Surface Modifications of Halloysite Nanotubes by Layered Double Hydroxide for Efficient removal of Dyes from Wastewater

A dissertation thesis submitted to

Chemistry Division

Indian Institute of Science Education and Research (IISER) Pune,

Dr. Homi Bhabha Road,

Pune-411008.

In partial fulfillment of the BS-MS dual degree programme

for the academic year 2016-2017

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(COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH)
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International Collaboration & Publicity Section

No.14-03-03-2016- 17- ICP

March 16, 2017

CERTIFICATE

This is to certify that this Dissertation entitled ***"Surface Modifications of Halloysite Nanotubes by Layered Double Hydroxide for Efficient Removal of Dyes from Waste Water"*** towards the partial fulfilment of the BS-MS (Chemistry) Dual Degree Programme at the Indian Institute of Science Education and Research (IISER), Pune - 411 008 represents original research carried out by **Mr. Santhosh.L** at CSIR-Central Electrochemical Research Institute, Karaikudi under the supervision of **Dr. B. Ramesh Babu, Senior Principal Scientist,** Pollution Control Division during the academic year **2016 - 2017.**

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Declaration

I hereby declare that the matter embodied in the report entitled "**Surface Modifications of Halloysite Nanotubes by Layered Double Hydroxide for Efficient removal of Dyes from Wastewater**" are the results of the investigations carried out by me at the Department of **Pollution control division**, **CSIR- Central Electrochemical Research Institute**, under the supervision of **Dr. B. Ramesh Babu** and the same has not been submitted elsewhere for any other degree.

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ACKNOWLEDGEMENT

I wish to express my sincere gratitude towards my project supervisor, **Dr. B. Ramesh Babu**, Senior Principal Scientist and Head of Pollution Control Division, CSIR-CECRI, Karaikudi for his valuable guidance and constant inspiration throughout the term of this project. Also I would like to thank **Dr. Vaidhyanathan Ramanathan**, Assistant Professor, Department of Chemistry, IISER Pune for critically evaluating my research work. I sincerely thank S. Vahidha Banu, Senior research Fellow for spending her valuable time for guiding me and helping me throughout this project.

I also thank all those who have directly involved or indirectly helped for the successful completion of this Project.

ABSTRACT

In the work, a facile and efficient synthesis of Fe_3O_4@HNT@LDH (FHL) composites has been successfully prepared via a layer-by-layer (LBL) deposition process followed by an insitu growth technique. The Fe_3O_4@HNT@LDH were characterized by XRD (x-ray diffraction), Fourier Transform infrared (FT-IR), Scanning Electron Microscopy (SEM) and surface area measurements. The application of synthesized FHLs for removing the Congo red (CR) from aqueous solution was described. The FHL composites showed strong magnetic response, high removal efficiencies for CR dye and could be simply regenerated by magnetic separation process. Moreover, Incorporation of magnetite particles and LDH with chemically and mechanically stable. Halloysite clay nanotubes dramatically enhanced the surface area. The rapid CR removal and adsorbent sorption efficiency of this system suggests that the FHLs composite are effective and promising materials in the pre-concentration of CR from aqueous solution in the larger volumes of wastewater treatment.

CONTENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

%	Percentage
°C	Degree Celcius
HNT	Halloysite Nano Tube
Conc.	Concentration
CR	Congo Red
FTIR	Fourier transform infrared spectroscopy
H2O	Water
JCDD	Joint Committee on Powder Diffraction Standards
ml	Millilitre
mm	Millimeter
BET	Brunauer-Emmett-Teller
SEM	Scanning Electron Microscopy
XRD	X Ray Diffraction
Ph	Potential of Hydrogen
ppm	Parts per million
UV	Ultra Violet
Nm	Nano Meter
Min	Minute
FHL	Fe_3O_4@HNT@LDH

1.INTRODUCTION

1.1 GENERAL

One of the major differences between the developed countries and the developing countries is the industrialization. Among different types of industries, textile industry is one of the major type of industry contributing more in terms of shelter, economy and environment. The wastewaters discharged from textile industry processes generally contain dyes with high intensity of colour and toxicity. This wastewater causes major environmental hazards and drinking water problems due to the presence of toxic organic, inorganic, acids, bases like contaminants and dissolved solids and colour. Because of toxicological and aesthetical reasons, discharging the dyes into the open environment is not advisable as it leads to the environmental degradation by reducing the quality of the receiving streams. It also disturbs the ecological balance disrupting the food chain contributors. These coloured dye compounds are not only aesthetically unpleasant to the environment but also blocks the sunlight into the streams reducing the natural photosynthetic activity.

Among various different coloured dye, Congo Red (CR) is one of the primary anionic acid dye which is most commonly used in the textile industries due to its strong affinity towards cellulose fibres and high solubility nature. [5] found that the Congo Red dye is a cognate of benzidine and napthoic acid which gets metabolized to form products of carcinogenic nature [4].It's been also found that its a mutagenic which leads to reproductive problems, causes eye, skin and gastrointestinal irritations when it is exposed. Also [2] says it also affects the blood clotting capacity and leads to respiratory problems as well. These said problems leads to the removal of such dyes from the environment as primary one.

There are different types of physical, chemical and biological dye removal techniques from the wastewater such as coagulation, flocculation, adsorption, bio-sorption, advanced oxidation, ozonation, biodegradation, extraction, membrane filtration etc. was shown by [7] has a opinion that among all these treatment techniques, Adsorption technique stands out at the top due to its effective separation technique, less capital cost, design simplicity, comfort of operation and maintenance and callous to toxic contaminants. [14].The morphological phase and the interfacial properties of the nanocomposites shows better properties than the conventional composites. Normally the Clay have a two types of layers namely silica tetrahedral and alumina octahedral sheets which can be used to remove dyes from wastewater with suitable surface modification.

