464
30	0.3899	0.2058	1.5390
45	0.3519	0.2438	1.8231
60	0.3387	0.2570	1.9218
90	0.3315	0.2642	1.9757
120	0.3269	0.2688	2.0101
150	0.3269	0.2688	2.0101

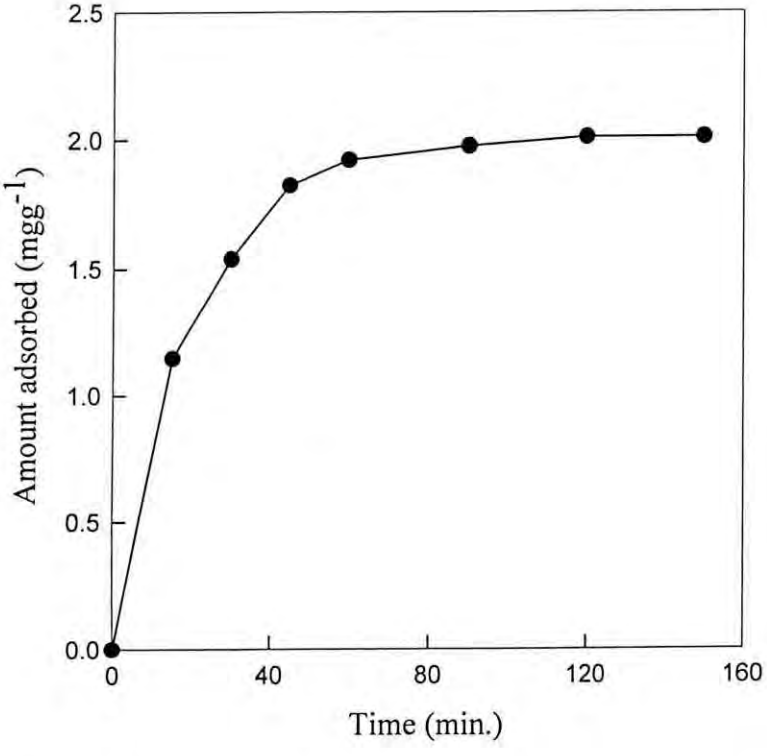


Fig. 3.3.17: Amount of MB adsorbed by neutral-PANI at different time of adsorption (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.18: Adsorption of MB dyestuff on neutral-PANI from 1.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 25 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.5×10^{-5}	0.02	15 30 45 60 90 120 150	0.7251 0.7169 0.6752 0.6515 0.6510 0.6508 0.6508	0.9285

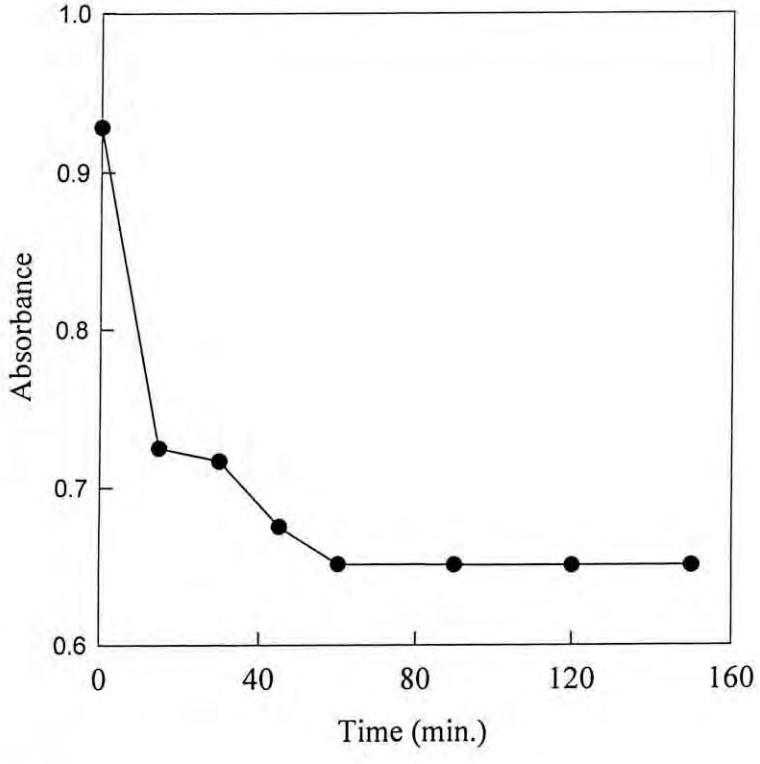


Fig. 3.3.18: Progress of MB adsorption with time on neutral-PANI (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.19 : Amount of MB dyestuff adsorbed by neutral -PANI from 1.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.7251	0.2034	1.5210
30	0.7169	0.2116	1.5823
45	0.6752	0.2533	1.8942
60	0.6515	0.2770	2.0714
90	0.6510	0.2775	2.0751
120	0.6508	0.2777	2.0766
150	0.6508	0.2777	2.0766

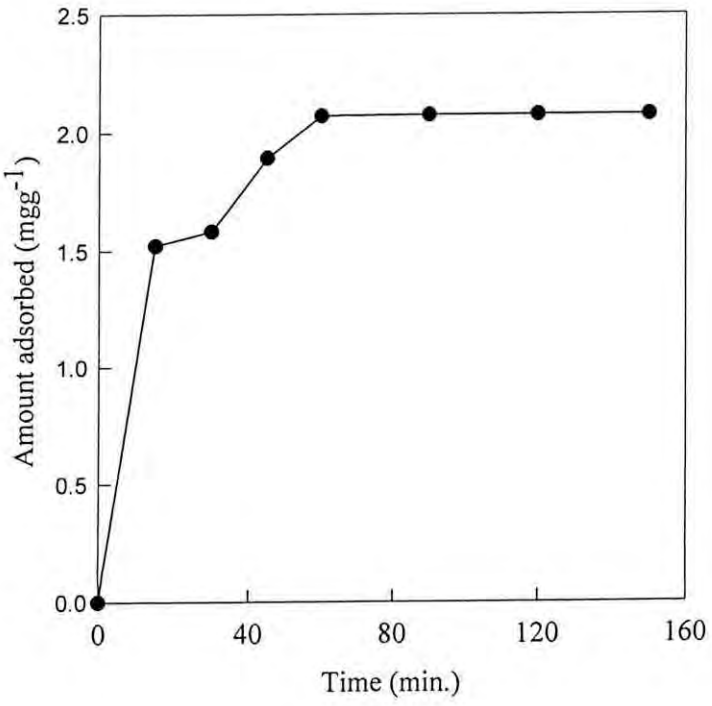


Fig. 3.3.19: Amount of MB adsorbed by neutral-PANI at different time of adsorption (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.20: Adsorption of MB dyestuff on neutral-PANI from 2.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 25 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.0×10^{-5}	0.02	15	0.9270	1.2063
		30	0.8809	
		45	0.8352	
		60	0.7963	
		90	0.7789	
		120	0.7646	
		150	0.7645	

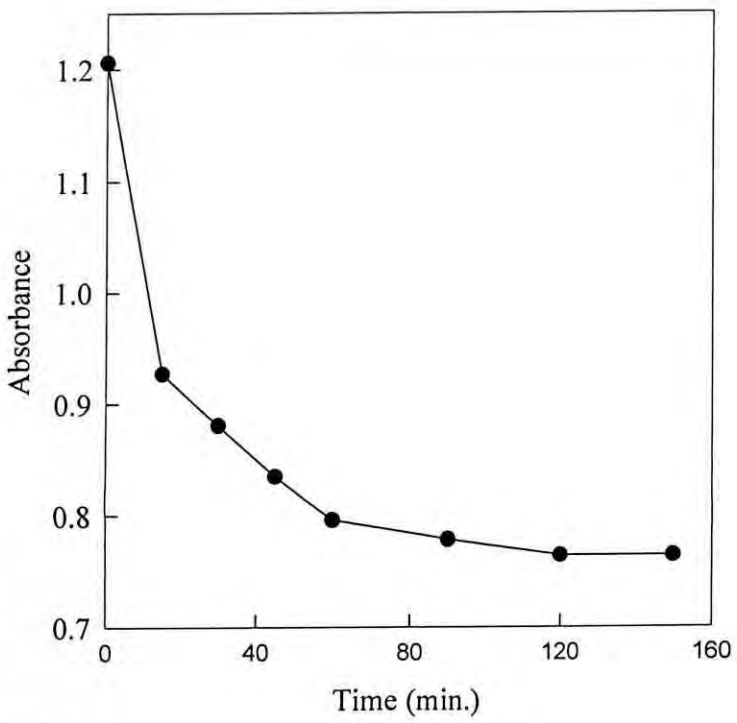


Fig. 3.3.20 : Progress of MB adsorption with time on neutral-PANI (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.21 : Amount of MB dyestuff adsorbed by neutral -PANI from 2.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.0×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.9270	0.2793	2.0886
30	0.8809	0.3254	2.4333
45	0.8352	0.3711	2.7751
60	0.7963	0.4100	3.0660
90	0.7789	0.4274	3.1961
120	0.7646	0.4417	3.3030
150	0.7645	0.4418	3.3038

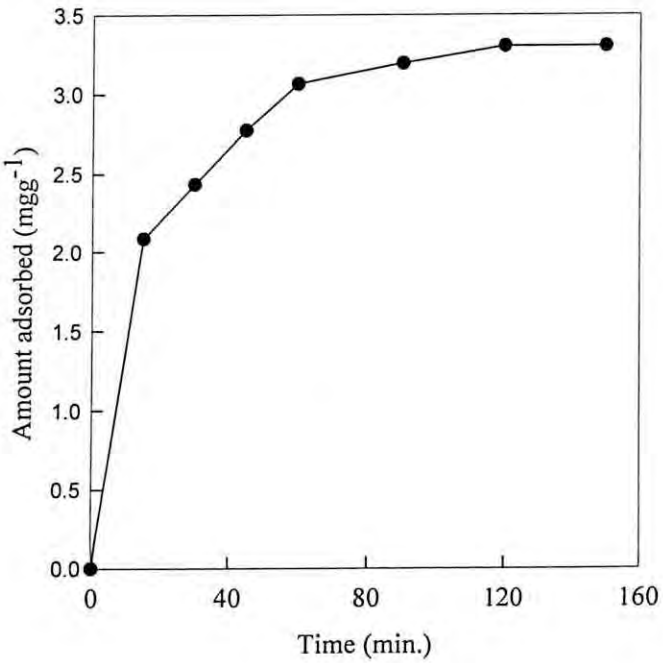


Fig. 3.3.21: Amount of MB adsorbed by neutral-PANI at different time of adsorption (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.22: Adsorption of MB dyestuff on neutral-PANI from 2.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 25 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.5×10^{-5}	0.02	15	1.2257	1.4823
		30	1.1759	
		45	1.1255	
		60	1.0890	
		90	1.0800	
		120	1.0747	
		150	1.0746	

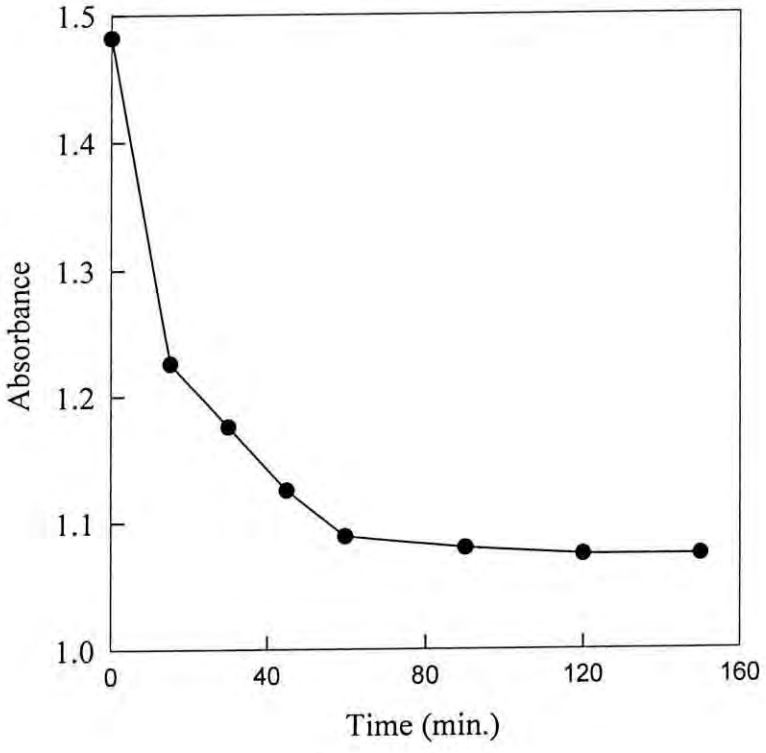


Fig. 3.3.22: Progress of MB adsorption with time on neutral-PANI (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.23 : Amount of MB dyestuff adsorbed by neutral -PANI from 2.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	1.2257	0.2566	1.9188
30	1.1759	0.3064	2.2912
45	1.1255	0.3568	2.6681
60	1.0890	0.3933	2.9411
90	1.0800	0.4023	3.0084
120	1.0747	0.4076	3.0480
150	1.0746	0.4077	3.0488

