Enhanced Removal of Cr (VI) ions from Industrial Wastewater using Functionalized HNTs

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A thesis submitted in partial fulfillment of the requirements

for the degree of Master of Science in

Chemistry

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2018

FORM TH-4

National University of Sciences & Technology

MS THESIS WORK

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Dedicated
to

My Parents

&

Siblings

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Abbreviations

AAS	Atomic Absorption Spectroscopy
AC	Activated Carbon
AMD	Acid Mine Drainage
APTES	3-Aminopropyltriethoxysilane
As	Arsenic
ASTDR	US Agency for Toxic Substances and Disease Registry
BSE	Back scattered electrons
C_2H_5OH	Ethyl alcohol
Cd	Cadmium
CEC	Cation Exchange Capacity
CMC	Critical Micelle Concentration
CNTs	Carbon Nanotubes
Co	Cobalt
COOH	Carboxylic acid
Cr	Chromium
Cu	Copper
DAF	Dissolved Air Flotation
DEA	Diethanolamine
DETA	Diethylentriamine
EDA	Ethylenediamine
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray Spectroscopy
EEA	European Environment Agency
EF	Electroflotation
$FeCl_3$	Ferric chloride
$FeSO_4$	Ferrous sulphate
f-HNTs	Functionalized Halloysite Nanotubes
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
H	HNTs (pristine)
H1	Amidoxime modified f-HNTs
H2	Hydrazine modified f-HNTs
H_2S	Hydrogen sulphide
H3	Ethylendiamine modified f-HNTs
H4	Diethylenetriamine modified f-HNTs
HDTMA	Hexadecyltrimethylammoniumbromide
Hg	Mercury
HM	Heavy Metals
HNTs	Halloysite Nanotubes (HNTs)
IR	Infrared

K_2CO_3	Potassium carbonate
MCl	Maximum Contaminant Level
MEUF	Micellar Enhanced Ultrafiltration
MF	Macromolecular flocculants
MMT	Montmorillonite
MV	Methyl violet
MWCNTs	Multi-walled carbon nanotubes
NCs	Nanocomposites
NH_2	Amine
NH_2NH_2	Hydrazine
NH_2OH	Hydroxylamine
Ni	Nickel
Nm	Nanometer
NMP	N-Methylpyrollidone
Pb	Lead
PEI	Polyethyleneimine
PEUF	Polymer Enhanced Ultrafiltration
ppm	Parts per million
PPy	Polypyrrole
RO	Reverse Osmosis
SE	Secondary electrons
SEM	Scanning Electron Microscopy
TEA	Triethanolamine
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XRD	X-Ray Diffraction
Zn	Zinc

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Acknowledgements

First, I would like to say my heartfelt thanks to the ALMIGHTY ALLAH who enabled me to accomplish this research, Whomade ways for me from blind alleys and Who cleared every obstacle I faced during my research phase. I am deeply thankful for the ALIMGHTY's blessings and for everything.

I am thankful to my supervisor ***Dr. Sonia Zulfiqar (Tamgha-i-Imtiaz)****who stood by my side through thick and thin, whose guidance and continuous support lead to the completion of this research.Besides, I am grateful to my Co-supervisor* ***Dr. MudassirIqbal*** *whose guidance, support and constructive criticism helped me a lot during my research. He alwayskepthisdooropenforany query regardingmy research work.*
I am also thankful to GEC members ***Dr. AzharMahmood*** *and* ***Dr. Syed RizwanHussain****for always being cooperative with me.*
Iwouldlike toexpressmy sincere gratitude to ***Prof. Dr. Muhammad IlyasSarwar****for providing me all the resources of his Lab in Quaid-i-Azam University and helped me in characterizations of samples. I would like to thank* ***Dr. Muhammad Rafiq*** *for his innovative ideas, guidance and being very supportive and kind.*

I would like to say my Special thanks to my friend ***Jahangeer Ali Patujo****for his sincere help and support and without him, this entire work would not have been turned into reality. Besides, I am grateful to my friends* ***Amaan, Umair, Nasir, Dr. Kashif, Ajmal*** *and all others for their kind support, wishes and prayers.*

I am also thankful to my ***office colleagues*** *for being supportive and kind.*

Lastly Iwouldlike tothank myparentsandmy siblingsfortheiraffection and continuoussupport during hard phase of my research.

