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Enhanced Adsorption Studies of Synthetic Dyes From Aqueous Solution By Polyaniline -Nickel Ferrite Composites And Its ConductivityStudies

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ABSTRACT
In this particular work, thecompsite of PANI with varying composition of nickel ferrite were prepared using HCl as the medium. The characterization was done using X-ray diffraction techniques and SEM analysis. These composites showed good adsorption properties towards water contaminants like malachite green and crystal violet. The electrical behavior shows increase in conductivity of pani when incorporated with ferrite, As ferrite concentration increases conductivity decreases.

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I. INTRODUCTION

The use of organic synthetic dyes has increased dramatically and uncontrollably in last few decades. Different types of dyes are frequently employed in plastics, paper, cosmetics, leather, and textile industries for colouring purposes. These dyes are released in water as effluents, which are of low biological oxygen demand (BOD) and high chemical oxygen demand (COD). Some of these dyes, such as azo-dyes, are toxic and carcinogenic in nature. Their addition into nearby streams and rivers contaminates water and greatly upsets the biological activities of aquatic life. It is highly desirable to explore efficient technologies for remediation and separation of these potential pollutants from effluents.

Various protocols and techniques, such as reverse osmosis, precipitation, coagulation, membrane filtration, chemical oxidation, electrochemical methods, ion exchange, and adsorption are used to remove these dyes and other hazardous materials from polluted water[1]. However, adsorption is the most frequently used technique to remove dyes from water, because this technique, in addition to easiness and low cost, causes low generation of residues and the adsorbent used may be regenerated and reused

Nanoparticles have distinct properties such as high surface area, high adsorption and special photo electric properties; and based on this, nanoparticles have applications in the removal of environmental pollutants. It is preferable to use magnetic nano particles which can be easily removed using external magnetic field. Magnetic nano materials possess adsorbent properties that qualify them as promising adsorbent materials, which open up wide field for emerging separation applications. The low potential pollutant removal ability is the main drawback of using magnetic nano particles. To invade this defect, the surface of magnetic nano particles can be modified using polymeric adsorbents such as polyaniline (PANI). The surface properties of nanoparticles can be greatly enhanced by this modification.

Due to unique characteristics, conductive polymers have been used in advanced technologies in recent years[2]. Among the various conductive polymers available polyaniline (PANI) has been widely studied not only because of its electrical resistivity, environmental stability and economic feasibility. It is highly stable in air and soluble in most of the solvents and exhibits dramatic changes in its electronic structure and physical properties in the protonated state.

In this present work , modification of nickel ferrite with PANI was used as an adsorbent for the adsorption of organic dyes such as malachite green and Crystal violet from effluent water.

II. Experimental

2.1 Methodology

2.1.1 SYNTHESIS OF PANI

Using APS as the oxidising agent, aniline is polymerized by chemical oxidation method keeping monomer to oxidant ratio as 1:1.25respectively. Freshly distilled aniline is dissolved in 200 ml 1M HCl. To get a homogeneous solution, the solution is made to stir for half an hour using mechanical stirrer. The solution is then kept under ice cold condition maintaining the temperature between 0-5°C. To this mixture, 200 ml aqueous solution of APS is added drop by drop using a burette. The reaction mixture is then kept for 12 hrs to complete the polymerization. It is then washed with distilled water, acetone and finally with diluted HCl. The green colouredpolyaniline is then dried under sunlight. [3][4]

2.1.2 SYNTHESIS OF NICKEL FERRITE

Ferric nitrate and nickel nitrate are dissolved in 50 ml natural bilimbi juice at 40°C in the molar ratio 2:1.This solution is then heated at 60°C and the temperature is kept constant till a wet gel of the metal nitrates is obtained. Which undergoes self-ignition to get fluffy product of nickel ferrite.Final homogenization is carried out by grinding it into a fine powder in smooth agate mortar using acetone as a moistening medium. It is then heated at 200°C in a muffle furnace to get fine particles. The chemical reaction leading to the formation of nickel ferrite is as follows,

$Ni(NO_3)_2 .7H_2O + 2Fe(NO_3).9H_2O \rightarrow NiFe_2O_4$ + volatilities. [5][6]

2.1.3 SYNTHESIS OF PANI FERRITE COMPOSITES

The solution of aniline in HCl is taken in a 500ml beaker. It is stirred for 15 minutes using mechanical stirrer. The beaker is kept in an ice bath to maintain a temperature of 0-5°C.To this, the oxidant, ammonium peroxydisulphate is added drop by drop using burette. Nickel ferrite powder is added occasionally with constant stirring in order to keep the nickel-ferrite powder suspended on the solution about 30 minutes. After the addition, the solution is kept stirring overnight then filtered and washed with distilled water, acetone and dil. HCl. It is then dried under sunlight. [7][8].