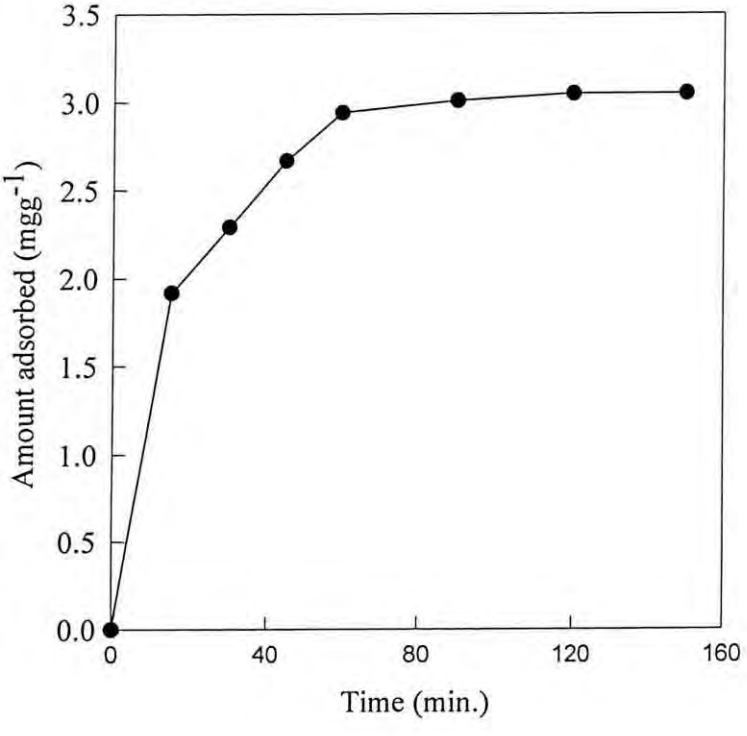


Fig. 3.3.23: Amount of MB adsorbed by neutral-PANI at different time of adsorption (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.24: Adsorption of MB dyestuff on neutral-PANI from 3.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 25 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
3.0×10^{-5}	0.02	15 30 45 60 90 120 150	1.4559 1.4254 1.3606 1.3431 1.3401 1.3324 1.3323	1.7594

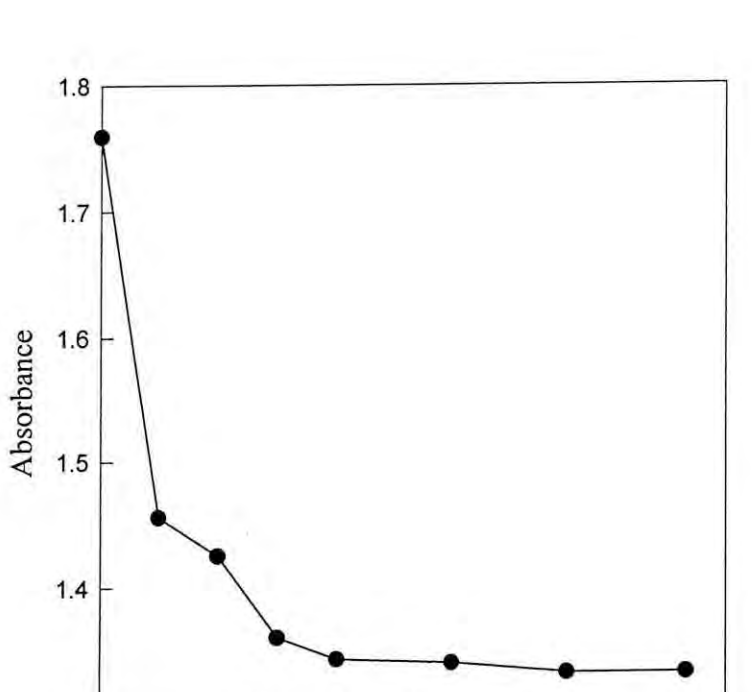


Fig. 3.3.24: Progress of MB adsorption with time on neutral-PANI (Initial concentration of MB = 3.0×10^{-5} M).

Table 3.3.25: Amount of MB dyestuff adsorbed by neutral-PANI from 3.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 3.0×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	1.4559	0.3035	2.2696
30	1.4254	0.3340	2.4976
45	1.3606	0.3988	2.9822
60	1.3431	0.4163	3.1131
90	1.3401	0.4193	3.1355
120	1.3324	0.4270	3.1931
150	1.3323	0.4271	3.1938

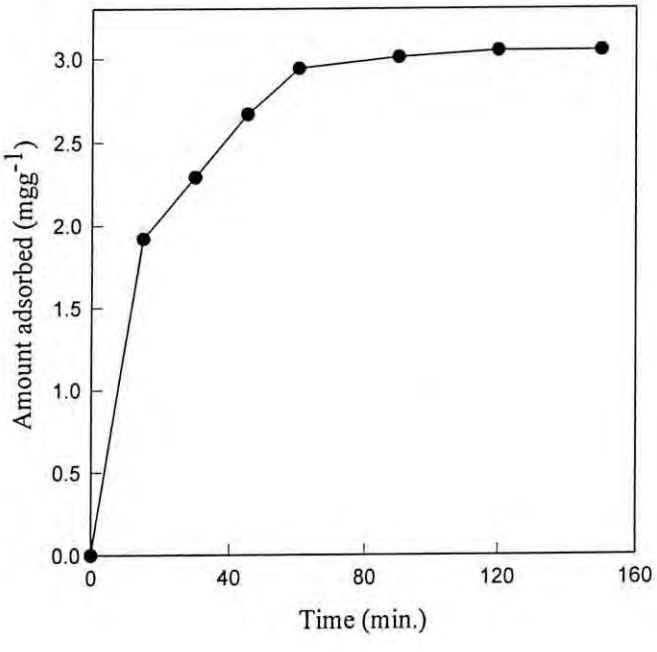


Fig. 3.3.25: Amount of MB adsorbed by neutral-PANI at different time of adsorption (Initial concentration of MB = 3.0×10^{-5} M).

Determination of monolayer capacity (χ_m) for neutral- PANI

Table 3.3.26: The amount of MB adsorbed on neutral-PANI at different equilibrium concentration of MB solution.

Initial concentration ($M/10^{-5}$)	Equilibrium time (min.)	Absorbance of the remaining MB solution at equilibrium time	Amount adsorbed at equilibrium time ($mg\ g^{-1}$)	Equilibrium concentration ($M/10^{-5}$)
0.5	120	0.1690	0.9916	0.2840
1.0	150	0.3269	2.0101	0.5494
1.5	150	0.6508	2.0766	1.0938
2.0	150	0.7645	3.3038	1.2849
2.5	150	1.0746	3.0488	1.8061
3.0	150	1.3323	3.1938	2.2392

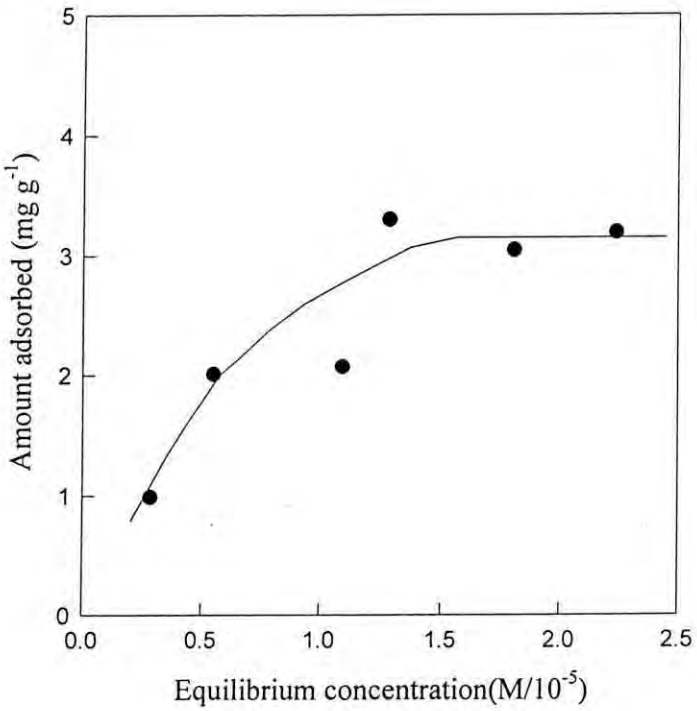


Fig. 3.3.26: Isotherm for the determination of monolayer capacity of MB at neutral-PANI.

Calculation of Specific Surface Area of neutral-PANI Substrate

The specific surface area of the neutral –PANI substrate can be calculated using the following equation,

$$\mathbf{S= (\chi_m /M) \times N \times A_m \times 10^{-20}}$$

Here,

Monolayer capacity $(\chi_m) = 3.19\ mgg^{-1} = 3.19 \times 10^{-3}\ g\ g^{-1}$

Molecular mass of MB (M) = 355.89 g mol^{-1}

Avogadro constant (N) = 6.023×10^{23}

(i) Cross-sectional area of MB ($\mathbf{A_m}$) = 130×10^{-20} $Å^2$ BET with N_2

(ii) Cross-sectional area of MB ($\mathbf{A_m}$) = = 78×10^{-20} $Å^2$ BET with Ar

Specific surface area = $\mathbf{S}\ (m^2 g^{-1})$ = ?

(i) $S = (3.19 \times 10^{-3} /355.89) \times 6.023 \times 10^{23} \times 130 \times 10^{-20}$

$= 7.019\ (m^2 g^{-1})$

(ii) $S = (3.19 \times 10^{-3} /355.89) \times 6.023 \times 10^{23} \times 78 \times 10^{-20}$

$= 4.211\ (m^2 g^{-1})$

Table 3.3.27: Adsorption of MB dyestuff on basic-PANI from 0.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
0.5×10^{-5}	0.015	10 30 60 90 120	0.0292 0.0172 0.0160 0.0160 0.0160	0.1665

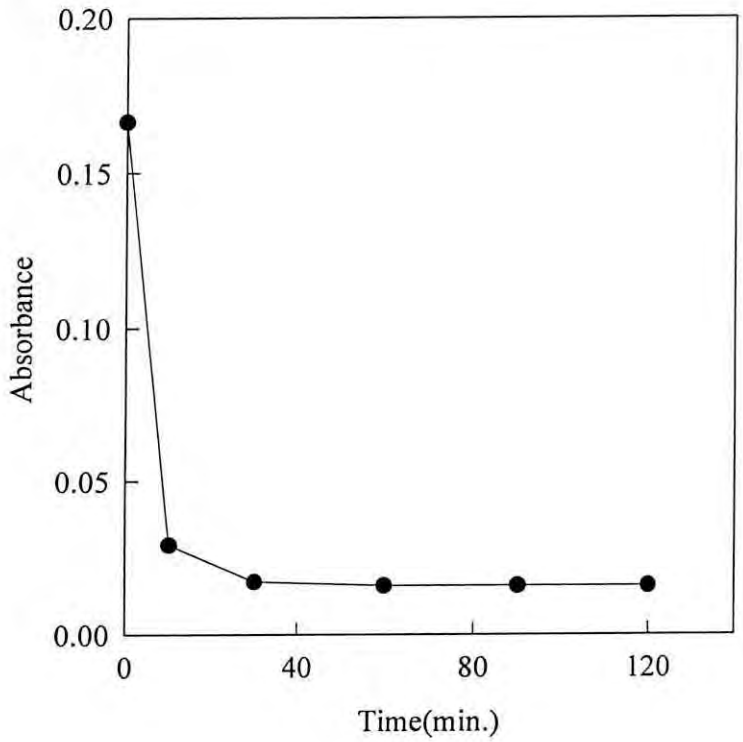


Fig. 3.3.27: Progress of MB adsorption with time on basic-PANI (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.28 : Amount of MB dyestuff adsorbed by basic -PANI from 0.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 0.5×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
10	0.0292	0.1373	5.1027
30	0.0172	0.1493	5.5487
60	0.0160	0.1505	5.5933
90	0.0160	0.1505	5.5933
120	0.0160	0.1505	5.5933

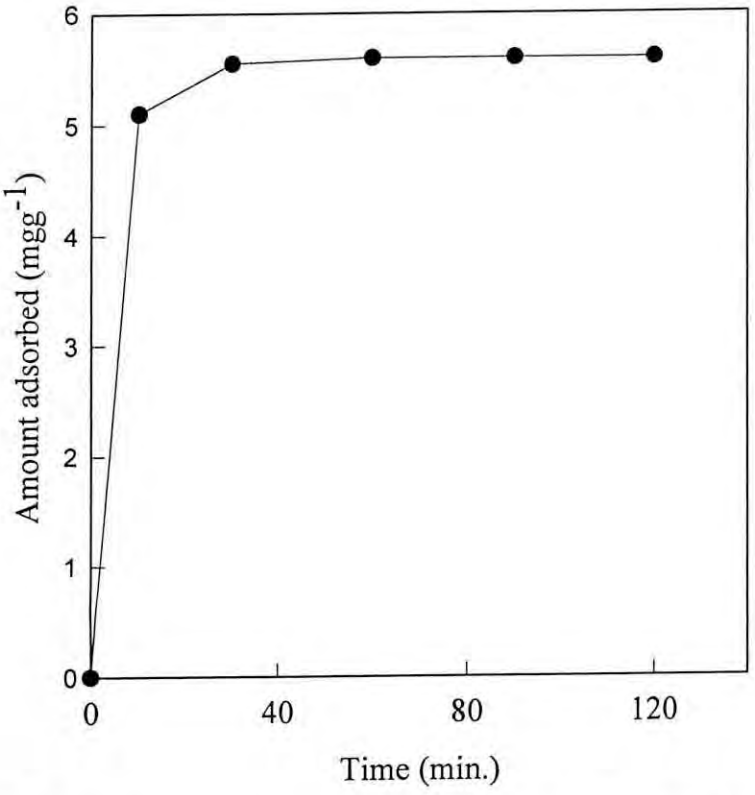


Fig. 3.3.28: Amount of MB adsorbed by basic-PANI at different time of adsorption (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.29: Adsorption of MB dyestuff on basic-PANI from 1.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.0×10^{-5}	0.015	15 30 45 60 90 120 150	0.0583 0.0343 0.0250 0.0220 0.0181 0.0154 0.0154	0.3120