1.2 ADSORPTION

The adhesion or retaining of molecules of gas, liquid or dissolved solids to the surface is known as adsorption. The material that adsorbs onto its surface is called adsorbate and the material on which gets adsorbed is called adsorbent. In this process, a film of the adsorbate is laid on the surface of the adsorbent. It is different from absorption, where the molecules permeate is dissolved by a liquid or solid. The term ‘sorption’ encompasses both adsorption and absorption, whereas the reverse of adsorption is the desorption.

Just like the surface tension, the adsorption process is a consequence of energy on the surface. In a bulk material, the requirements of bonding (ionic, covalent or metallic) constituent atoms of a material are replaced by other atoms present in the material. Hence, there will be a disequilibrium of inward attraction of forces from the free valances at the surface (ie., atoms of the surface are not fully surrounded by the other adsorbent atoms) have the characteristic to attract and clutch the molecules onto its surface when they come into contact. The adsorption process can be classified into physisorption (characteristic of van der Waals forces) and chemisorptions (characteristic of covalent bonding).

The physisorption can be characterized by low heats and is generally reversible in nature. It is also known as “Ideal adsorption”. The chemisorptions can be characterized by high heats which is generally irreversible in nature. It is sometimes known as “Activated adsorption”.

Some of the factors that influence the process adsorption and its efficiency are

- pH
- Temperature

- Adsorbate solubility
- Presence of other solutes
- Surface area
- Nature of the adsorbent
- Active carbons

Some of the common types of adsorbents are Activated Alumina, Polymeric resins, Ion exchange resins etc., At present, there is a burgeoning interest in using low – cost raw materials which are also available commercially from the market for the adsorption of contaminants from the wastewater. A broad range of materials like Activated carbon, rice husk, coconut husk, papaya seeds, fly ash, wood ash, holly oak etc., are used as substitute to luxury adsorbents.

Some of the characteristics of the adsorbents are thermal stability, surface area, density, size, pore volume, abrasion resistance, sieve analysis, pore size, Ash percent, etc.,

Adsorption characteristic can be seen in many natural systems including physical, chemical and biological. Adsorption is widely used in the various industrial applications like for the removal of colour from textile industries, chemical and fertilizer industries, sugar industry etc. Its capacity goes even upto removing trihalomethanes which are toxic and carcinogenic.

"Adsorption process can operate independently for removal of colour. It has the capability of degrading organic compounds that are chemically and biologically stable"was said by [7] The adsorption process is influenced by some parameters such as concentration of the dye, dosage of adsorbent, time of contact, pH and temperature affect the removal efficiency of dyes from the effluent.

1.3 ADVANTAGES OF ADSORPTION

The adsorption is one of the desired process used for the removal of dye from the effluent than the conventional treatment methods due to its high adeptness and performance, simple and quick ease of operation with flexibility in the design. Furthermore, the adsorbent which is used can be recouped and reused for the other processes. [6]

According to the [15] observations, due to the low capital cost of the setup and the easy availability of the adsorbent, the adsorption process is the most common method adopted in the removal of the textile industries contaminants from the wastewater. From the [16] point of view Adsorption is free from harming the environment causing no problems by not even generating sludge.[5] “The effluent produced after adsorption is generally high quality” was stated by Nandi et al.[4]. The pollutant present in the wastewater gets sticked to the adsorbent surface due to the synergy between the adsorbent and the adsorbate which can also be definitive by the physical properties and the adsorptive characteristics was shown [3]

When the methods treating dye effluents are compared based on its simplicity and feasibility, physicochemical methods offers plenty of advantages due to its wide range of applicability. And moreover the adsorbent capacities can be easily embellished by some facile and fiscal methods.

1.4 ADSORBENT

Nanocomposites are an example of applications in the real time rapidly growing industrialization world. The composites materials like Carbon nanotubes, metals, nano particles, minerals etc., Nanocomposites standout from the conventional composites due to its effective morphological phase and its interfacial properties. Due to this, nanostructured organic-inorganic composites have attracting great interest from both research and its applications and even some are available in the commercial market.

Each year the need for absorbent clay minerals is increasing. The main advantage of the absorbent clay minerals are it is being used all over the world due to its diverse application in the industries. The Clay mineral has layered sheets of silica tetrahedral and alumina octahedral sheets where silica is the dominant constituent of clay and alumina being essential, as well. In the silica tetrahedral sheet, the repeating units of composition Si_4O_{10} consists of a hexagonal network formed by the SiO4 groups linked together. Whereas in the alumina octahedral sheet, it consists of octahedral coordination between the oxygen or hydroxyl’s and the aluminium atoms such that they are placed in the equidistant manner. Hence, in the Clay mineral, both the layers share their apex oxygen within themselves. The new class of Nanocomposites can be made with the help of Montmorillonite which is a type of clay consists of magnesium aluminium silicate."The rheological benefits of the montmorillonite can be due to its higher surface area of 750m^2/g and the aspect ratio of (70 – 150)" was found by [17]. Halloysite nanotube (HNTs), a clay mineral which has one-dimensional tubular structure, has interesting application in material science due to its high adsorption capacity, tunable surface chemistry and environmental friendly properties. [11]

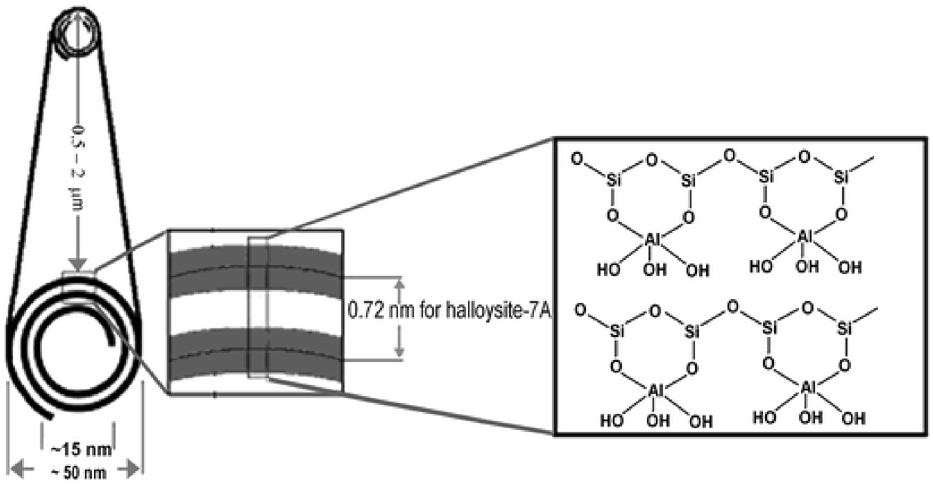


Fig. 1 Schematic representation of halloysite-7 Å <u>nanotubes</u> [Image source- 12]