Syed Nadeem Ahmad Shah

Abstract

The surface of raw halloysite nanotubes (HNTs) were functionalized with four different kinds of groups to produce four different functionalized halloysite nanotubes (f-HNTs) namely H1, H2, H3 and H4. The prepared f-HNTs were characterized using various techniques like FTIR, XRD, EDS and SEM. FTIR results confirmed that grafting has been accomplished successfully on the external surface of HNTs. SEM and XRD also verified that only outer surface has been modified rather than interlayer or lumen. These f-HNTs were used as adsorbents for Cr (VI) ions uptake present in wastewater. Batch adsorption was employed to optimize conditions like pH, contact time and metal ions concentration. Functionalized HNTs displayed excellent adsorption and adsorption efficiency of more than 90% was noticed within first 10-15 minutes for H1 and H2 and 66% and 58% for H3 and H4 respectively. Maximum % removal falls in broader pH range of 3-5. The model of Langmuir isotherm provided the nearest fit to the data suggesting the monolayer adsorption of Cr (VI) ions. Langmuir isotherm suggests that adsorption process was favorable (R_L between 0 and 1). The adsorption mechanisms involved are quite complicated.Yet possible mechanism involved may be the electrostatic interaction of negatively charged Cr (VI) ions and positively charged amine groups on the surface of f-HNTs. All these results testified that functionalized HNTs may be used as highly efficient and cost-effective adsorbent for wastewater treatment.

Chapter 1

INTRODUCTION

1.1 Heavy metals:

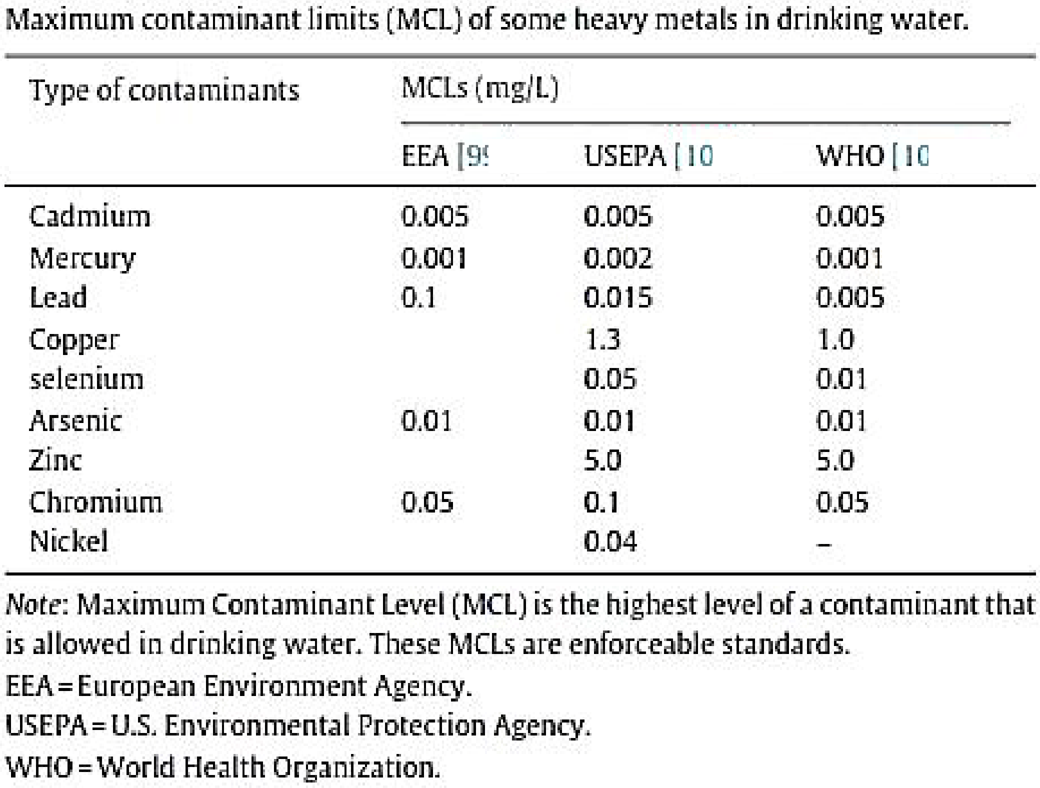
The word “heavy metal” (HM) covers those elements whose specific gravity is five times greater than that of water like lead, arsenic, cadmium and mercury.[1] Among 35 metals which are of ecological concern, 23 of them represent heavy metals. Chromium, arsenic, mercury, leadand cadmiumare rated among 20 most harmful substances as per ATSDR / US EPA.[2]