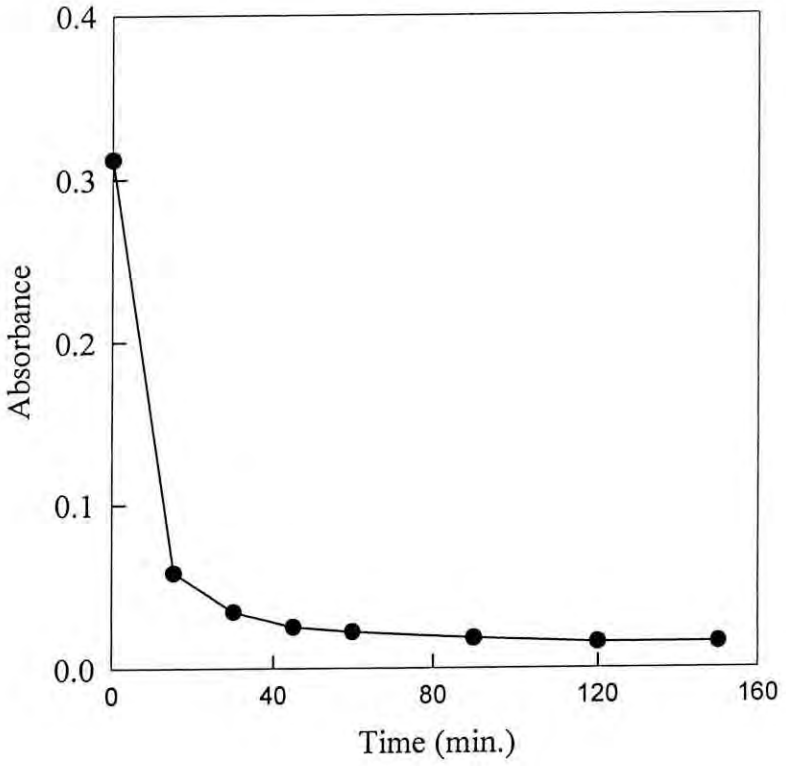


Fig. 3.3.29: Progress of MB adsorption with time on basic-PANI (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.30 : Amount of MB dyestuff adsorbed by basic -PANI from 1.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.0×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.0583	0.2537	9.4287
30	0.0343	0.2777	10.3207
45	0.0250	0.2870	10.6663
60	0.0220	0.2900	10.7778
90	0.0181	0.2939	10.9227
120	0.0154	0.2966	11.0231
150	0.0154	0.2966	11.0231

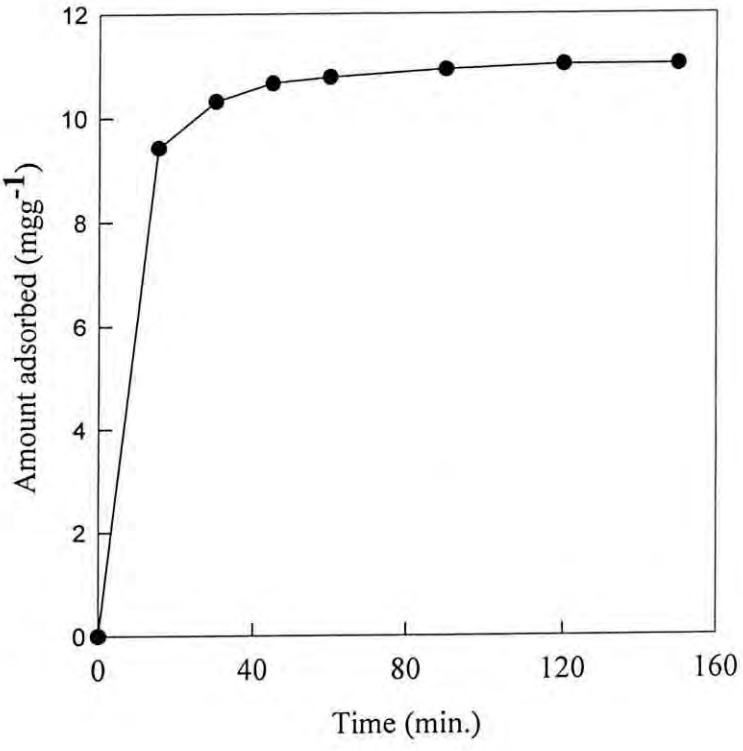


Fig. 3.3.30: Amount of MB adsorbed by basic-PANI at different time of adsorption (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.31: Adsorption of MB dyestuff on basic-PANI from 1.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.5×10^{-5}	0.015	15 30 45 60 90 120 150	0.0853 0.0618 0.0489 0.0370 0.0296 0.0287 0.0287	0.4955

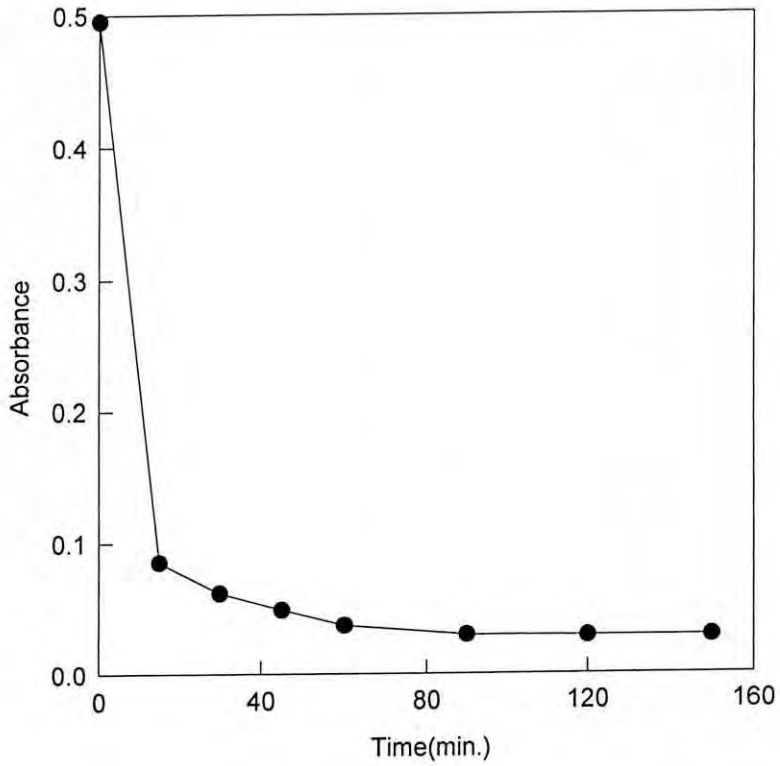


Fig. 3.3.31: Progress of MB adsorption with time on basic-PANI (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.32 : Amount of MB dyestuff adsorbed by basic -PANI from 1.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 0.5×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.0853	0.4102	15.2450
30	0.0618	0.4337	16.1184
45	0.0489	0.4466	16.5978
60	0.0370	0.4585	17.0401
90	0.0296	0.4659	17.3151
120	0.0287	0.4668	17.3485
150	0.0287	0.4668	17.3485

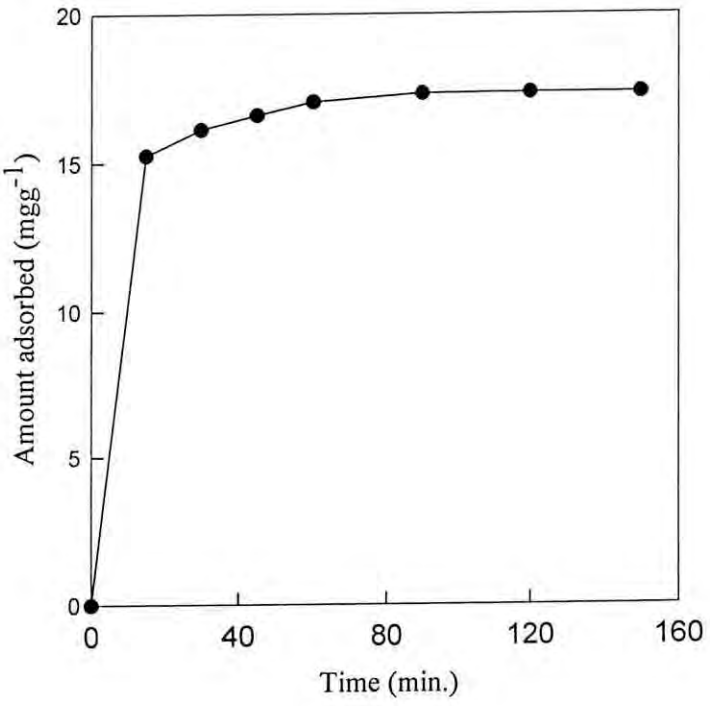


Fig. 3.3.32: Amount of MB adsorbed by basic-PANI at different time of adsorption (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.33: Adsorption of MB dyestuff on basic-PANI from 2.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.0×10^{-5}	0.015	15 30 45 60 90 120 150	0.1340 0.0985 0.0735 0.0459 0.0349 0.0355 0.0354	0.6638

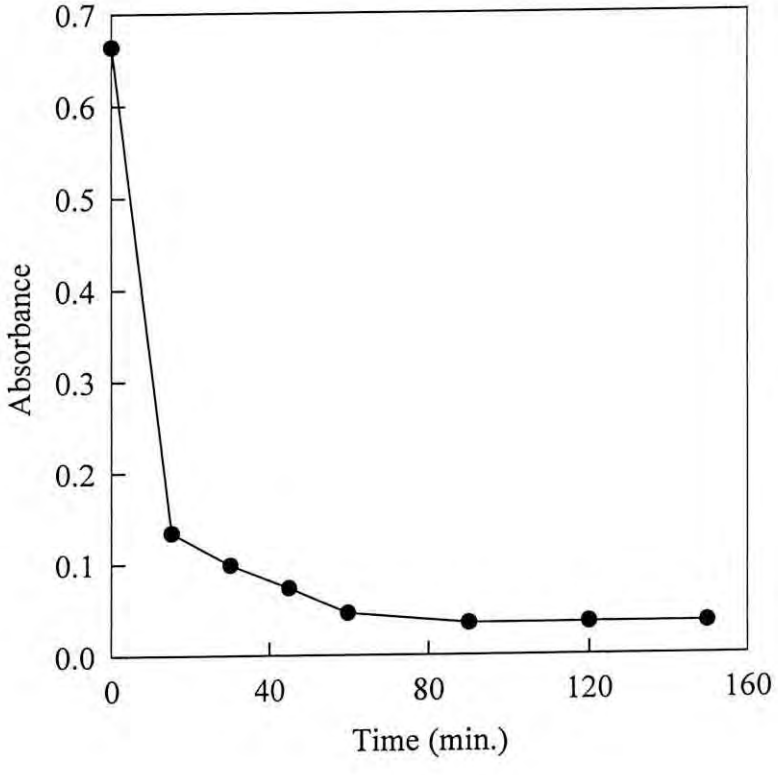


Fig. 3.3.33: Progress of MB adsorption with time on basic-PANI (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.34 : Amount of MB dyestuff adsorbed by basic -PANI from 2.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 0.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.1340	0.5298	13.7829
30	0.0985	0.5653	14.7065
45	0.0735	0.5903	15.3569
60	0.0459	0.6179	16.0749
90	0.0349	0.6289	16.3611
120	0.0355	0.6283	16.3454
150	0.0354	0.6284	16.3480

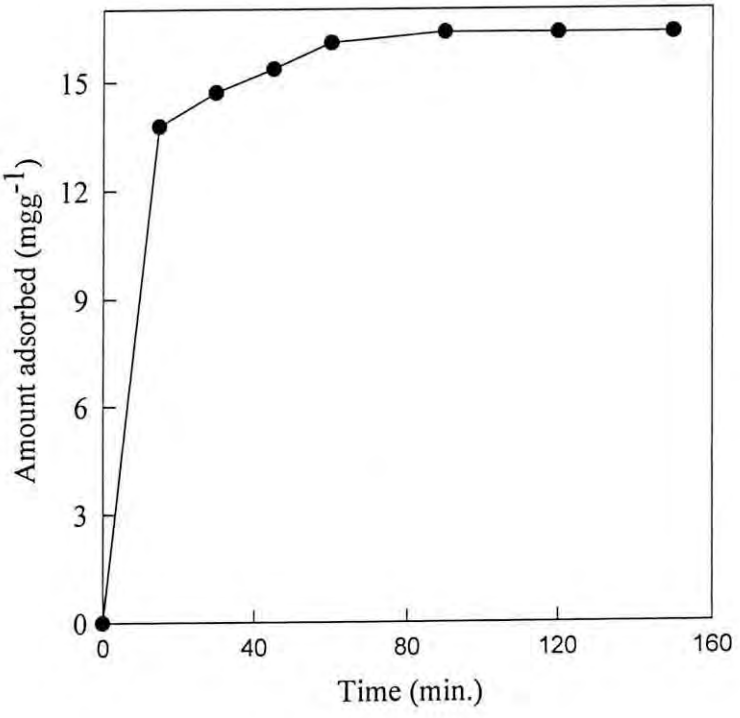


Fig. 3.3.34: Amount of MB adsorbed by basic-PANI at different time of adsorption (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.35: Adsorption of MB dyestuff on basic-PANI from 2.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.5×10^{-5}	0.015	15 30 45 60 90 120 150	0.2041 0.1101 0.0755 0.0549 0.0511 0.0480 0.0480	0.7932