1.5ADSORBATE

1.5.1 CONGO RED

Congo red (CR) is a dye which is emulsifiable to a greater extent in the water. It belongs to the anionic group and has a strong inclination towards the cellulose which makes it a wonderful prospect to be used in the textile industries. It is a connate of benzidine and napthoic acid and degrades to form the pernicious products [10] It's been also found that its a mutagenic which leads to reproductive problems, causes eye, skin and gastrointestinal irritations when it is exposed. Also [17] says it also affects the blood clotting capacity and leads to respiratory problems as well.[11]These said problems leads to the removal of such dyes from the environment as primary one. The chemical formula of CR is $C_{32}H_{22}N_6Na_2O_6S_2$ with colour Index 22120 and molecular weight of 696.663g.mol^{-1} (see fig. 2.). [18] found that the sodium salts present in the Congo Red which is the reason for the dying cotton. [6]. When the inorganic acids are present, there is a transformation of color from red to blue which is caused by the reverberation of vitalized canonical structures. [3].

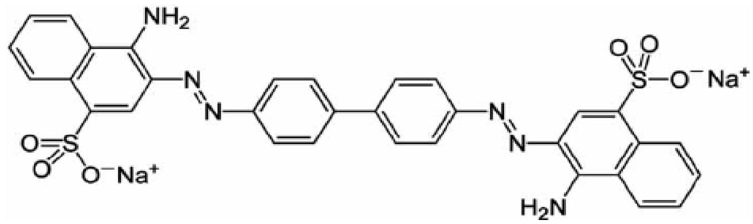


Fig 2: Chemical structure of Congo red dye [Image source-13]

1.5.2 NANOCOMPOSITES FOR ADSORPTION

The materials that we can use in the Adsorption can be classified into two types: Organic materials like Polymers and elastomers which carry advantages like its flexible and elastic nature, less weight and are soft in nature which make them not difficult to make use of and progress despite having a poor electronic properties (e.g. dielectric constant, conductivity, etc.), and prudent optical properties (e.g. refractive index) compared to their inorganic counterparts. The second type is the Inorganic materials such as glasses, ceramics, metals and some natural clays have high adsorption capacity, hardness, firmness, and thermal resistance; but are much more difficult to process into films, coatings, fibers, or extruded shapes. When the organic material with flexibility is combined with the adsorptive inorganic materials, we attain a product with favourable properties in a single combined system. Nanocomposites are composites that have at least one characteristic scale in the order of nanometers.

Nanocomposites are an example of applications in the real time rapidly growing industrialization world. The composites materials like Carbon nanotubes, metals, nano particles, minerals etc., Nanocomposites standout from the conventional composites due to its effective morphological phase and its interfacial properties. Due to this, nanostructured organic-inorganic composites have attracting great interest from both research and its applications and even some are available in the commercial market. From the discussion of [13] “Nanocomposites couple the most eloquent properties of their components such as low processing temperature (polymeric), thermal stability (metal oxides) and high transparency.

2. METHODS

2.1 MATERIALS

2.1.1 ADSORBENT

The morphology of Halloysite nanoclay is a tube like structure. It's surface hydroxyl groups has lower stability than the inner hydroxyl groups. Its low electrical, strong hydrogen interactions and thermal conductivity allows the Halloysite to be used in various applications.

Composition: Molecular Weight = 258.16 gm

Aluminium 20.91 % Al 39.51 % Al_2O_3

Silicon 21.77 % Si 46.56 % SiO_2

Hydrogen 1.57 % H 13.97 % H_2O

Oxygen 55.79 % O

2.1.2 ADSORBATE

An anionic dye, Congo Red (CR), having molecular formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol) was chosen as adsorbate. Congo red dye was purchased from Sigma Aldrich chemical company. The Congo red is a red colloidal solution and organic solvents such as ethanol is better for solubility. Because of the known strong adsorption on to solids, the Congo red dye was chosen for this study. The dye stock solution was prepared by mixing accurately Congo red in distilled water with respect to the concentration of 100 mg L^{-1}.

2.1.3 PREPARATION OF DYE SOLUTION

The dye Congo red (C.I name = Direct Red 28, C.I No. = 22120, Chemical formula = $C_{32}H_{22}N_6O_6S_2Na_2$, Formula weight = 696.65) is supplied by Sigma Aldrich Chemicals, India. To prepare the stock solution (1000 ppm) a precise quantity of dye are diluted with double distilled water.

2.2 EXPERIMENT

2.2.1 Synthesis of HNT@ Fe_3O_4

1g HNT in 180 ml of FeCl3.6H2O (4.72)g & FeCl2.4H2O (2.1)g at 60°C under Nitrogen atmosphere. Then NH3.H2O added dropwise. And the PH should be maintained between 9-11 under 70°C for 4 hours. We have to centrifuge by washing 3 times with d.H2O and kept in oven at 60°C till it gets dried.

2.2.2 Synthesis of HNTs@AlOOH

5.8 g of solid boehmite was dispersed in 107 mL of deionized water, and solution was mixed for 1 hour at 85°C. then HNO3 (0.0095L, 1.0 M) was slowly added dropwise, and the mixture was mixed using a magnetic pellet for a further period of 6 hours. After cooling to the solution under room temperature the AlOOH primer sol was obtained. After that, the AlOOH primer sol which we have obtained will be added with the HNTs with intense stirring for 1 hour. The products were cooled by precipitating and washing repeatedly with ethanol, followed by keeping it under room temperature for 30 min. The whole process dispersion, withdrawing, drying was repeated multiple cycle until the product contained no white AlOOH by centrifugation. The resulting material, HNTs@AlOOH, was kept in a vacuum at 35 °C for 24 h.