The release of wastewater from industries containing heavy metals is one of the most sensitive ecological issues worldwide.[3] Industrial wastes that carry heavy metals usually present in water are chromium (Cr), cadmium (Cd), lead (Pb), arsenic (As) and copper (Cu).[4, 5]Due to increased rigorous protocols and laws, HM are treated as priority pollutants. Presence of such poisonous metals in wastewater pose a great threat to the humans as well as environment. Consequently, their extraction from wastewater should be carried out with low cost and eco-friendly adsorbents.[6]

1.2 Heavy metal hazards:

Removal of HM is the need of hour as it results in serious health issues which include disorders of central nervous system, stunted growth and development, organ damage, cancer and sometimes even death[7]. Heavy metals like lead and mercury in wastewater may lead to the phenomena of autoimmunity by which immune system destroys itself on its own.[8, 9]Besides, this may result in multiple diseases like malfunction in nervous system, fetal brain, circulatory system, kidney diseases and rheumatoid arthritis [10].Heavy metals in excessive amounts may cause permanent damage to brain.The MCL standards of heavy metals as per WHO, USEPA, EEA are given in the following Table 1.1[11, 12]

Table 1.1 MCL standards[11]



Maximum contaminant limits (MCL) of some heavy metals in drinking water.

Type of contaminants	MCLs (mg/L)		
	EEA [9	USEPA [10	WHO [10
Cadmium	0.005	0.005	0.005
Mercury	0.001	0.002	0.001
Lead	0.1	0.015	0.005
Copper		1.3	1.0
selenium		0.05	0.01
Arsenic	0.01	0.01	0.01
Zinc		5.0	5.0
Chromium	0.05	0.1	0.05
Nickel		0.04	–

Note: Maximum Contaminant Level (MCL) is the highest level of a contaminant that is allowed in drinking water. These MCLs are enforceable standards.
EEA = European Environment Agency.
USEPA = U.S. Environmental Protection Agency.
WHO = World Health Organization.

The hazards of various metals are given below:

Chromium (Cr):

Chromium usually exists in Cr (VI) and Cr (III) oxidation states. Nevertheless, Cr (VI) ions are 500 times more dangerous as compared to Cr (III) [13]. Due to this reason, Cr (VI) ions stand out among the most deadly pollutant. Cr (VI) ions present in wastewater are coming from variety of sources like tanneries, textile industries, photography, dyeing, batteries, paints, plastics and nuclear plants. [14]Because of its non-biodegradable property, it intrudes the food chain and subsequently led to many health issues like skin cancer, damage to kidneys and liver, vomiting, stunted breathing.[15] Cr (VI) ions from the industrial discharges have the concentration range from 15-300 mgL^{-1}.In case of tanneries waste, Cr (VI) ions level may go up 1300-2500 mg/L in extreme cases. MCL value in case of Cr (VI) as per USEPA and WHO is 0.1 mg/L and 0.05 mg/L for surface water and drinking water respectively. (EPA, 1990; WHO, 2006).[16]

Cadmium (Cd)