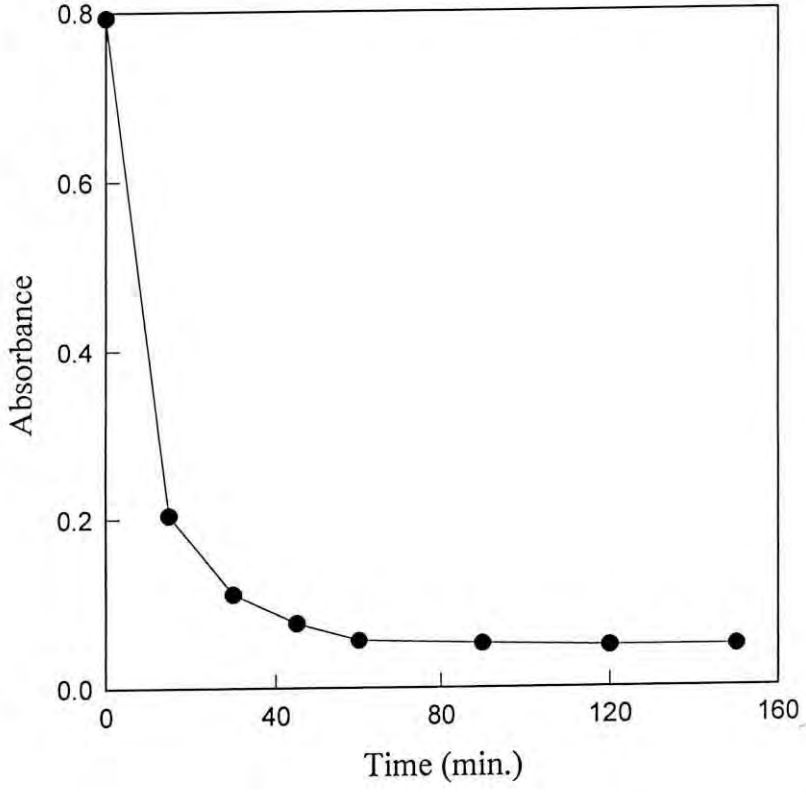


Fig. 3.3.35: Progress of MB adsorption with time on basic-PANI (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.36 : Amount of MB dyestuff adsorbed by basic -PANI from 2.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.2041	0.5891	21.8938
30	0.1101	0.6831	25.3873
45	0.0755	0.7177	26.6732
60	0.0549	0.7383	27.4388
90	0.0511	0.7421	27.5800
120	0.0480	0.7452	27.6952
150	0.0480	0.7452	21.8938

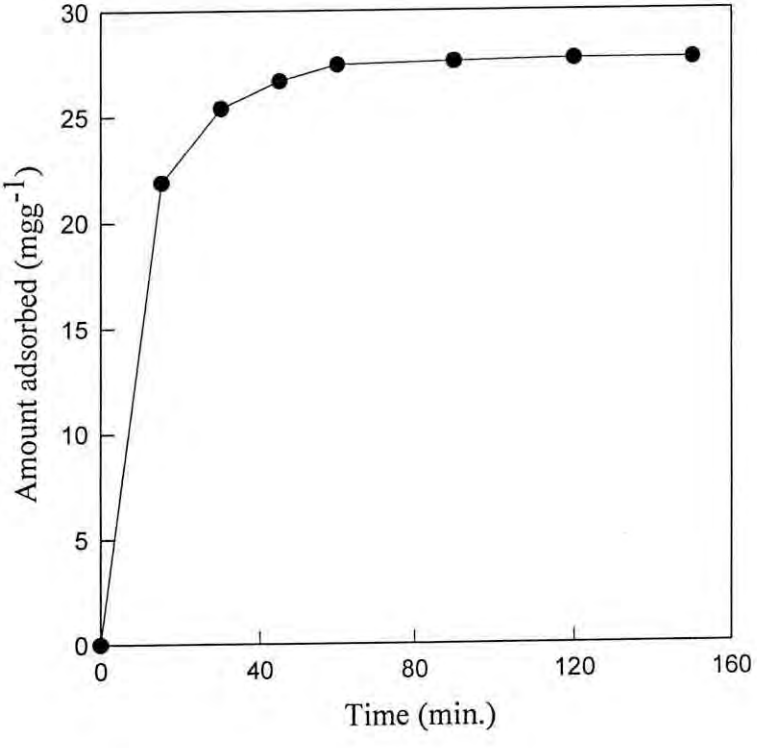


Fig. 3.3.36: Amount of MB adsorbed by basic-PANI at different time of adsorption (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.37: Adsorption of MB dyestuff on basic-PANI from 3.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
3.0×10^{-5}	0.015	15 30 45 60 90 120 150	0.2593 0.1718 0.1246 0.0856 0.0769 0.0607 0.0606	0.9377

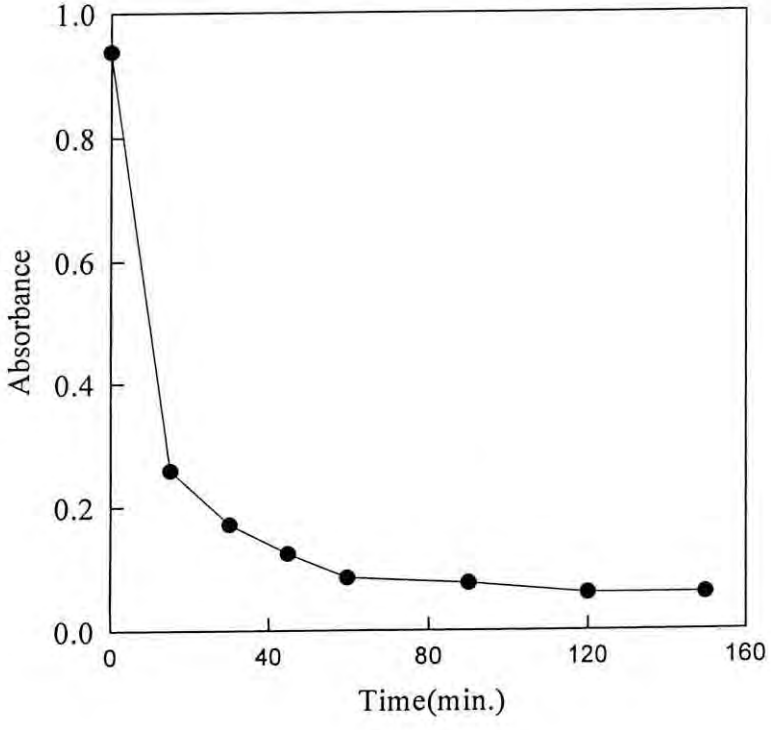


Fig. 3.3.37: Progress of MB adsorption with time on basic-PANI (Initial concentration of MB = 3.0×10^{-5} M).

Table 3.3.38 : Amount of MB dyestuff adsorbed by basic -PANI from 3.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 3.0×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.2593	0.6784	25.2126
30	0.1718	0.7659	28.4645
45	0.1246	0.8131	30.2187
60	0.0856	0.8521	31.6681
90	0.0769	0.8608	31.9914
120	0.0607	0.8770	32.5935
150	0.0606	0.8771	32.5972

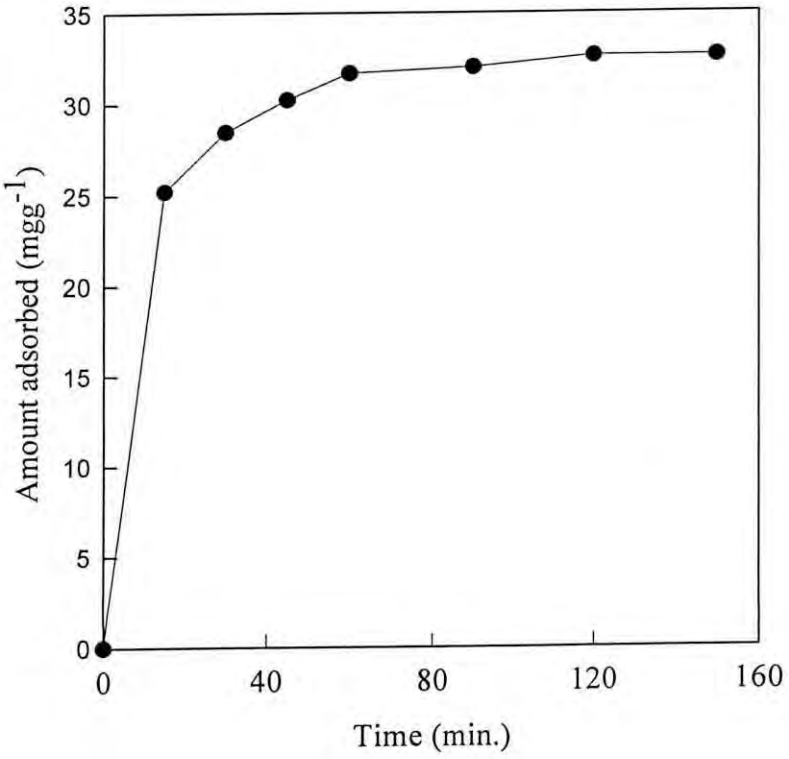


Fig. 3.3.38: Amount of MB adsorbed by basic-PANI at different time of adsorption (Initial concentration of MB = 3.0×10^{-5} M).

Determination of monolayer capacity (χ_m)for basic- PANI

Table 3.3.39: The amount of MB adsorbed on basic-PANI at different equilibrium concentration of MB solution.

Initial concentration ($M/10^{-5}$)	Equilibrium time (min.)	Absorbance of the remaining MB solution at equilibrium time	Amount adsorbed at equilibrium time (mgg^{-1})	Equilibrium concentration ($M/10^{-5}$)
0.5	120	0.0104	5.8010	0.0325
1.0	150	0.0154	11.0231	0.0482
1.5	150	0.0287	17.3485	0.0899
2.0	150	0.0354	23.3543	0.1112
2.5	150	0.0480	27.6952	0.1504
3.0	150	0.0606	32.5935	0.1898

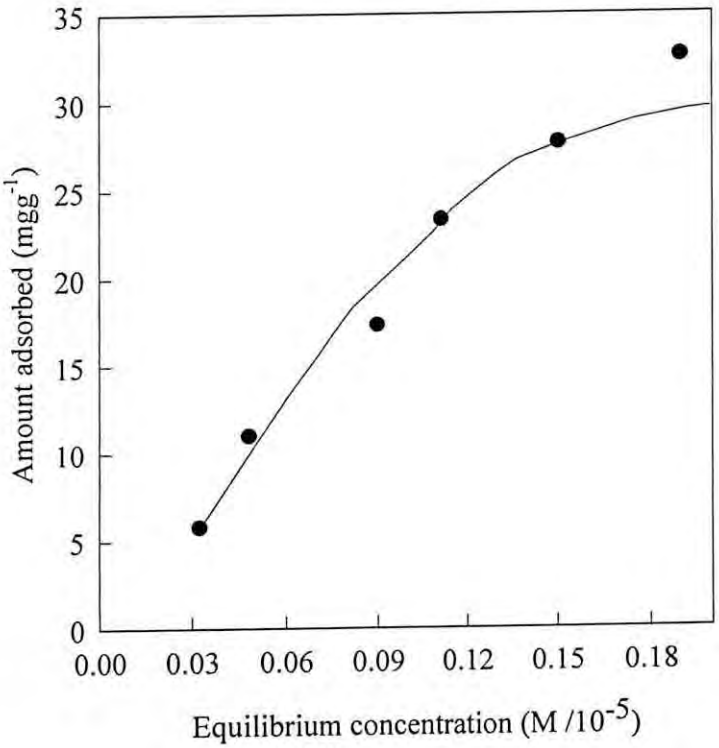


Fig. 3.3.39: Isotherm for the determination of monolayer capacity of MB at basic-PANI.

Calculation of Specific Surface Area of basic-PANI Substrate

The specific surface area of the basic –PANI substrate can be calculated using the following equation,

$$S = (\chi_m / M) \times N \times A_m \times 10^{-20}$$

Here,

Monolayer capacity $(\chi_m) = 30.0\ mgg^{-1} = 30.0 \times 10^{-3}\ g\ g^{-1}$

Molecular mass of MB (M) = 355.89 g mol^{-1}

Avogadro constant (N) = 6.023×10^{23}

(i)Cross-sectional area of MB $(A_m) = 130 \times 10^{-20}$ $Å^2$ BET with N_2

(ii)Cross-sectional area of MB $(A_m) = 78 \times 10^{-20}$ $Å^2$ BET with Ar

Specific surface area = $S\ (m^2 g^{-1})$ = ?