2.2.3 Synthesis of HNT@ Fe_3O_4 @LDH

0.3 g of HNTs@AlOOH was supplemented to a solution containing 0.005 mol +Mg(NO3)2·6H2O, 0.04 mol urea and 200 mL of deionized water. After that, the mixture was heated to 80 °C and constantly stirred for 24 hour, and then it was maintained under room temperature. Finally, HNT@Fe3O4@MgAl−LDH was isolated by centrifuging and rinsing repeatedly with ethanol.

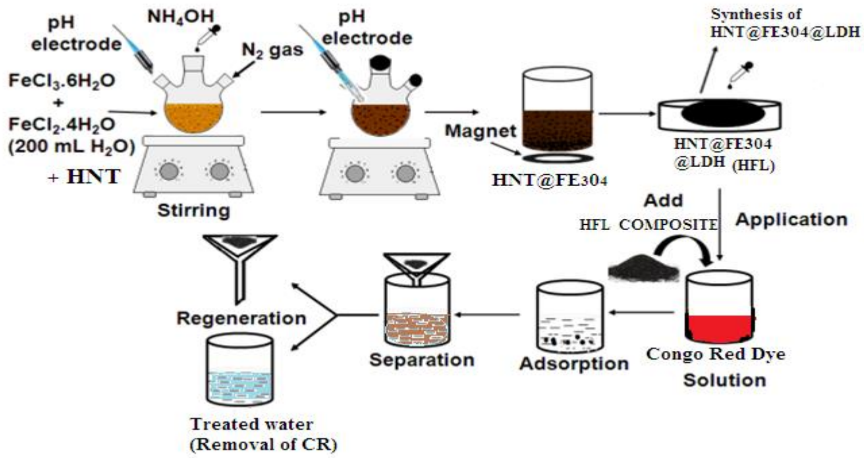


Fig 3. Overall experimental diagram

2.3 ADSORPTION STUDIES

The batch equilibrium technique was attempted in adsorption for HNT@LDH. These studies were carried out by varying initial concentrations of the dye and pH values and also varying times of contact. At initial concentration of 100 mg/L, the effect of time of contact was in the range between 5-120 min for the adsorption capacity of modified HNT.

For the degradation studies, by diluting the stock solution of 1000 mg L^{-1} five sets of 25 mL solutions of Congo Red (CR) dye of concentration 100 mg L^{-1} were obtained. Congo Red (CR) dye of different concentrations of 50, 75, 100, 150 and 200ppm were prepared by this dilution formula

Required ppm* required volume/ Stock.

In a adsorption experiment, 0.01 g of the synthesized nanocomposites under stirring were added to aqueous solution of 25 mL, and under UV-vis spectroscopy at 496nm adsorption spectra were recorded at varying intervals of 5, 10, 15, 20, 30, 60, 120minutes respectively to monitor the degradation process.

2.3.1 EFFECT OF CONTACT TIME

In a conical flask 100ml of dye solution will be placed on the shaker with the concentration of adsorbent (10mg/L). The concentration of Dye is predicted using a spectrophotometer at the wavelength corresponding to maximum absorbance, λmax (Jasco UV/Vis-550). With the help of a micropipette at fixed time intervals the samples will be taken from the shaker (Deneb instruments) the dye solution and the adsorbent will be separated. Then, the absorbance of solution is measured until equilibrium reaches the concentration of the dye is measured after 5, 10, 15, 20, 30, 60, 120 minutes.

2.4 CHARACTERISATION METHOD

2.4.1 XRD ANALYSIS

X-ray diffraction (XRD) is a powerful analytical technique for characterizing and determining the unknown crystalline materials. It offers different kinds of data on the structures, phases of the crystal orientations such as average grain size, purity, crystalline, strain, and crystal defects. When the monochromatic beam of X – rays are scattered at certain angles from set places, there is a X-ray diffraction peaks due to its interference. The distribution of the atoms in the lattice can be found from the peak intensities.

ADVANTAGES OF XRD ANALYSIS

- The crystalline nature of an unknown mineral can be identified or quantified.
- The average bulk composition samples can be used for the analysis of crystalline size, strain etc.,
- Less quantity of sample is enough
- Results are direct

2.4.2 SEM ANALYSIS

The scanning electron microscope (SEM) uses a concentrated aimed ray of high-energy electrons to produce an image of the sample including its topography, morphology, chemistry, grains orientation, composition, and crystalline structure and orientation of materials making up the sample. A 2-dimensional image data is produced are collected which displays spatial variations over a selected area of the surface of the sample. Areas for magnification is between 1 cm to 5 microns in width using conventional SEM techniques. This approach is used to determine chemical compositions, crystalline structure, and crystal orientations.

2.4.3 BET ANALYSIS

The evaluation of materials for a specific surface area by nitrogen multilayer adsorption can be done by BET analysis using a fully automated analyser. The technique used to evaluate external area and pore area to find the total specific area in terms of m2/g resulting information regarding the surface porosity and particle size in various applications.

To determine the specific surface area the macroporous and mesoporous materials,the external surface area along with area distribution and pore volume that characterise porosity below the effective range of mercury.

2.4.4 FTIR ANALYSIS

A analytical technique which measures the absorption of infrared radiation by material vs wavelength for organic and inoraganic materials was carried out by Fourier Transform-Infrared Spectroscopy (FTIR). The energy difference between lower and the excited vibrational state when a material is irradiated with infrared radiation absorbed by the material are characteristic of its molecular structure. The signal obtained using a detector must be analyzed to get single- beam infrared spectrum using Fourier transform. The collection of sample information can be done without any harm to the sample with high speed and the measurement of the sample with high precision.