Cadmium (Cd), a trace metal present in wastewater comes from many factories like fertilizer industries, welding, plastics, Ni and Cd batteries. Besides, electroplating industries generate cadmium in considerable proportions. The rust in water pipes is also the source of cadmium in water.It is to be noted that the epidemic of Itai-Itai that spread in Japan is also attributed to the presence of cadmium. Continuous exposure to cadmium may result in liver and renal damage, seizures, diarrhea, cardiovascular problems, muscle spasms, vomiting, lower RBC count and osteoporosis.[17]Cadmium halts the enzymatic activity in humans by changing their stereo-structure leading to multiple issues. It is also reported that around 8% pulmonary tumor is caused by cadmium.MCL value in case of Cd as per USEPA and WHO is 0.005 mg/L.[2, 11]

Mercury (Hg)

Naturally, mercury (Hg) is present in some of the ores. However, the chief sources of industrial origin are batteries, pharmaceutical and electronics industries, dental fillings, photography, alloy based plants and power plants of coal.[18] Mercury present in wastewater may also be taken up by aquatic animals like fish, whales etc. Being a neurotoxin, it leaves detrimental effects on the central nervous system. It damages neonate’s brain by interfering blood-brain barrier. This results in mental retardation which in case of adults leads to Alzheimer, Parkinson and other diseases. The level of damage caused by methyl mercury can be imagined that if just a single dose of itpenetrates across skin may even result in death. Owing to such risks, USEPA has set MCL value for mercury to be 2 ppb. [2]

Arsenic (As)

Arsenic (As) poses a great threat to many countries like USA, India, Thailand, Vietnam, Nepal, Bangladesh and Canada. It causes widespread “arsenic poisoning” and various diseases may outbreak like skin and bladder cancer, pulmonary cancer.[19] Industrial processes from where the arsenic comes are casting and smelting of various metals and combustion of fossil fuels. Indications for arsenic poisoning are diarrhea, muscle spasms, speech disorders, vomiting, restlessness, intense stomach pain and death. Due to these prevalent risks, arsenic tops in the list of 20 most harmful substances as per ATSDR/USEPA. MCL value for As as per USEPA and WHO is 0.01 mg/L.[2, 11]

Copper (Cu)

Although presence of copper (Cu) in trace amounts serves a vital role in humans to maintain sound health.[20] Nevertheless, its uptake beyond nominal concentration may be hazardous. Copper contamination in water may come from electrical factories. It may cause vomiting, convulsions, diarrhea, muscular cramps and atrophy. MCL value for Cu as per USEPA and WHO is 1.3 mg/L and 1.0 mg/L respectively.[2, 11]

Lead (Pb)

Lead is considered as the most dangerous pollutant present in industrial wastewater. Its presence may have various origins like batteries, petroleum, mining and paint factories.[21-23]It may concentrates in the body of humans in the form of neurotoxin leading towards renal failure. Chronic lead poisoning may result inserious damage to liver, genital system and kidneys. Besides, it is also noted that presence of lead in children may induce mental retardation.The presence of lead in water may cause vertigo, headache, restlessness, delirium, muscle atrophy, anemia and renal failure. Due to such risks, lead (Pb) is rated among 20 most harmful substances as per ATSDR /USEPA. MCL value for Pb as per USEPA and WHO is 0.015 mg/L and 0.005 mg/L respectively.[2]

Zinc (Zn)

Zinc as a trace metal plays an important role in living organisms by initiating many enzymatic reactions. Nevertheless, its excess level may be hazardous since it possesses carcinogenic properties. It may lead to many health concerns like anemia, cramps, vomiting and skin itching. MCL value for zinc as per WHO is 5.0 mg/L.[11]

Cobalt (Co)

Cobalt is an essential metal which has both positive and negative effects upon human health. On one side where it plays a vital role in the production of vitamin B12, its excess amount may have disastrous consequences on the other side.[24]Application of Co (II) in electroplating industries, batteries, pigments, electronics manufacturing factories, petroleum and nuclear plants may discharge cobalt in significant proportions in wastewater. This may lead to multiple health issues like skin diseases, diarrhea, asthma, vomiting, weight loss and malfunctioning of kidneys. MCL value for Co is 0.01 mg/L.