(i) $S = (30.0 \times 10^{-3} / 355.89) \times 6.023 \times 10^{23} \times 130 \times 10^{-20}$

$= 66.002\ (m^2 g^{-1})$

(ii) $S = (30.0 \times 10^{-3} / 355.89) \times 6.023 \times 10^{23} \times 78 \times 10^{-20}$

$= 39.601\ (m^2 g^{-1})$

Table 3.3.40: Adsorption of MB dyestuff on doped-PANI from 0.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
0.5×10^{-5}	0.015	15 25 35 45 60	0.0569 0.0509 0.0500 0.0498 0.0498	0.1665

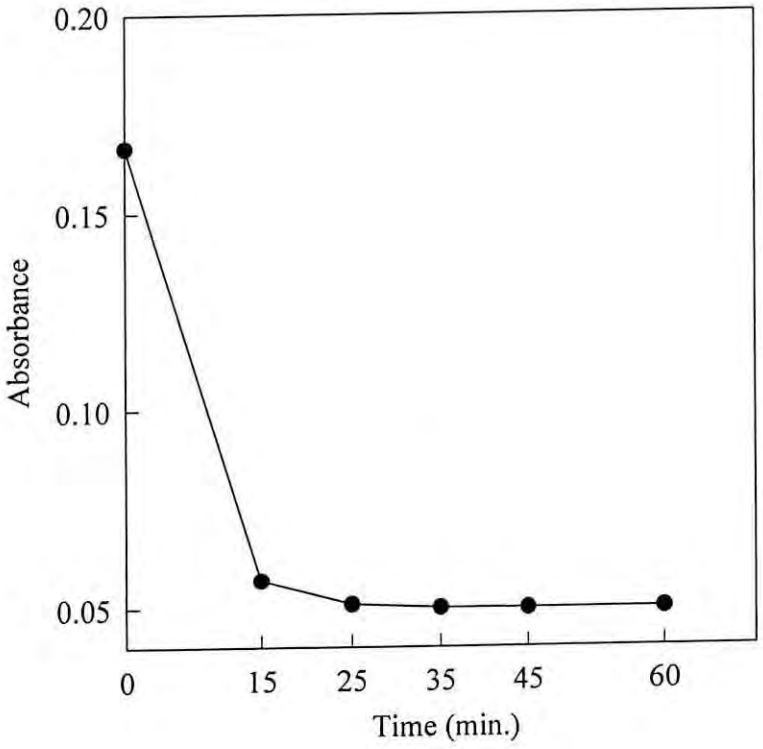


Fig. 3.3.40: Progress of MB adsorption with time on doped-PANI (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.41 : Amount of MB dyestuff adsorbed by doped -PANI from 0.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 0.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.0569	0.1096	4.0733
25	0.0509	0.1156	4.2962
35	0.0500	0.1165	4.3297
45	0.0498	0.1167	4.3371
60	0.0498	0.1167	4.3371

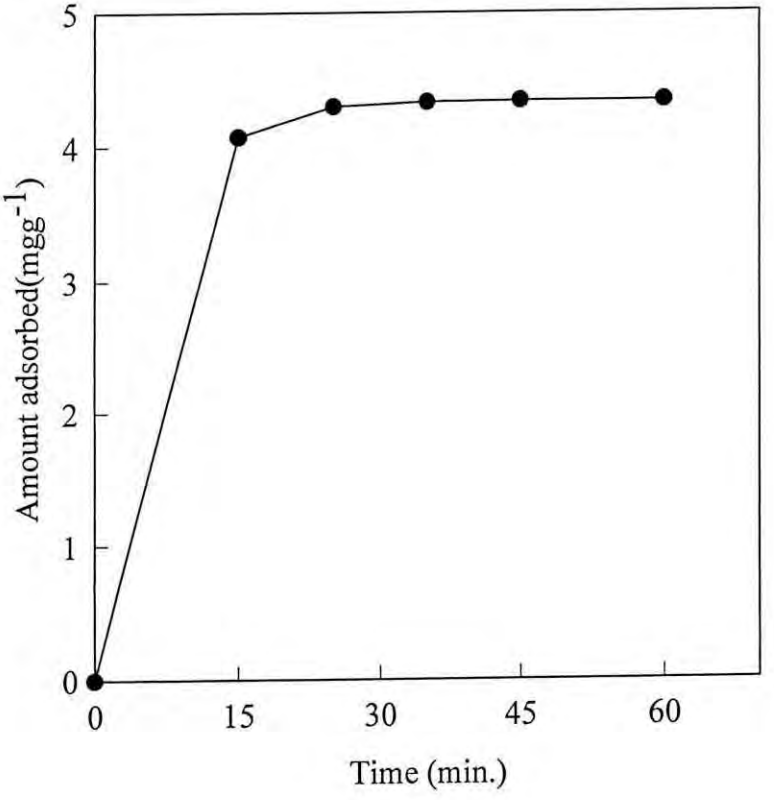


Fig. 3.3.41: Amount of MB adsorbed by doped-PANI at different time of adsorption (Initial concentration of MB = 0.5×10^{-5} M).

Table 3.3.42: Adsorption of MB dyestuff on doped-PANI from 1.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.0×10^{-5}	0.015	15 30 45 60 90 120 150	0.1221 0.0909 0.0825 0.0791 0.0611 0.0564 0.0563	0.3120

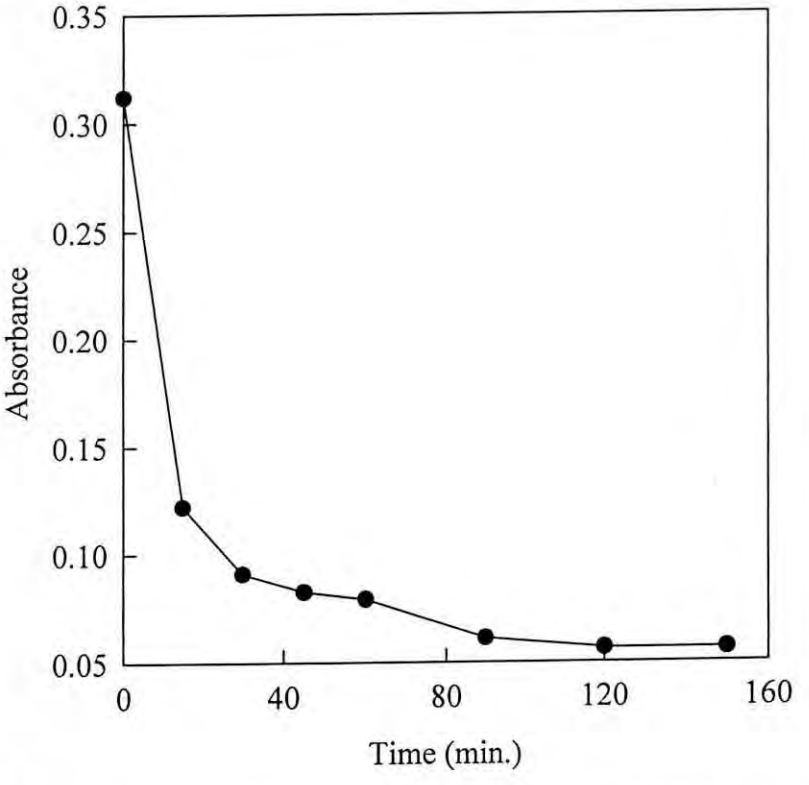


Fig. 3.3.42: Progress of MB adsorption with time on doped-PANI (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.43 : Amount of MB dyestuff adsorbed by doped -PANI from 1.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.0×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.1221	0.1899	7.0575
30	0.0909	0.2211	8.2171
45	0.0825	0.2295	8.5293
60	0.0791	0.2329	8.6550
90	0.0611	0.2509	9.3246
120	0.0564	0.2556	9.4993
150	0.0563	0.2557	9.5030

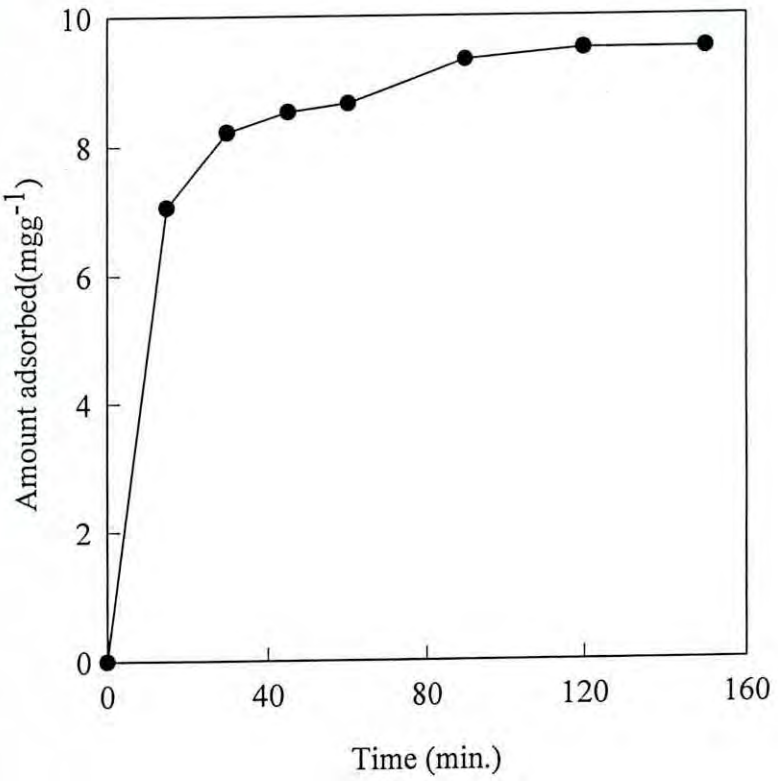


Fig. 3.3.43: Amount of MB adsorbed by doped-PANI at different time of adsorption (Initial concentration of MB = 1.0×10^{-5} M).

Table 3.3.44: Adsorption of MB dyestuff on doped-PANI from 1.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
1.5×10^{-5}	0.015	15 30 45 60 90 120 150	0.1711 0.1156 0.1086 0.0963 0.0802 0.0786 0.0786	0.4955

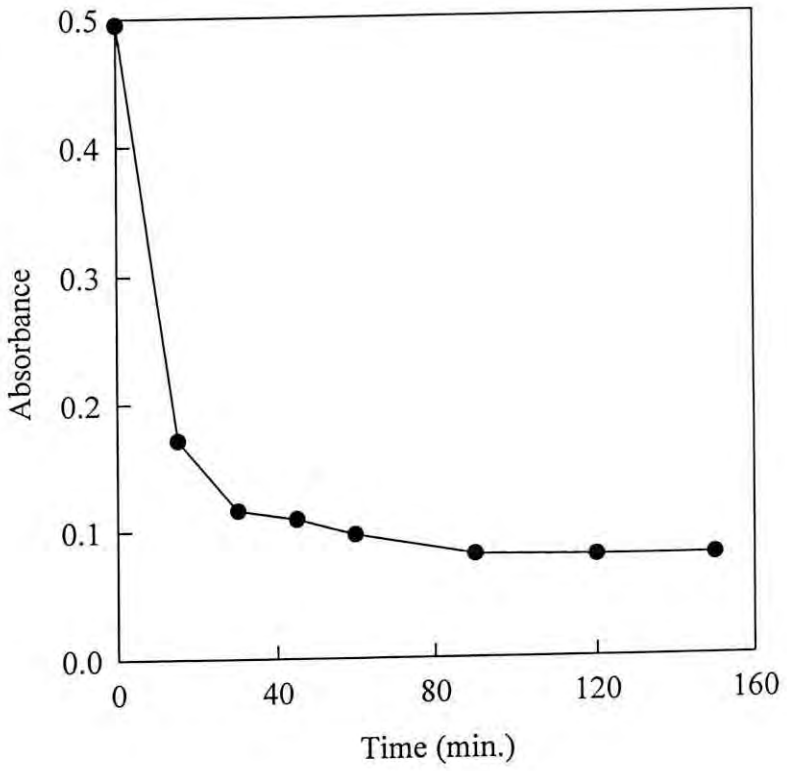


Fig. 3.3.44: Progress of MB adsorption with time on doped-PANI (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.45 : Amount of MB dyestuff adsorbed by doped -PANI from 1.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 1.5×10^{-5} MMB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.1711	0.3244	12.0563
30	0.1156	0.3799	14.1189
45	0.1086	0.3869	14.3791
60	0.0963	0.3992	14.8362
90	0.0802	0.4153	15.4345
120	0.0786	0.4169	15.4940
150	0.0786	0.4169	15.4940

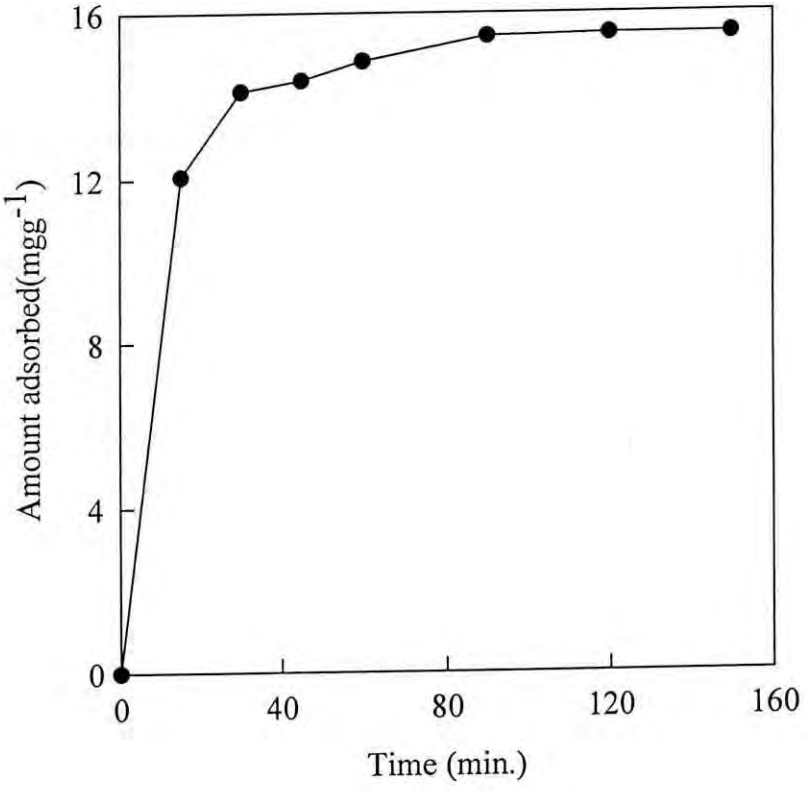


Fig. 3.3.45: Amount of MB adsorbed by doped-PANI at different time of adsorption (Initial concentration of MB = 1.5×10^{-5} M).