Table 1: Composite with different amount of ferrite

SAMPLE	PANI(M)	FERRITE(g)
fe1	0.4	2.5
fe2	0.4	5
fe3	0.4	7.5
fe4	0.4	10

2.2 ADSORPTION EXPERIMENTS

The adsorption experiments were performed with the PANI and PANI-ferrite composites to investigate their capacity of removing contaminants from waste water. The experiments were performed with stock solutions of Crystal Violet and Malachite Green in deionized water. All adsorption experiments were carried out by placing 2 g of adsorbent (PANI, fe1, fe2, fe3 and fe4) in 10 mL of the test solution contained in different volumetric flasks.

2.2.1. Spectrophotometric determination Crystal violet

1ppm solution of crystal violet was prepared using distilled water. To 5 ml of each solution taken in five separate test tubes, 2 g of PANI added in each test tubes, fe1(2.5g ferrite), fe2 (5g ferrite), fe3 (7.5g ferrite and fe4 (10g ferrite) are added respectively and shaken well, centrifuged and centrifugate is analyzed. [9]

2.2.2. Spectrophotometric determination Malachite green

1ppm solution of Malachite green dye was prepared using distilled water. To 5 ml of each solution taken in five separate test tubes, 2 g of PANI added in each test tubes, fe1(2.5g ferrite), fe2 (5g ferrite), fe3 (7.5g ferrite and fe4 (10g ferrite) are added respectively and shaken well, centrifuged and centrifugate is analyzed. [10]

2.3 CHARACTERISATIONTECHNIQUES

Structural characterisation of the samples were carried out using Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation (=1.5406 A^o) over a 2θ range of 20-80^o. Optical properties of the samples were determined using Shimadzu UV-VIS spectrophotometer (UV 2600), in the Department of Physics S. D. College, Alappuzha. The morphology and composition were analysed by Scanning electron microscope (SEM-EDAX :Jeol 6390LA/ OXFORD XMX N).

DC conductivity of the sample was determined using disc shaped samples of 8mm diameter and about 2mm thickness. The samples were placed in a conductivity/dielectric cell. A bias voltage in the range of 0-30 V is applied and the current flowing across the sample was measured by a Keithley2001 multimeter, which is a fully programmable instrument capable of sourcing and measuring voltage or current simultaneously with accuracy.

The measurements were done at room temperature. The conductivity of the samples calculated by the following formula.

$$\sigma(S/cm) = (I/V) x (l/A),$$

where,σ is the electrical conductivity, I is the current through probe in amperes, V is the voltage across the probe in volts, l is the spacing between the probes in centimeters and A is the area of contact of the probes with the sample in centimeter square.

III. RESULTS AND DISCUSSION

3.1. Structural & Morphological analysis

XRD is used to determine the crystalline structure of metal oxide and polymer coated metal oxide by comparing the diffraction angle (2θ) with that of metal oxide of known composition. Figure 1 shows the XRD pattern of PANI, NF and fe2. In the pattern of PANI a broad 2θ peaks was observed at $2\theta = 25^o$(110plane) which is due to the periodicity perpendicular to PANI chain and no sharp peak is observed which indicates the amorphous nature and emeraldine salt form of PANI. XRD of NF represents sharp diffraction peaks at 30.3^0(220), 35.70(311), 43.40(400), 57.4^0(511), 63.00(440), 75.2^0(622).