3. RESULTS AND DISCUSSION

3.1STRUCTURE AND MORPHOLOGY OF ADSORBENT:

The XRD patterns of HNT, HNT-$Fe_3O_4$and HNT-Fe_3O_4@LDH. The diffraction peaks that HNT and HNT-Fe_3O_4@LDH show are in good agreement with the characteristic peaks of the standard compound Halloysite-7 Å (JCPDS Card No. 29-1487) and Mg 0.667 Al 0.33 (OH) 2 (CO 3) 0.167 (H 2 O) 0.5 (JCPDS Card No.89-0460). Compared with that of HNT, XRD patterns of HNT-Fe3O4 and HNT- Fe_3O_4@LDH display relatively strong diffraction peaks at 2θ values of 12.3°, 20.2°, 30.1°, 35.9°, 43.6°, 57.5° and 62.8°,with planar values (001),(002),(220),(311),(400),(511),(440) which is consistent with the standard XRD data for the magnetite phase(JCPDS No. 19-062) After the in situ growth process, the XRD pattern of the resulting HNTs- Fe_3O_4@LDH composites exhibits superimposition of reflections of a HNTs phase and a LDH phase. The diffraction peaks for the (003), (006), (009), (015) and (018) crystal planes are clearly observed, indicating the well-formed crystalline layered, demonstrating the successful growth of LDH crystallization on the modified HNTs.

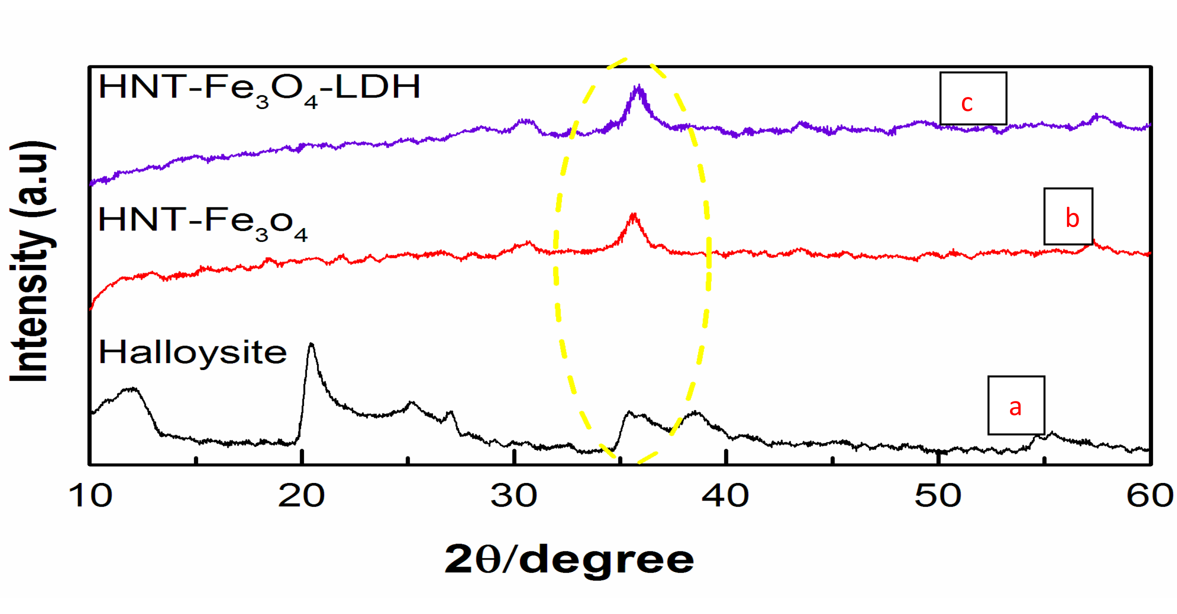


Fig 4: XRD a) HNT b) HNT@Fe3O4 c) HNT@Fe3O4@LDH

By using the SEM and EDX analysis the morphologies of HNT, HNT-Fe3O4 can be observed. We can really observe the difference between raw HNT and modified HNT by noting that no nanoparticles are observed on the surface of raw HNT whereas many nanoparticles are uniformly fixed on the surface or in the lumen of HNT in HNT-Fe_3O_4 The **fig5.c** clearly demonstrated that lots of flower petals like architectures with a high crystallinity quality were synthesized.