Nickel (Ni)

The chief sources of presence of nickel in industrial wastewater are batteries, electroplating factories andalloy based manufacturing units.[25]It causes skin allergy, pulmonary problems and renal failure. Besides, it is reported as a potent carcinogen. Due to this reason, WHO has set the MCL value for nickel to be 2 mg/L in industrial wastewater and 0.1 mg/L in drinking water. Table 1.2 lists the effects of HM upon human health along with their MCL values: [6]

Table 1.2 HM Effects with MCL values [6]

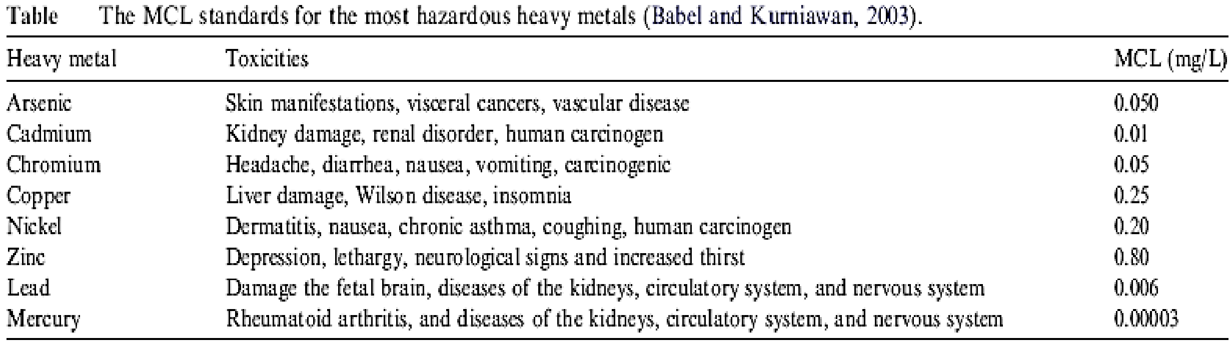


Table The MCL standards for the most hazardous heavy metals (Babel and Kurniawan, 2003).

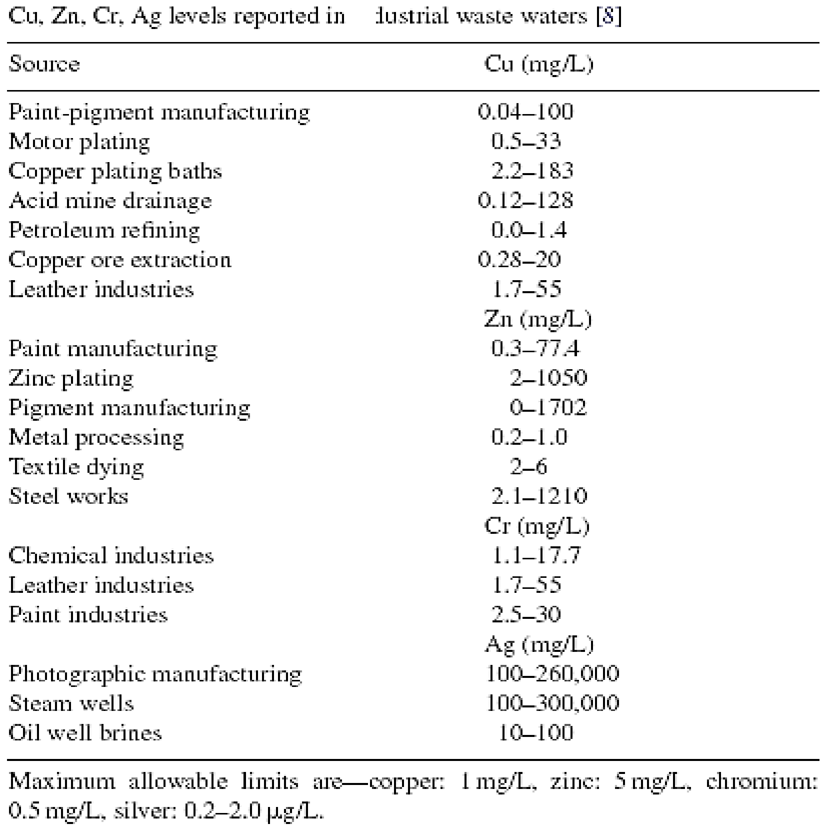
Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