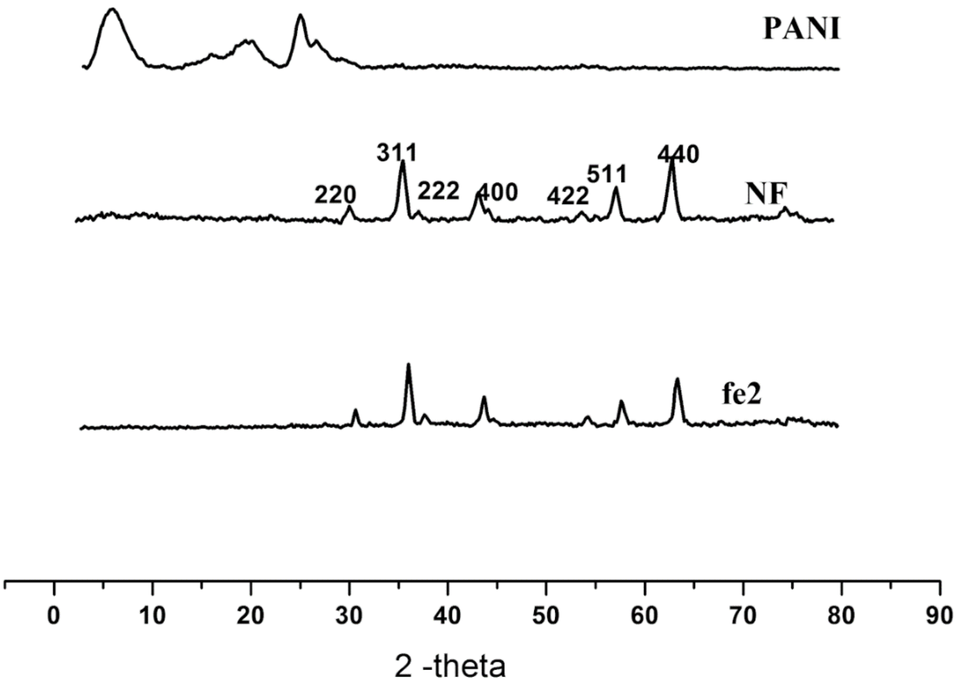
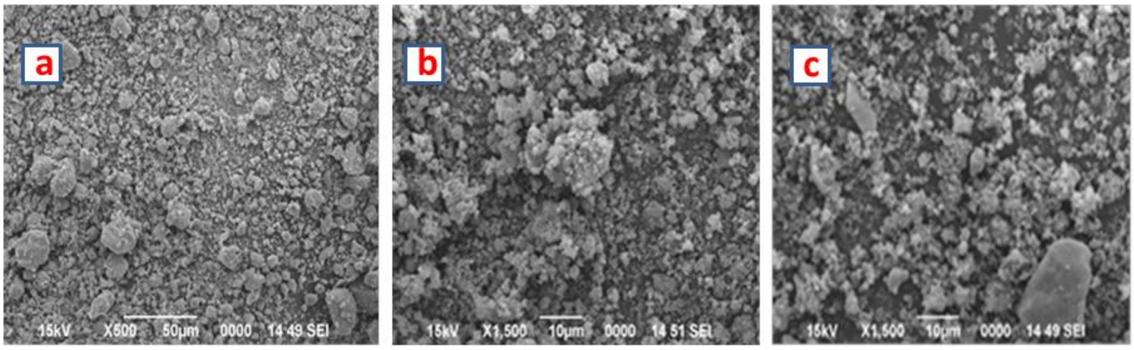


Figure 1 :XRD of PANI, NF and Ferrite (Fe)

The fe2 sample also gives the above mentioned characteristics peaks of NF. The peak intensity of the composites decreased compared to that of pure NF, due to polymerization of PANI on the surface of NF. Average particle size of NF and fe2 calculated using Debye-Scherrer formula are about 13nm and 13.07nm respectively.

Morphological studies of the material were studied by SEM analysis. SEM images of ferrite,PANI and PANI-ferrite were shown in figure 2. From the SEM images, relatively amorphous nature of the polymer sample and crystalline nature of ferrite was evident. After the polymerization on the surface of ferrite, the morphology changes significantly with highly porous structure.

Figure 2: SEM images of (a) ferrite (b) PANI (c) PANI-ferrite



3.2 Adsorption of Water contaminants by PANI, ferrite and PANI-ferrite composites

3.2.1 Malachite green adsorption

Adsorption of Malachite green by the samples was carried out as explained in section 2.2.2. UV spectrum recorded in the range of 617 nm is shown in figure 3.From the intensity of the λmax of absorption peak the adsorption capacity of the samples can be analysed. All the samples exhibit a broad peak in the range of 617. Intensity of λmax directly related to the concentration of the dye. Decrease in intensity indicates the decrease in concentration of dye in test solution. So the change in intensity of the peak directly gives an idea about the adsorption capacity of the sample towards Malachite green dye.