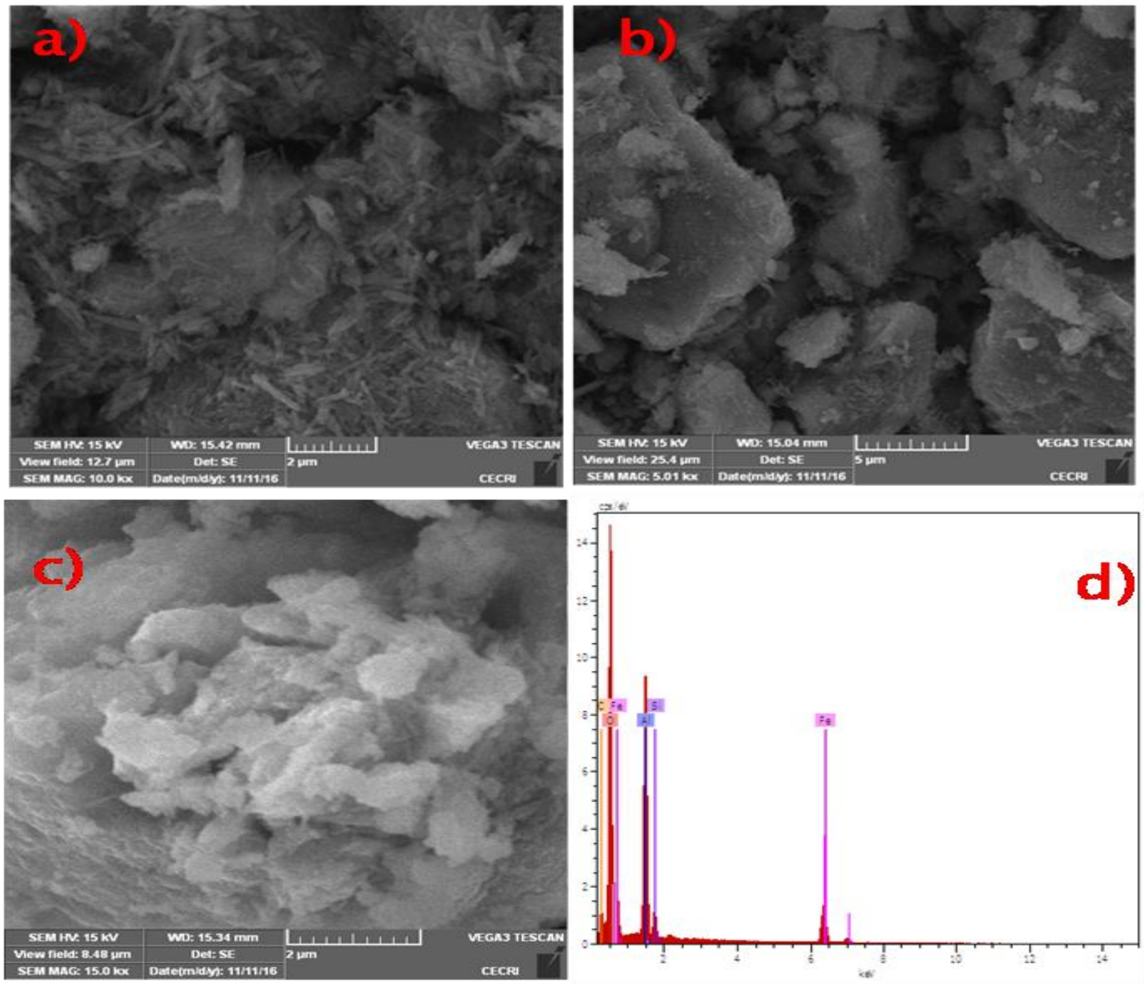


Fig 5: SEM a)HNT b)HNT@Fe3O4 c) HNT@Fe3O4@LDH d) EDAX for HNT@Fe3O4@LDH

HNT, HNT –Fe_3O_4 nanoparticles and HNT-Fe_3O_4 @LDH layers, as well as their interactions were characterized by FTIR spectra **(Fig.6).** Several new adsorption peaks were appeared at 1260—1530, 640—660 and 420 cm –1 when compared to pristine HNT, HNT-$Fe_3O_4$and HNT-Fe_3O_4 @LDH. It indicates the interaction between iron oxide and HNT because of Fe—O stretching. For HNT-Fe_3O_4@LDH, the peaks at around 1722 cm –1 assigned to C=O stretching vibrations. The peaks were superpositioned between the LDH phase and two substrates due to that HNT characteristic band not clearly observed.