Table 3.3.46: Adsorption of MB dyestuff on doped-PANI from 2.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.0×10^{-5}	0.015	15	0.2983	0.6638
		30	0.2227	
		45	0.2059	
		60	0.1978	
		90	0.1869	
		120	0.1811	
		150	0.1810	

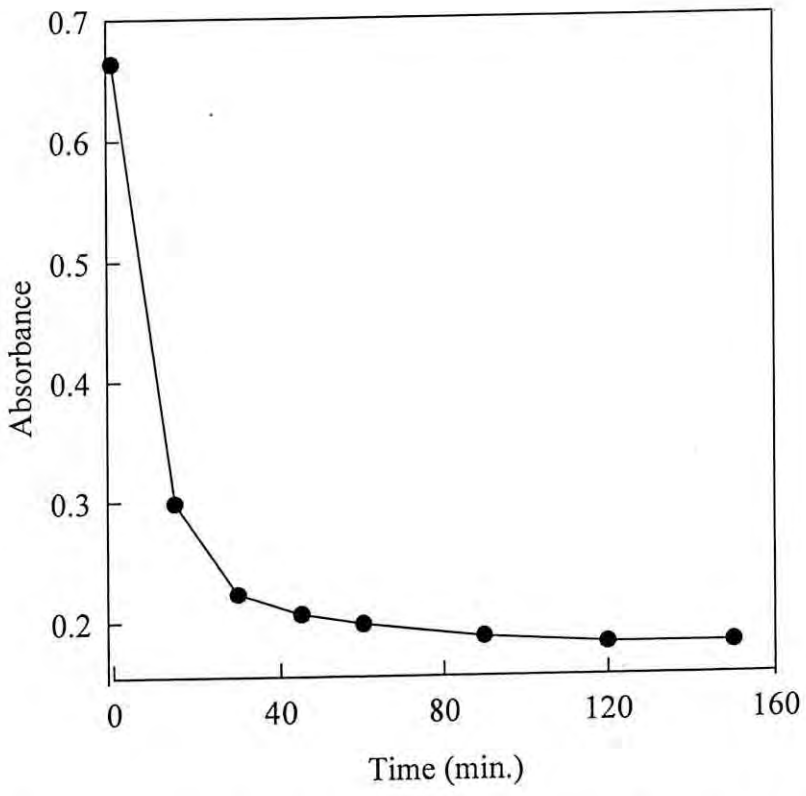


Fig. 3.3.46: Progress of MB adsorption with time on doped-PANI (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.47 : Amount of MB dyestuff adsorbed by doped -PANI from 2.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.0×10^{-5} MMB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.2983	0.3655	13.5837
30	0.2227	0.4411	16.3934
45	0.2059	0.4579	17.0178
60	0.1978	0.4660	17.3188
90	0.1869	0.4769	17.7239
120	0.1811	0.4827	17.9394
150	0.1810	0.4828	17.9432

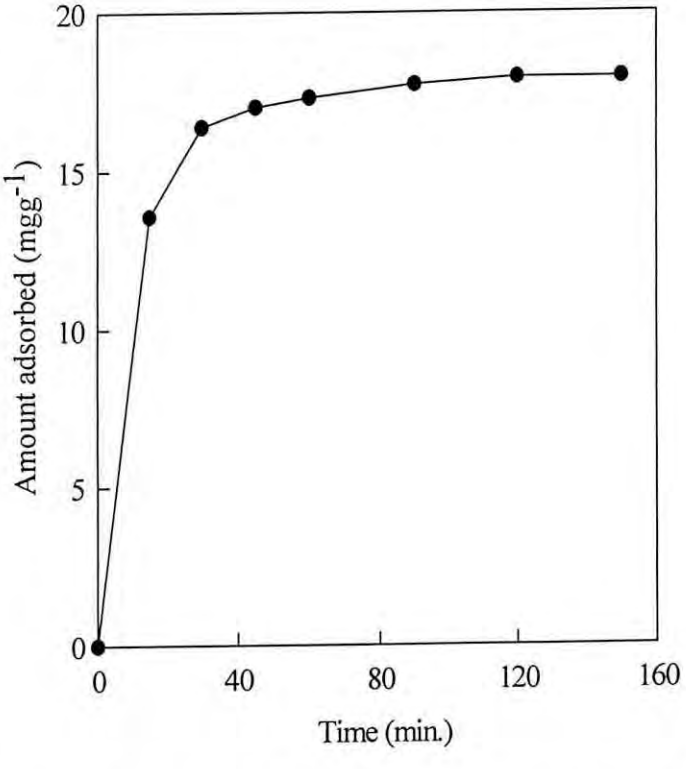


Fig. 3.3.47: Amount of MB adsorbed by doped-PANI at different time of adsorption (Initial concentration of MB = 2.0×10^{-5} M).

Table 3.3.48: Adsorption of MB dyestuff on doped-PANI from 2.5×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
2.5×10^{-5}	0.015	15	0.3761	0.7932
		30	0.2990	
		45	0.1822	
		60	0.1465	
		90	0.1217	
		120	0.1001	
		150	0.1008	

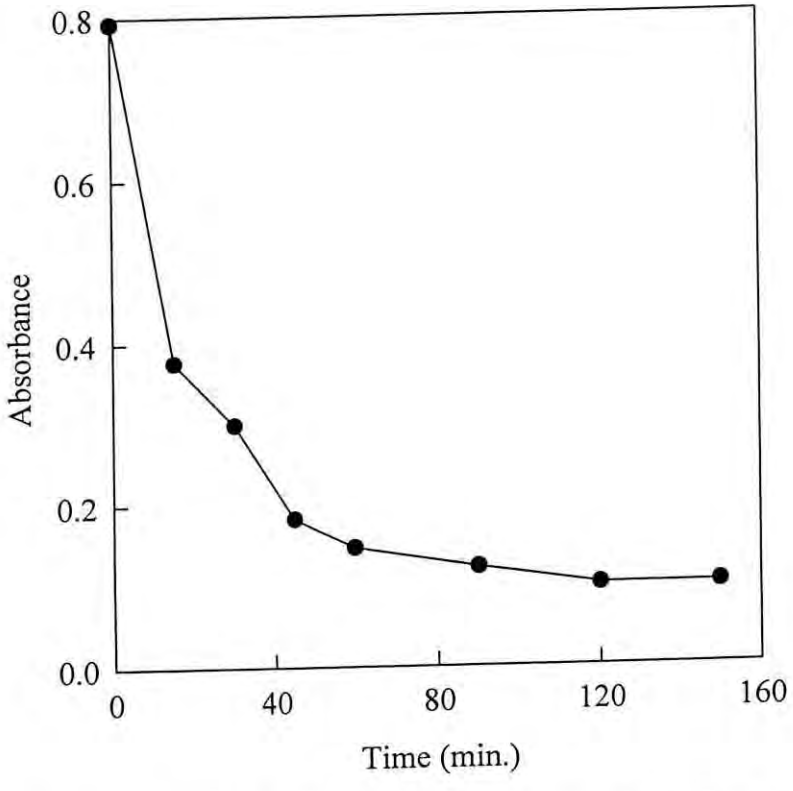


Fig. 3.3.48: Progress of MB adsorption with time on doped-PANI (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.49 : Amount of MB dyestuff adsorbed by doped -PANI from 2.5×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 2.5×10^{-5} M MB solution)- (Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.3761	0.4171	15.5014
30	0.2990	0.4942	18.3668
45	0.1822	0.6110	22.7077
60	0.1465	0.6467	24.0345
90	0.1217	0.6715	24.9562
120	0.1001	0.6931	25.7589
150	0.1008	0.6931	25.7589

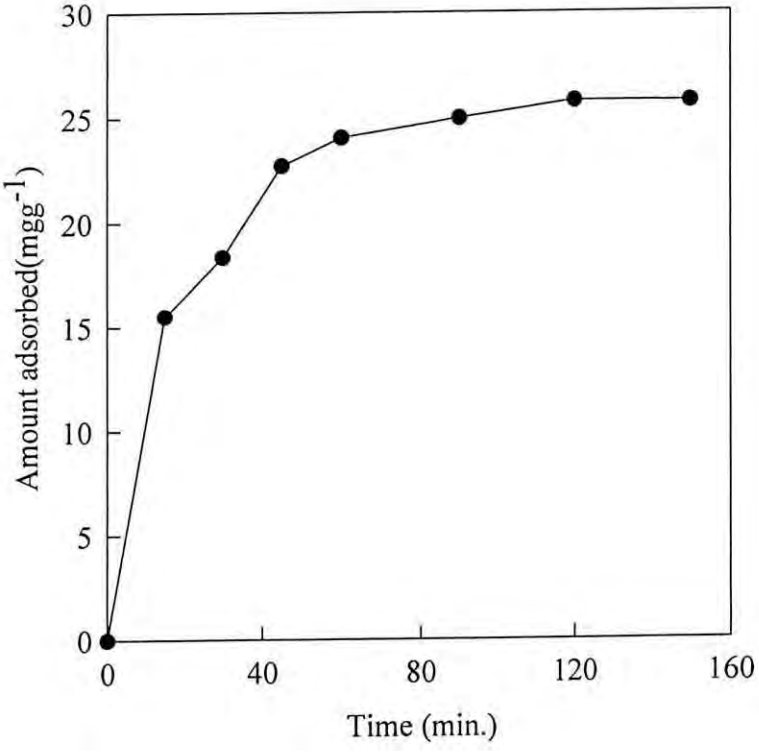


Fig. 3.3.49: Amount of MB adsorbed by doped-PANI at different time of adsorption (Initial concentration of MB = 2.5×10^{-5} M).

Table 3.3.50: Adsorption of MB dyestuff on doped-PANI from 3.0×10^{-5} M MB solution.

Initial conc. of MB solution (M)	Amount of sample taken in 50 mL MB solution (g)	Time of adsorption (min.)	Corresponding absorbance	Initial absorbance of MB solution before adsorption
3×10^{-5}	0.015	15 30 45 60 90 120 150	0.3795 0.3438 0.2541 0.2107 0.2112 0.2064 0.2063	0.9377

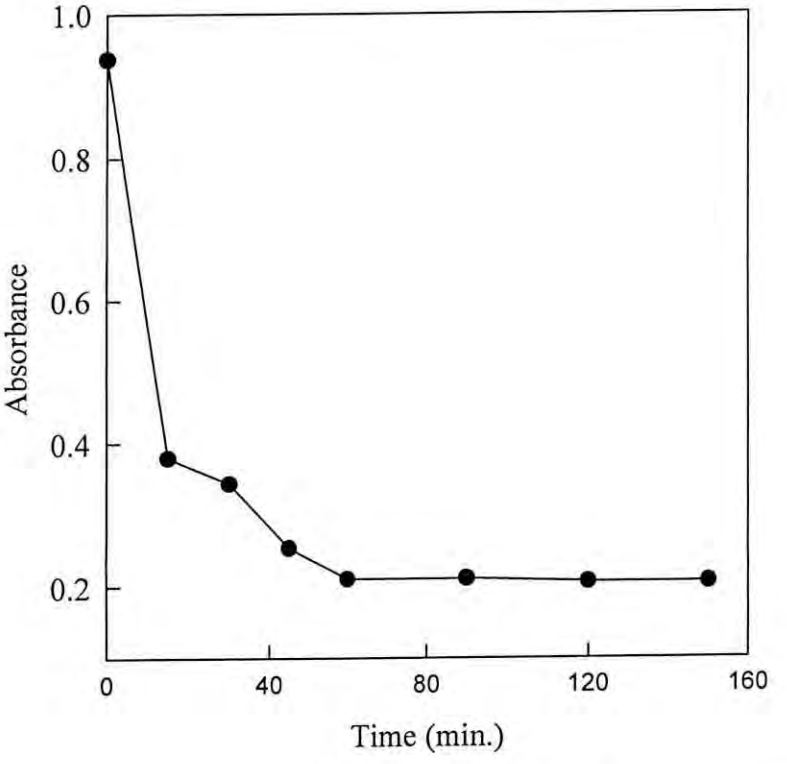


Fig. 3.3.50: Progress of MB adsorption with time on doped-PANI (Initial concentration of MB = 3.0×10^{-5} M).

Table 3.3.51 : Amount of MB dyestuff adsorbed by doped -PANI from 3.0×10^{-5} M MB solution.

Time of absorption (min.)	Absorbance of remaining MB solution after adsorption	Difference of absorbance (Initial absorbance of 3.0×10^{-5} M MB solution)-(Absorbance of remaining MB solution after adsorption)	Amount of MB adsorbed by the sample at the corresponding time (mg g^{-1})
15	0.3795	0.5582	20.7454
30	0.3438	0.5939	22.0722
45	0.2541	0.6836	25.4058
60	0.2107	0.7270	27.0188
90	0.2112	0.7265	27.0002
120	0.2064	0.7313	27.1786
150	0.2063	0.7314	27.1823

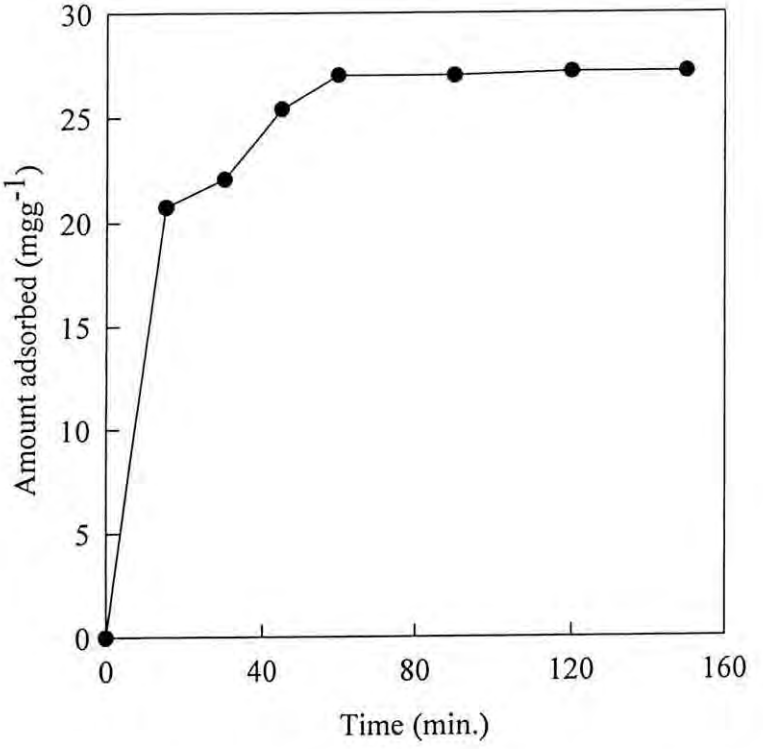


Fig. 3.3.51: Amount of MB adsorbed by doped-PANI at different time of adsorption (Initial concentration of MB = 3.0×10^{-5} M).

Determination of monolayer capacity (χ_m)for doped- PANI

Table 3.3.52 : The amount of MB adsorbed on doped-PANI at equilibrium concentration of MB solution.