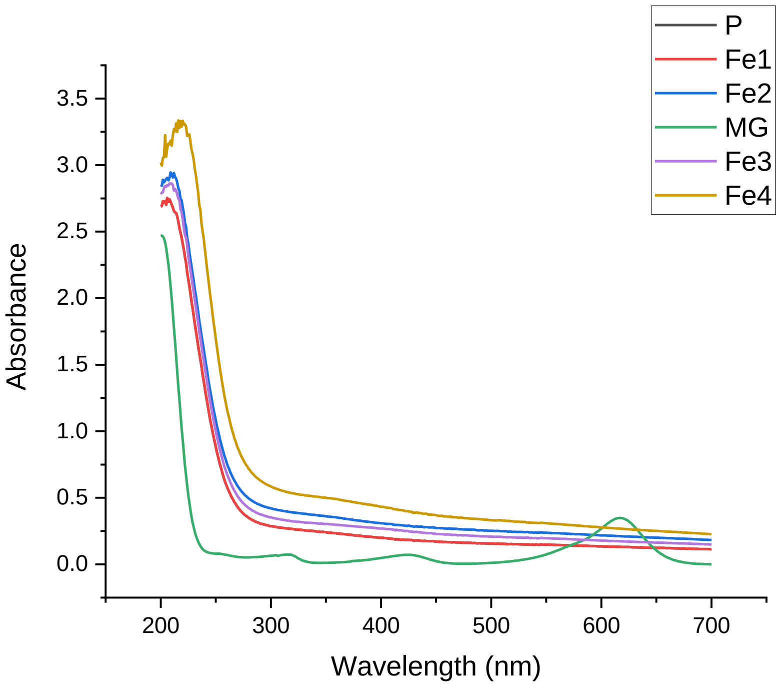


Fig 3. Malachite green adsorption of PANI,Ferrite,andfe(2.5g,5g,7.5g,10 g)

3.2.2 Crystal violet adsorption

Adsorption of crystal violet by the samples was carried out as explained in section 2.2.1. UV spectrum recorded in the range of 400- 700 is shown in figure 4.6.From the intensity of the λmax of absorption peak the adsorption capacity of the samples can be analysed. All the samples exhibit a broad peak in the range of 400-700 nm. Intensity of λmax directly related to the concentration of the dye. Decrease in intensity indicates the decrease in concentration of dye in test solution. So the change in intensity of the peak directly gives an idea about the adsorption capacity of the sample towards crystal violet dye.

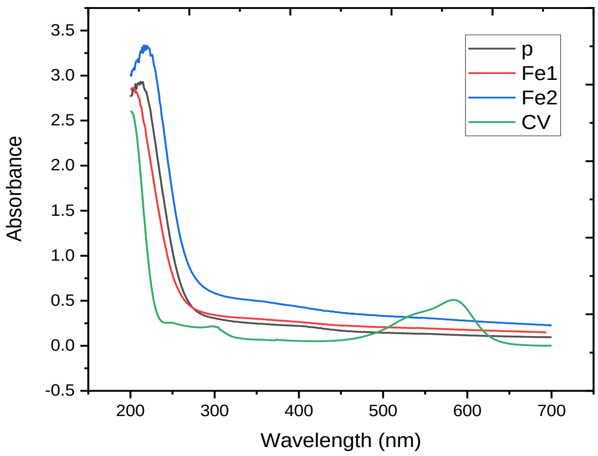


Fig 4.Crystal violet adsorption of PANI,Ferrite,andfe(2.5g,5g,7.5g,10 g)

3.3DC CONDUCTIVITY STUDIES

Current –voltage curve as measured by a for probe method is depicted in figure 5 and 6.The conductivity is calculated and is given in table 2. All the samples exhibit conductivity in the range $10^{-5}Scm^{-1}$. Conductivity of pure pani is 1.2x10 ¯5. By incorporating ferrite into the composite a further improvement in conductivity is observed. As the concentration of ferrite is raised up to 7.5g slight decrease is observed. At high amount of ferrite, decreases conductivity.

Table 2. DC Conductivity of samples

SL No	Samples	Conductivity (Scm^{-1})
1	PANI	1.2×10^{-5}
2	Fe1	1.22×10^{-5}
3	Fe2	1.35×10^{-5}
4	Fe3	1.17×10^{-5}
5	Fe4	1.12×10^{-5}