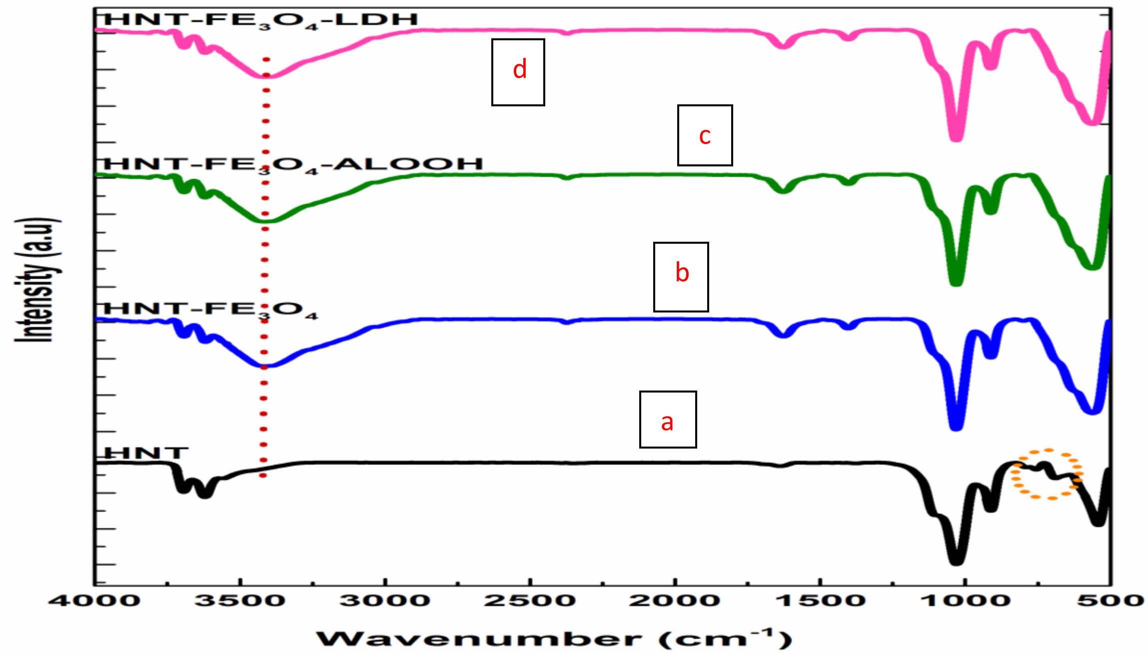


Fig 6: FTIR a) HNT b) HNT@Fe3O4 c) HNT@Fe3O4@ALOOH d) HNT@Fe3O4@LDH

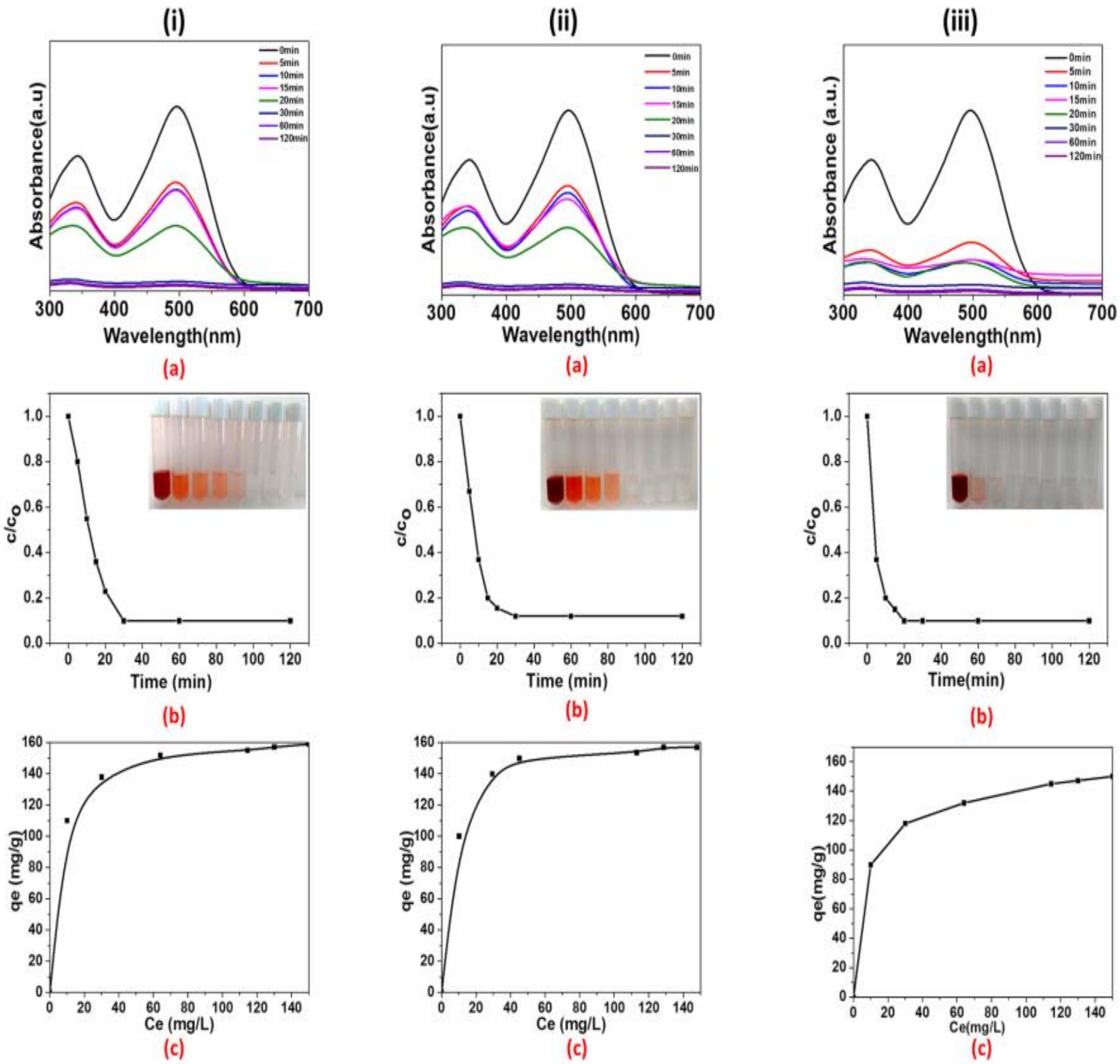
3.2 ADSORPTION KINETICS AND ISOTHERMS:

The performance of FE3O4@HNT@LDH (FHL) as adsorbent was measured through the removal of Congo red dye in an aqueous solution. The initial concentration of CR dye in water is 90 mg L^{-1}. To estimate the adsorption process of CR using nanocomposites at different time interval UV-vis spectroscopy was used. UV-vis absorption spectra of aqueous CR dye in the presence of nanocomposites at different time interval were provided in Fig. 6 (i),(ii),(iii): (a). CR dye alone gives two characteristic absorption peaks at 350 and 496 nm, which corresponds to π-π^* transition of N-H and π-π^* transition of azo groups.[8] The absorption maxima at 496 nm chosen for monitoring the adsorption process with different time duration. After 20 min, the intensities of the peaks become too weak were observed irrespective of the nanocomposites. For comparison pure HNT, HNT-Fe_3O_4 and Fe_3O_4@HNT@LDH (FHL) has been analysed. Whereas, faster removal efficiency was observed in the case of Fe_3O_4@HNT@LDH (FHL) . The intensity of peaks was weakened immediately after 5 min of Fe_3O_4@HNT@LDH (FHL) compared to HNT and HNT-Fe_3O_4. This means that addition of LDH provides very faster removal efficiency over CR dye from an aqueous solution. Over all, the prepared nanocomposites can able to remove 98% of CR dye from an aqueous solution within 120 min under room temperature without adding any additives.

The colour changes occurred during adsorption process was captured using a camera and the images of the original and treated dye solutions over time [inset in the Fig.7 (i), (ii), (iii) (b). The colour of CR dye solution is initially red and intensity of the colour decreased as the adsorption starts and completely fades at the end.

The adsorption isotherms for the removal of CR dye was fitted by the Langmuir isotherm model and provided in Fig.7 (i), (ii), (iii): (c). The maximum adsorption capacities of adsorbent were found to be 256.72 mgg^{-1} (HNT), 289 mgg^{-1} (HNT-Fe_3O_4) and 342.69 mgg^{-1} (HNT-Fe_3O_4-LDH). The correlation coefficient obtained from Langmuir isotherm is $R^2 > 0.99$. This indicates that CR dye adsorption over adsorbent fitted well with Langmuir isotherm model.

Fig.7. **UV** (i), (ii), (iii): (a) UV-vis absorption spectra of the aqueous CR solution (90 mg L-1, 25mL) in the presence of adsorbent at different time intervals; (i)(HNT), (ii)(HNT-Fe_3O_4), (iii)(HNT-Fe_3O_4-LDH): (b) Adsorption rates of the CR on adsorbent [The insets present the photographs of the adsorption progress of HNT, HNT-Fe_3O_4 and Fe_3O_4@HNT@LDH (FHL) over CR]; and (i), (ii), (iii): (c) Adsorption isotherms of CR on HNT, HNT-Fe_3O_4 and Fe_3O_4@HNT@LDH (FHL) .