1.3 Wastewater sources:

HM removal from wastewater is of great concern because of their non-biodegradable nature. With the continuous expansion of industries like steel and electroplating factories,batteries, fertilizers manufacturing plants, tanneries, pigments and ink related factories, petroleum refining,oil spills,[21-23]heavy metals are progressively released into the surroundings by various direct or indirect means, especially in developing countries like Pakistan. Heavy metals are not degradable biologically, therefore they remain present in the soft tissues of living organisms.[26]These heavy metals pose a great threat as they possess carcinogenic properties.[20]HM usually present in wastewater are Cu, Cd, Cr, Hg, Zn and Ni [6]

Table 1.3 lists the sources of HM present in wastewater along with their MCL levels:[27]

Table 1.3 Wastewater sources [27]



Cu, Zn, Cr, Ag levels reported in dustrial waste waters [8]

Source	Cu (mg/L)
Paint-pigment manufacturing	0.04–100
Motor plating	0.5–33
Copper plating baths	2.2–183
Acid mine drainage	0.12–128
Petroleum refining	0.0–1.4
Copper ore extraction	0.28–20
Leather industries	1.7–55
	Zn (mg/L)
Paint manufacturing	0.3–77.4
Zinc plating	2–1050
Pigment manufacturing	0–1702
Metal processing	0.2–1.0
Textile dying	2–6
Steel works	2.1–1210
	Cr (mg/L)
Chemical industries	1.1–17.7
Leather industries	1.7–55
Paint industries	2.5–30
	Ag (mg/L)
Photographic manufacturing	100–260,000
Steam wells	100–300,000
Oil well brines	10–100

Maximum allowable limits are—copper: 1 mg/L, zinc: 5 mg/L, chromium: 0.5 mg/L, silver: 0.2–2.0 µg/L.

1.4 Methods for wastewater treatment:

Various techniques and approaches have been designed for the enhanced elimination of heavy metals which are precipitation, ion-exchange, electrochemical method, flotation, flocculation, coagulation, membrane filtration technique, osmosis and adsorption.[27-32]

1.4.1 Precipitation:

The most usual technique which is used in wastewater treatment is precipitation since it is comparatively simple and gives high yield. By the addition of precipitating reagent into the water containing heavy metal ions, insoluble precipitates are produced. This may be removed either by sedimentation or by filtration. Both cations and anions can be precipitated out by this process. Generally, precipitation process is of two kinds:

1. Hydroxide precipitation
2. Sulfide precipitation

1.4.1.1 Hydroxide precipitation

A simple and cost-effective procedure used for wastewater treatment involves hydroxide precipitation. In this method, alkaline agent is added so as to increase the pH which subsequently leads to decreased solvation of heavy metal ions. Thus, metal hydroxides will precipitate out which may be separated via flocculation or sedimentation. Although various kinds of hydroxides may be used for the process of precipitation, usually lime or caustic soda is used.

Chen et al., 2009b employed fly ash so as to boost lime precipitation.[33] The use of fly ash in addition to lime results in larger particle size and more precipitates that considerably enhanced the HM removal. Nevertheless, metal concentration of zinc, copper, lead and chromium in wastewater was decreased from 100 mg/L to 0.45, 0.14, 0.03 and 0.08 respectively.Mirbagheri and Hosseini (2005) reported the extraction of Cr (VI) and Cu (II) ions from water by the process of hydroxide precipitation involving lime and sodium hydroxide.[34] Cr (VI) was transformed into Cr (III) by the addition of ferrous sulphate. When $Ca(OH)_2$ was used, Cr (III) concentration fall from 30 to 0.01 mg/L. At this point, maximum precipitation took place at pH 8.7. While Cu (II) concentration falls from 48.51 to 0.694 mg/L when $Ca(OH)_2$ and NaOH were used simultaneously. Thenceforth, the pH 12.0 was the point where highest precipitation of Cu (II) happened.