Initial concentration ($M/10^{-5}$)	Equilibrium time (min.)	Absorbance of the remaining MB solution at equilibrium time	Amount adsorbed at equilibrium time ($mg\ g^{-1}$)	Equilibrium concentration ($M/10^{-5}$)
0.5	120	0.0498	0.1560	4.3371
1.0	150	0.0563	0.1764	9.5030
1.5	150	0.0786	0.2462	15.4940
2.0	150	0.1810	0.5639	17.9432
2.5	150	0.1008	0.3136	25.7329
3.0	150	0.2063	0.6463	27.1823

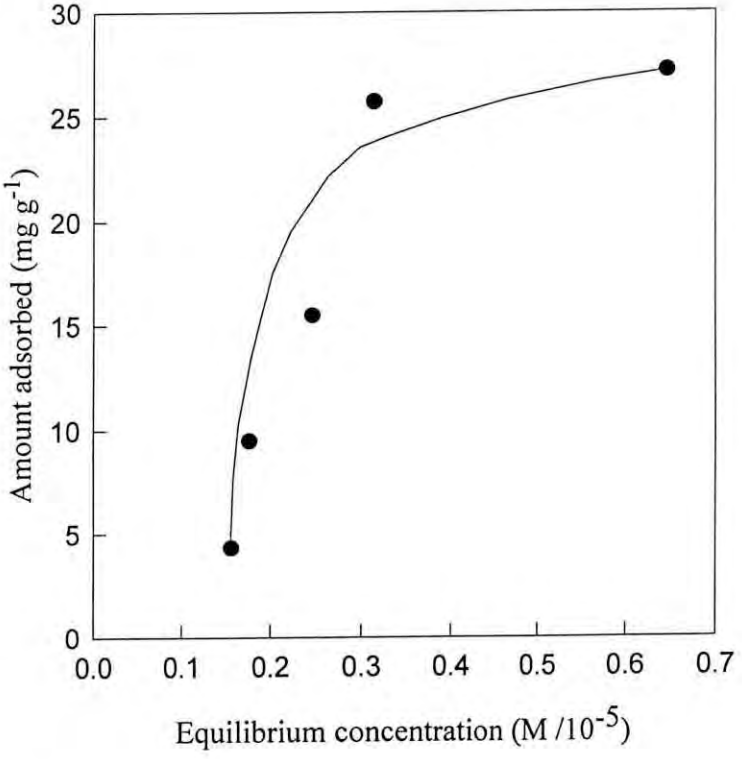


Fig. 3.3.52: Isotherm for the determination of monolayer capacity of MB at doped-PANI.

Calculation of Specific Surface Area of doped-PANI Substrate

The specific surface area of the doped –PANI substrate can be calculated using the following equation,

$$\mathbf{S = (\chi_m / M) \times N \times A_m \times 10^{-20}}$$

Here,

Monolayer capacity $(\chi_m) = 27.18 mg g^{-1} = 27.18 \times 10^{-3}\ g\ g^{-1}$

Molecular mass of MB (M) = 355.89 g mol^{-1}

Avogadro constant (N) = 6.023×10^{23}

(i) Cross-sectional area of MB ($\mathbf{A_m}$) = 130×10^{-20} $Å^2$ BET with N_2

(ii) Cross-sectional area of MB ($\mathbf{A_m}$) = 78×10^{-20} $Å^2$ BET with Ar

Specific surface area = $\mathbf{S}$ $(m^2 g^{-1})$ = **?**

(i) $S = (27.18 \times 10^{-3} / 355.89) \times 6.023 \times 10^{23} \times 130 \times 10^{-20}$

$= 59.798\ (m^2 g^{-1})$

(ii) $S = (27.18 \times 10^{-3} / 355.89) \times 6.023 \times 10^{23} \times 78 \times 10^{-20}$

$= 35.879\ (m^2 g^{-1})$

Calculated Specific Surface Area of Adsorbents

The calculated specific surface area of acidic-PANI, neutral- PANI, basic PANI and doped-PANI are given in the Table. Calculation was performed by using the two different A_m values.

Table 3.3.53: Calculated specific surface area of the PANI matrices studied.

Matrices	Derived monolayer coverage, χ_m (mg g^{-1})	Adsorption Capacity, K_L ($LMol^{-1}$)×10^5	Calculated specific surface area, S ($m^2 g^{-1}$)	
			A_m=130 Å^2	**A_m=78 Å^2**
Acidic –PANI	4.17	0.34	9.174	5.504
Neutral-PANI	3.19	0.27	7.019	4.211
Basic-PANI	30.00	2.44	66.002	39.601
Doped-PANI	27.18	2.38	59.798	35.879

From the above result, it can be seem that the monolayer capacity of MB on the basic-PANI is 7 and 9 times higher than that on the acidic- and neutral-PANI, respectively. On the other hand, monolayer capacities of the basic- and doped-PANI are nearly comparable. The specific surface area of the basic-PANI is also 7 and 9 times higher than that of acidic- and neutral-PANI. The higher monolayer capacity and surface area of the basic-PANI has also been reported earlier [45] ascribing electrostatic attraction and the morphological change of the PANI by basic treatment. The present results seems to follow the following order:

Monolayer capacity:

basic - PANI ≈ doped - PANI > acidic - PANI ≈ neutral - PANI

Specific surface Area

(A_m = 130 Å^2): basic-PANI ≈ doped-PANI > acidic-PANI ≈ neutral-PANI

3.4 Evaluation of Adsorption Capacity

Adsorption capacity is one of the important characteristics of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent per unit mass or volume of the adsorbent. It depends on the fluid-phase concentration, pH, temperature and other conditions such as nature of the adsorbent and the molecular structure of the adsorbate. Usually, adsorption capacity decreases with increasing temperature although rate of adsorption may increase with increasing temperature. The character of the adsorbent has a profound effect on the adsorption capacity. Typically, adsorption capacity data are collected at a fixed temperature and the data are plotted as an isotherm at various adsorbate concentrations (or partial pressures for a gas or vapor). In the present work, the adsorption capacities of ionic dye MB onto the surface of the electrochemically prepared PANI matrices were analyzed using the following Langmuir adsorption isotherm equation:

$$\frac{C_e}{x/m} = \frac{1}{K_L k_L} + \frac{C_e}{k_L}$$

Where C_e is the concentration of dyes (MB) after attaining the adsorption equilibrium onto the PANI matrices, x is the mass in grams of the dye adsorbed onto m grams of the adsorbent, k_L is the proportionality constant and K_L is the adsorption coefficient that indicates the affinity of the dye to the adsorbent. K_L is also termed as adsorption capacity. The plot of $Ce/(x/m)$ *vs* C_e should give a straight line with a slope = $1/k_L$ and an intercept = $1/K_L k_L$ from which the value of K_L can be evaluated. The plots are shown in Figs. 3.4.1-3.4.4 for different PANI adsorbent at 30 °C. The corresponding data are given in Table 3.4.1-3.4.4.

Table 3.4.1: Data for the evaluation of adsorption coefficient, K_L for the acidic- PANI

Initial concentration of MB ($M/10^{-5}$)	Equilibrium concentration, C_e ($M/10^{-5}$)	Amount adsorbed at quilibrium,(x/m) ($g\ g^{-1}$) / 10^{-3}	$C_e/(x/m)$ ($M/10^{-2}$)	Adsorption Coefficient, K_L ($L\ mol^{-1}$)
0.5	0.2121	1.2331	0.1720	0.34×10^5
1.0	0.4499	2.2390	0.2009	
1.5	0.6228	2.9971	0.2078	
2.0	0.9824	3.7735	0.2603	
2.5	1.1705	4.6166	0.2535	
3.0	1.5257	5.1768	0.2947	

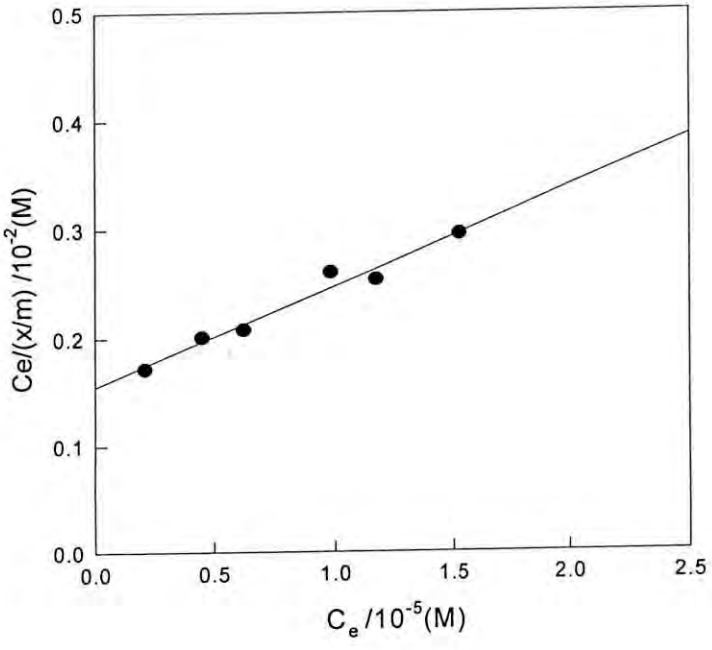


Fig 3.4.1: Langmuir plot for acidic PANI to calculate the adsorption coefficient, K_L

Table-3.4.2: Data for the evaluation of adsorption coefficient, K_L for the neutral- PANI

Initial concentration of MB ($M/10^{-5}$)	Equilibrium concentration, C_e ($M/10^{-5}$)	Amount adsorbed at equilibrium ,(x/m) ($g\ g^{-1}$) / 10^{-3}	$C_e/(x/m)$ ($M/10^{-2}$)	Adsorption Coefficient, K_L ($L\ mol^{-1}$)
0.5	0.2840	0.9916	0.2864	0.27×10^5
1.0	0.5494	2.0101	0.2733	
1.5	1.0938	2.0766	0.5267	
2.0	1.2849	3.3038	0.3889	
2.5	1.8061	3.0488	0.5924	
3.0	2.2392	3.1938	0.7011	

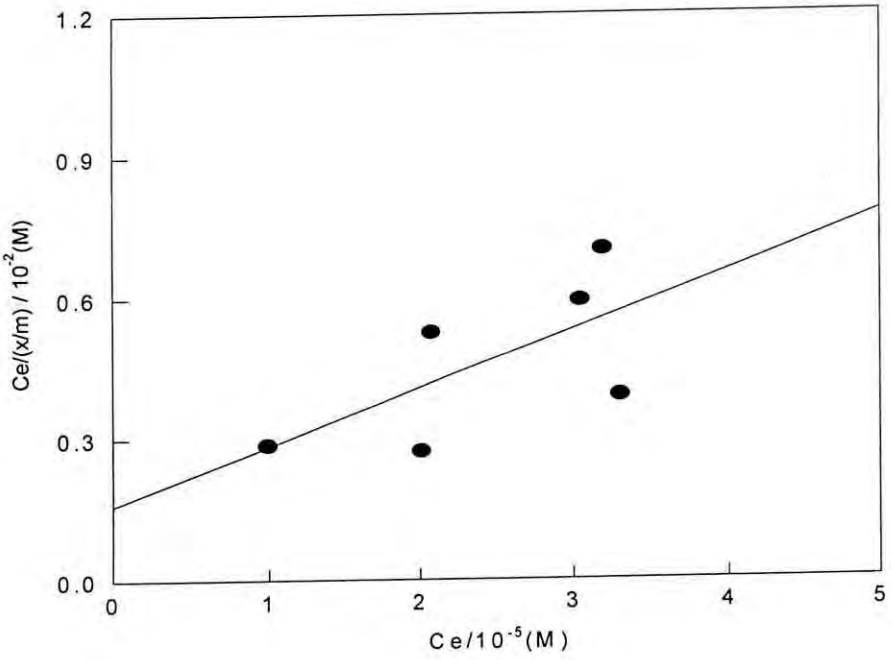


Fig. 3.4.2: Langmuir plot for neutral PANI to calculate the adsorption coefficient, K_L

Table 3.4.3: Data for the evaluation of adsorption coefficient, K_L for the basic - PANI.

Initial concentration of MB ($M/10^{-5}$)	Equilibrium concentration, C_e ($M/10^{-5}$)	Amount adsorbed at equilibrium, (x/m) ($g\ g^{-1}$) / 10^{-3}	$C_e/(x/m)$ ($M/10^{-2}$)	Adsorption Coefficient, K_L ($L\ mol^{-1}$)
0.5	0.0325	5.8010	5.6025e-3	2.44×10^5
1.0	0.0482	11.0231	4.3726e-3	
1.5	0.0899	17.3485	5.1820e-3	
2.0	0.1112	23.3543	4.7614e-3	
2.5	0.1504	27.6952	5.4305e-3	
3.0	0.1898	32.5935	5.8232e-3	

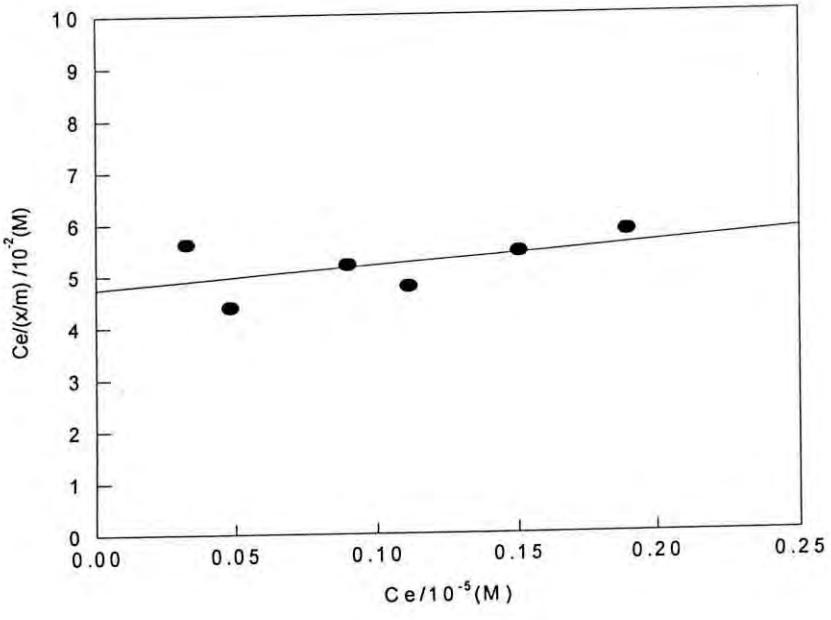


Fig. 3.4.3: Langmuir plot for basic PANI to calculate the adsorption coefficient, K_L

Table 3.4.4: Data for the evaluation of adsorption coefficient, K_L for the doped- PANI.