To understand the adsorption process and its characteristics the kinetics of CR adsorption of Fe_3O_4@HNT@LDH (FHL) was considered. The adsorption process can be described using Pseudo first order and second order and the linear expression is as follows, [1]

$$\ln (q_e-q_t) = \ln q_e - k_1 \quad (1)$$

Where,

q_e and q_t (mg g^{-1}) - amounts of adsorbate adsorbed at equilibrium at time t, respectively.

k_1 - pseudo-first order rate constant.

The pseudo-second order model proposed by [12] on the basis of that the adsorption obeys second order chemisorptions [2]. The linear equation is as follows:

$$t/q_t = 1/k_2 q^2_{e+} t/q_e \quad (2)$$

Pseudo second order was fitted well with experimental data. The R^2 (correlation coefficient) values for pseudo first order models were lesser than the pseudo second order model. For relating the adsorption behaviour of CR on to Fe_3O_4@HNT@LDH (FHL) adsorbent it shows that the pseudo second order model is the most suitable one.

In this study, we have selected two isotherm models Langmuir and Freundlich. The analysis of isotherm data is important step to find suitable model for designing of adsorption system.

The Langmuir isotherm equation is, [3]

$$C_e/q_e = 1/Q_0 b + C\,e/Q_0 \quad (3)$$

The Freundlich isotherm equation is, [4]

$$Q_e = k_F C_e^{1/n} \quad (4)$$

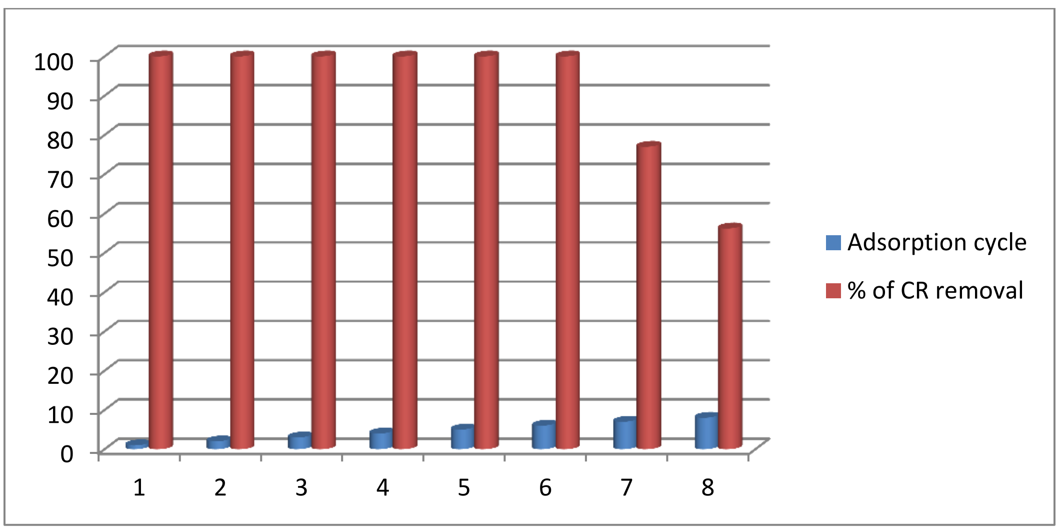
According to the values of R^2 the Langmuir isotherm model was fitted well on the adsorption process of CR.

The BET (Brunauer-Emmett-Teller) surface areas for neat Halloysite and HNT-Fe_3O_4 and FE_3O_4@HNT@LDH (FHL) were found to be 47, 84 and 152 m^2/g, respectively. The maximum adsorption capacity q_m for Halloysite , HNT-Fe_3O_4 and Fe_3O_4@HNT@LDH (FHL) were 256.72 mg g^{-1}, 289 mg g^{-1} and 342.69 mg g^{-1}, respectively. Hence, Langmuir equation better represents the adsorption process.

3.3 REGENERATION STUDY

It is crucial to investigate the reusability of adsorbents for practical applications to address ecological and economic demands for sustainability[8]. In this regard, desorption studies were performed as follows: Initially, 0.05 g of Fe_3O_4@HNT@LDH (FHL) nanocomposites was contacted with 50 mL of CR dye (90 mg/L) at pH 2 over the duration of 6 h. The desorption studies of CR dye loaded Fe_3O_4@HNT@LDH (FHL) nanocomposites were performed by using 50 mL of 0.1 M NaOH solution. Thereafter, the regeneration of active sorption sites was achieved by treating with 2 M HCl solution. The reusability of Fe_3O_4@HNT@LDH (FHL) nanocomposites was scrutinized by using regenerated adsorbents for seven consecutive adsorption-desorption cycles. The verifying experiment found that the removal efficiency (100%) of Fe_3O_4@HNT@LDH (FHL) nanocomposites remained almost same for the first five cycles. After sixth cycles, there was a gradual decrease in removal efficiency for the subsequent seventh (77%) and eighth cycles (56.2%).It is due to the fact that nano composites surface gets saturated after sixth cycles. Hence, we observe that Fe_3O_4@HNT@LDH (FHL) nanocomposites can be successfully reused for the six adsorption cycles with no loss of removal efficiency.

Fig:8 Adsorption cycle



4. CONCLUSION:

In the present investigation, Fe_3O_4@HNT@LDH (FHL) nanocomposites has prepared via a layer-by-layer (LBL) deposition process followed by an insitu growth technique. The prepared nanocomposites has been well characterized through different techniques and also applied as an effective adsorbent for the removal of CR (anionic dye) without adding any additives. XRD studies showed that the resulting HNTs- Fe_3O_4@LDH composites exhibits superimposition of reflections of a HNTs phase and a LDH phase indicating the well-formed crystalline layered, demonstrating the successful growth of LDH crystallization on the modified HNTs. The adsorption isotherm for CR dye removal was fitted well with Langmuir model. The removal efficiency of the adsorbent have been performed through regeneration studies. The removal efficiency was found to be 100% up to fifth cycle. Later, it was found to be 77% and 56.2% for seventh and eightth cycles, respectively .Hence, this could be an effective nanocomposites adsorbent exhibiting exemplary performance for the removal of the Congo red dye (also other toxic dyes) in an industrial effluent.

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