To boost the efficiency of hydroxide precipitation, various kinds of coagulants like polymers, alum etc may be added. Charerntanyarak (1999) used the technique of hydroxide precipitation for HM extraction. It was noticed that at optimized pH of 9.5, concentrations of Cd, Zn, Mg and Mn were 150, 450, 3154 and 1085 mg/L respectively. Besides, percentage efficiency can be further improved by the addition of coagulant.[35]

Though hydroxide precipitation is quite useful technique, yet it has various flaws. The sludge is being produced in large amounts which often pose a disposal problem. Besides due to amphoteric nature of metal hydroxides, efficiency of precipitation is affected as the optimum pH for a certain metal cannot be the pH for other metal.Furthermore, when agents for complexation like ethylenediaminetetraacetic acid (EDTA) is introduced into the solution, HM extraction is greatly affected.

1.4.1.2 Sulfide precipitation

Sulfide precipitation, a method considered as far more suitable than that of hydroxide precipitation because of various reasons. First, precipitates formed by this method are not amphoteric. Secondly, solubility of the resulting precipitates is considerably lower than that of hydroxide precipitation. Thirdly, its sludge shows enhanced decantation and thickness. All these factors contribute to higher extraction of heavy metal ions.Özverdi and Erdem (2006) worked upon iron sulfide and pyrite for the extraction of Cd (II),Pb (II) and Cu (II) [36]. At low pH, mechanism of HM removal was chemical precipitation while at high pH, adsorption plays a role. Nowadays, this process has been modified by sulfate reducing bacteria (SRB). SRB oxidizes sulfates to H_2S when oxygen is absent. Alvarez et al., 2007 used SRB to treat AMD (Acid Mine Drainage). Similarly, Kousi et al. (2007) employed SRB to treat Zn (II) in wastewater. Zn (II) were successfully removed up till 400 mg/L. [37]

Apart from being a useful technique, sulfide precipitation faces many risks. The presence of HM-sulfide particles in the acidic environment may lead to the release of dangerous fumes of H_2S. Besides, this process results in colloidal aggregates which makes separation cumbersome.

1.4.2 Ion-Exchange:

For HM extraction, this technique is often used because of various reasons like greater % efficiency and higher ion-exchange capacity. In this, ion-exchange resins are involved by which various metal ions are extracted from water when ions are exchanged. Both cations and anion exchange resins may be used for the removal of lead, copper, iron as well as sulfate, nitrate etc. respectively. Few contaminants like fluoride, arsenic etc. are hard to extract by ion-exchange because selectivity of resins is poor.Cation exchangers which are usually used in this technique are resins (highly acidic) having groups of sulfonic acid ($-SO_3H$) and resins (weakly acidic) having groups of carboxylic acid ($-COOH$).

Various constraints affect the HM removal by this technique like pH, contact time, metal ion concentration and temperature. Moreover, the presence of ionic charge on metals also affects the ion-exchange mechanism. In this regard, Abo-Farha et al. (2009) employed purolite resin in his work to assess the extraction of Fe^{3+}, Pb^{2+} and Ce^{4+} and found the ion-exchange efficiency in the manner as $Pb^{2+} < Fe^{3+} < Ce^{4+}$[38].Likewise, Kang et al. (2004) used Amberlite resin for Cr^{3+}, Ni^{2+}, Co^{2+} and obtained same results[39]

Apart from using resins, zeolites and various silicates are also extensively employed by researchers for HM removal since they possesses good CEC (Cation Exchange Capacity)[40] In this regard, Clinoptilolite is the zeolite upon which extensive research has been done. Its CEC has been improved considerably by its modification with iron oxide.[41]Heavy metals like Mn, Cu and Zn in drinking water has been extracted effectively by this method.