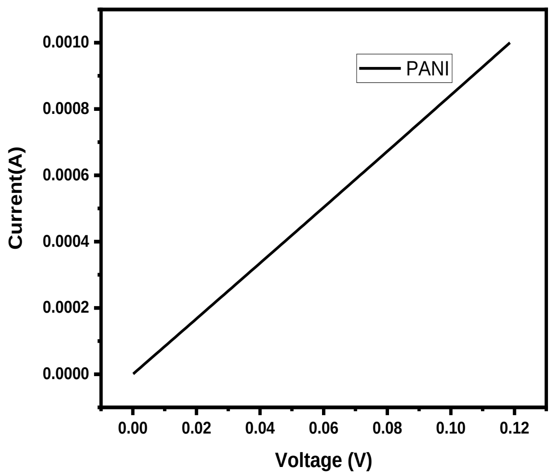


Fig 5. Conductivity of pure PANI

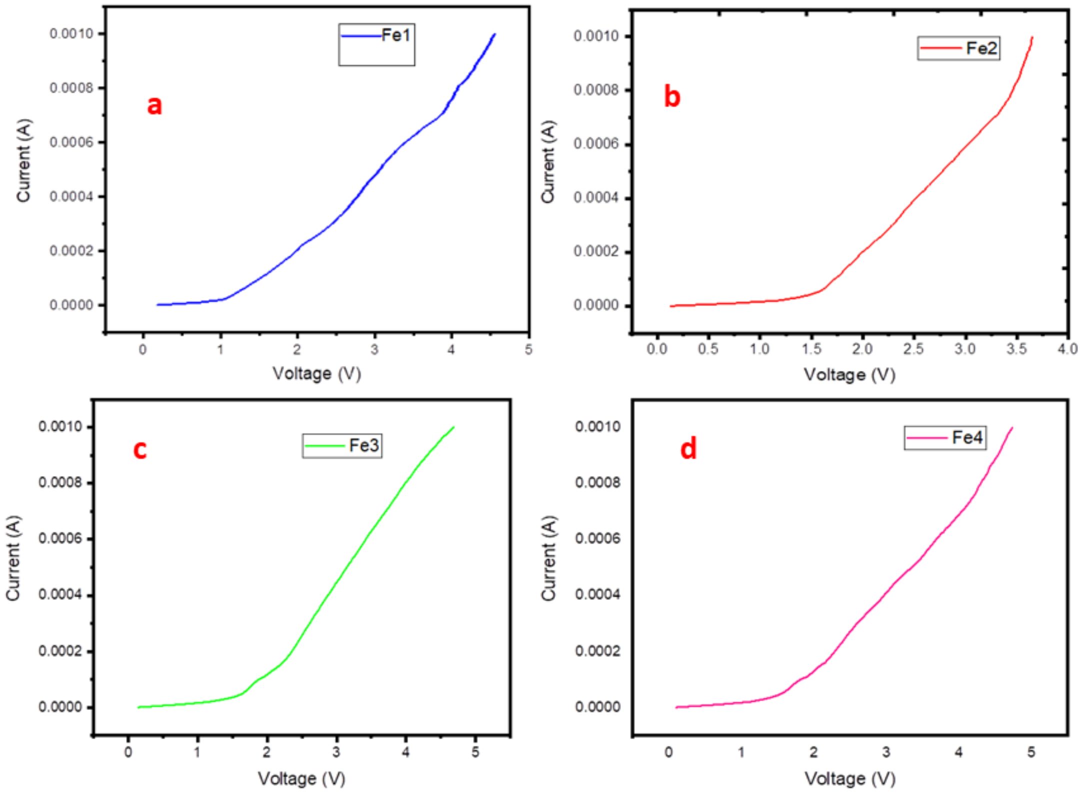


Figure 6: Conductivity of PANI-Ferrite Composite

IV. CONCLUSIONS

In this particular work Bilimbi fruit extract, an easily available natural fruit is used for the synthesis of nickel ferrite, PANI and PANI-ferrite composites. In situ chemical oxidative polymerization is adopted for the synthesis of PANI and PANI-ferrite composites.

XRD studies reveal the complete phase formation of nickel ferrite and also the blending of ferrite with PANI. Crystalline nature of ferrite is retained even after incorporation in PANI matrix. FTIR spectra confirm the presence of PANI in the most conductive emeraldine salt form and its interaction with the ferrite particles in composites.

PANI serves as better adsorbent than composites in the case of dyes such as Malachite green and Crystal violet, where as in the case of phosphate adsorption PANI ferrites composites exhibits good adsorbent characteristics. So natural resources such as Bilimbi fruit extract can be economically utilized for the synthesis and designing of efficient adsorbents for water body treatment.

Electrical studies show that pure PANI is conducting. Incorporation of ferrite into the pani increases the conductivity. At high concentration of ferrite conductivity deceases. At high amount of ferrite the decrease in conductivity may due to agglomeration of ferrite particles in the composite matrix.

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