Initial concentration of MB ($M/10^{-5}$)	Equilibrium concentration, C_e ($M/10^{-5}$)	Amount adsorbed at equilibrium time,(x/m) ($g\ g^{-1}$) $/10^{-3}$	C_e/ (x/m) ($M/10^{-2}$)	Adsorption Coefficient, K_L ($L\ mol^{-1}$)
1.0	9.5030	0.1764	0.0186	2.38×10^5
1.5	15.4940	0.2462	0.0159	
2.0	17.9432	0.5639	0.0314	
2.5	25.7329	0.3136	0.0122	
3.0	27.1823	0.6463	0.0238	

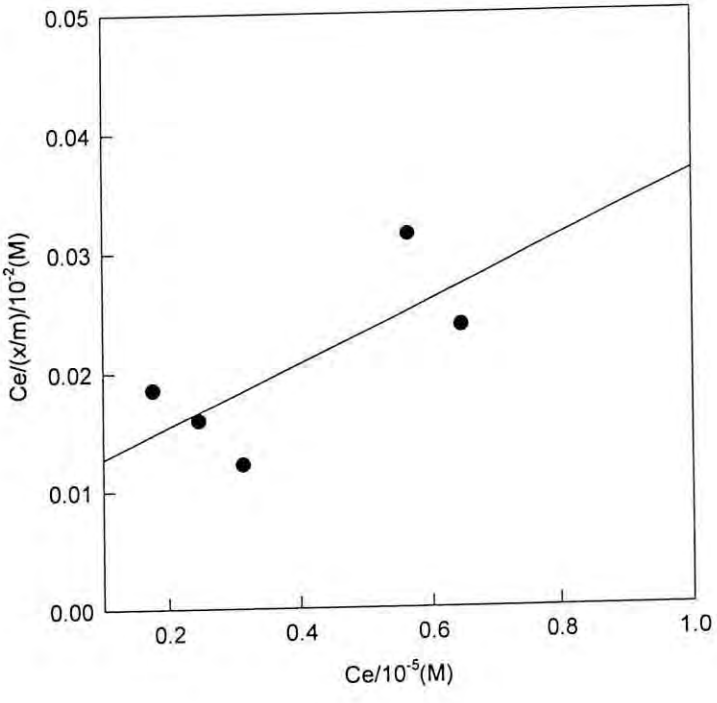


Fig. 3.4.4: Langmuir plot for doped PANI to calculate the adsorption coefficient, K_L

It can be seen from the above results of adsorption capacity, K_L for various PANI matrices that the value of K_L varies from adsorbent to adsorbent. The basic- and doped-PANI shows the highest values of K_L compared to that of acidic- and neutral-PANI. The order of the K_L for various PANI matrices studied can be arranged as:

basic-PANI ≈ doped-PANI > acidic-PANI ≈ neutral-PANI.

Similar order are also found in respect to monolayer capacity and specific surface area. The higher adsorption capacity of the basic- or doped-PANI indicates the higher affinity of MB dye toward them. The comparable adsorption capacity of the basic- and doped-PANI indicates that the incorporation of the dopants in the PANI matrix substantially negligible effect towards the Pain's surface activity. However the higher adsorption capacity of the basic-PANI may consider primarily due to the modification of PANI surface by electrochemical mode of synthesis and its treatment with base. The basic-PANI, as electrosynthesized and treated may contains a greater number of pores in it. Indeed, SEM observation of the basic-PANI samples also predicted a highly porous morphology of the basic-PANI. The high adsorption capacity of the basic-PANI may also results from the electrostatic attraction of cationic MB dye and the negative charged surface of the basic-PANI. The possibility of developing negative surface charge on the PANI by base treatment has indeed reported [46] previously.

3.5 Comparison of Surface Capacities Between Chemically and Electrochemically Prepared Polyaniline Matrices

Materials property strongly depends on the mode of synthesis and the route by which it is processed. Chemical and electrochemical means are widely used in preparing the polymeric matrices. The electrochemical method of preparation is highly sensitive to the material properties because during the electro-synthesis, it involves an electrolytic medium containing solvent, electrolytes and electrical force to drive a reaction to give the products. As a result, it is expected that the electrochemically prepared materials should have some significant characteristics which are not available by employing a chemical route. In the present work, PANI was prepared electrochemically in order to examine its surface characteristics. The analysis of the electrochemically prepared PANI revealed that quite a dissimilar surface morphology and superior adsorption capacities toward MB adsorption. The SEM observations of PANI prepared chemically and electrochemically are depicted in Fig 3.5.1. By comparing the SEM observation, it can be seen that surface morphology, particle size are different between the chemically and electrochemically prepared PANI. Moreover, the surface capacities, i. e. surface area (S), adsorption capacity (K_L) look to be dramatically superior when PANI is prepared electrochemically. The results are summarized in Table 3.5.1. The observed higher surface area and adsorption capacity for the PANI samples may be due to the surface modification of PANI as deposited electrochemically. Furthermore, the probability of highly porous structure is also possible as the insertion and rejection of electrolyte anion from the PANI matrix is occurred during its electrochemical preparation. Indeed, high porosity usually results in high surface area and thus high adsorption capacities. [47]. The results of surface capacity of the PANI prepared electrochemically and that of PANI obtained chemically are summarize further in the following Table 3.5.1.

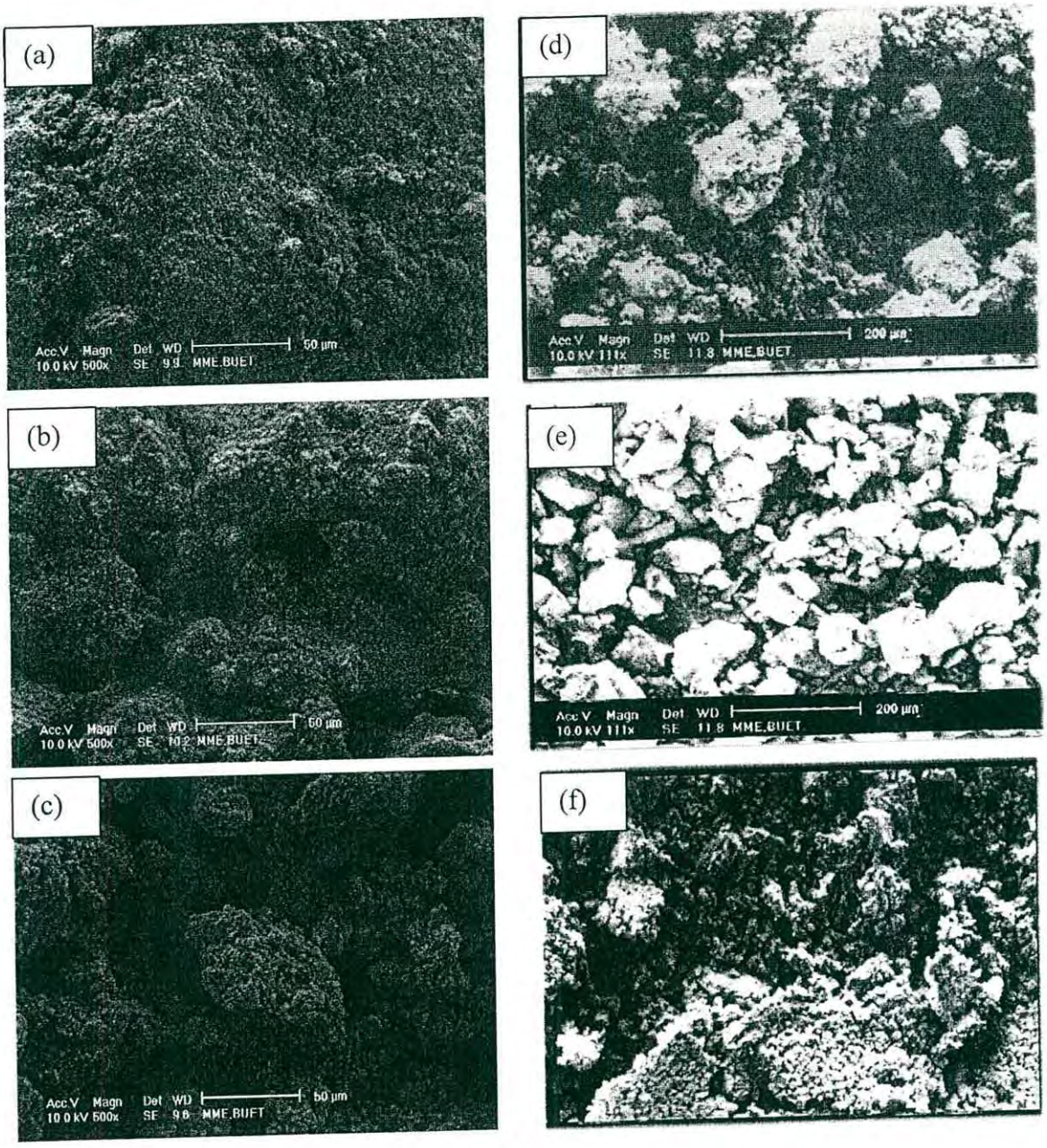


Fig. 3.5.1: SEM micrographs of electrochemically prepared (a) acidic-PANI, (b) neutral-PANI, (c) basic-PANI and chemically prepared (d) acidic-PANI, (e) neutral-PANI and (f) basic-PANI.

Table 3.5.1: The comparison of surface capacities between chemically and electrochemically prepared PANI matrices.

PANI	Electrochemically Prepared PANI				Chemically Prepared PANI			
	Mono-layer capacity, χ_m, (mg g^{-1})	Surface Area, S(m^2 g^{-1})		Adsorption Capacity, K_L (L Mol^{-1})	Mono-layer capacity, χ_m, (mg g^{-1})	Surface Area, S (m^2 g^{-1})		Adsorp-tion Capacity, K_L (L Mol^{-1})
		A_m=130 Å^2	A_m=78 Å^2			A_m=130 Å^2	A_m=78 Å^2	
Acidic	4.17	11.3745	6.825	0.34×10^5	6.95	15	9	0.50×10^5
Neutral	3.19	7.019	4.211	0.27×10^5	4.95	11	7	0.49×10^5
Basic	30.0	63.8026	38.282	2.44×10^5	13.0	29	17	1.39×10^5
Doped	27.18	59.798	35.879	2.38×10^5	-	-	-	-

Conclusion

The present investigation suggests that electrochemically synthesized conducting polymer PANI can be utilized as an effective adsorbent for the removal of cationic dyes *e.g*, MB from aqueous solution. The ability of MB adsorption of the adsorbent is largely governed by the pH of the solution with which PANI is treated. The electrochemical mode of synthesis and the treatment with both acidic and basic solutions, the PANI surface seems to modified greatly than the PANI prepared chemically. The treated PANI surfaces seems to behave as a charged adsorbent and their ability of MB adsorption largely differs. The SEM images of acidic- and neutral-PANI show almost uniform surface morphology with compact and evenly distributed particles, while the basic- and doped-PANI surfaces show irregularly shaped three-dimensionally organized bodies with huge porosity available for adsorption. By controlling the pH of the solutions with which the PANI matrices treated, the morphology and surface property can be modified.

The equilibrium adsorption times required for basic- and doped-PANI are found to be shorter than those of the acidic- and neutral-PANI surfaces, indicating that MB shows stronger affinity towards basic- and doped-PANI surfaces.

The monolayer capacity (χ_m) of acidic- and neutral- PANI was found to be comparatively less than the basic- and doped-PANI. Where as the monolayer capacity of acidic-and neutral-PANI was 4.17 mg g^{-1} and 3.19 mg g^{-1}, respectively. The monolayer capacity of basic- and doped-PANI was 30.00 mg g^{-1} and 27.18 mg g^{-1}, respectively.

The surface area of modified basic- and doped-PANI was found to be 66.002 $m^2 g^{-1}$ and 59.798 $m^2 g^{-1}$ in 130 $Å^2$, BET with N_2 .These values were found to be comparatively higher than those of the acidic- and neutral-PANI for which the surface areas were found to be 9.17 $m^2 g^{-1}$ and 7.019 $m^2 g^{-1}$, respectively. The surface area as a consequence of adsorption of the MB dye appears to be emphasized due to the electrostatic interaction between the ionic dye adsorbate and the charged-PANI adsorbent. For each PANI matrix, two different cross-sectional area of MB used. That was 130 $Å^2$, BET with N_2 and the other was 78 $Å^2$, BET with Ar.

The adsorption capacity (K_L) of basic- and doped-PANI was found to be more than the acidic- and neutral-PANI. The value of adsorption capacity (K_L) for acidic-,neutral-,basic-and doped-PANI was found $0.34\times10^5 Lmol^{-1}$, $0.27\times10^5 Lmol^{-1}$,$2.44\times10^5 Lmol^{-1}$ and $2.38\times10^5 Lmol^{-1}$ respectively.

The greater adsorption capacities of the basic- and doped-PANI thus suggest that the MB dye can be preferentially removed from the aqueous solution by using the basic- and doped-PANI matrices.

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