Although this technique offers various advantages like resin regeneration and others, its usage is limited recently since it cannot remove microbes and bacteria in water efficiently. Besides, polymers used in this technique are by nature biodegradable whose chemical resistance is quite fair but the thing which hampers its usage is microbial sensitivity. Lastly, the factor which carries a great significance is that if ion-exchange is used on a large scale in wastewater treatment then it involves high costs. Due to this reason, its use is discouraged nowadays and its use in wastewater treatment gets limited.

1.4.3Membrane filtration:

The most suitable and cost-effective technique for wastewater treatment is membrane filtration because of easy operation and greater efficacy. A variety of procedures used in membrane filtration involves: nanofiltration, reverse osmosisand ultrafiltration.[31]

1.4.3.1 Ultrafiltration:

Ultrafiltration (UF) is aprocess which is operational at relatively smaller trans-membrane pressure for the extraction of colloidal substances. The metal ions easily get through the membranes because of the fact that pore sizes are bigger as compared to metal ions. Ultrafiltration can be of two kinds: micellar enhanced (MEUF) and polymer enhanced (PEUF).Both MEUF and PEUF have great potential to extract metal ions from wastewater. In MEUF, surfactants are added to the wastewater containing heavy metals. As the surfactant concentration gets greater than that of micelle concentration (critical) or CMC, metal ions agglomerate with micelles to generate big surfactant-metal assemblies. Those metal ions are hold by the membrane having lesser pore size as compared to size of micelles while the rest get through the membrane. To boost the efficiency, such surfactants are used whose electric charge is antagonistic to metal ions. The % efficiency of MUEF is affected by many parameters like pH, nature of metal as well as surfactant.Landaburu-Aguirre et al. (2009) applied MEUF by involving SDS for the extraction of zinc from industrial wastewater.[42]Likewise, Sampera et al. (2009) have also applied MEUF by applying two different kinds of anionic surfactants like LAS and SDS for the extraction of Cu(II), Pb(II), Cd(II), Zn(II) and Ni(II)from industrial wastewater.[43]

Besides,PEUF is also treated as the reasonable process for the extraction of metal ions from industrial wastewater. PEUF involves polymer which make a complex with metal ions to produce a macromolecule when pumped via membrane of ultrafiltration. Molinari et al. (2008) applied polymer (PEI) for the metal uptake of Cu (II) via technique of ultrafiltration. The optimized pH where efficiency was maximum for Cu (II) was 6[44]. Similarly, Aroua et al. (2007) worked upon the extraction of chromium by three different polymers (PEI, pectin and chitosan) via PEUF technique. The % efficiency was higher when the pH was greater than 7[45]

PEUF offers many benefits like greater % efficiency, greater selectivity of binding etc. Nevertheless, this method is not widely used in the industry.

1.4.3.2. Reverse Osmosis:

RO is a prevalent treatment for industrial wastewater in chemistry and environmental sciences. The volume of world's desalination is around 20% by reverse osmosis.[46] RO involves a semipermeable membrane which permits the water to get through it while eliminating the pollutants.Various RO procedures have been applied to extract metal ions. Ni(II) and Cu(II) have been extractedby Na_2EDTA and the % efficiency reached up till 99%[47].The use of RO is discouraged because of high electricity costsand membrane re-building.

1.4.3.3Nanofiltration:

Nanofiltration is widely used for the extraction of heavy metals like chromium[48], arsenic[49],nickel[50]and copper[51].Two different effects are involved in this technique, one is electrical effect and the other one is steric hindrance.Since the pores of the membrane are charged in nature, therefore electric potential helps to separate the charged cations and anions by extracting the charged ions whose size is lesser than the membranes' pores. NF is preferable because of its consistency, simplicity and lesser electricity costs. As (V) was extracted from wastewater using two different nanofiltration membranes by Figoli et al. (2010). Many parameters like pH, temperature and concentration of Asaffected the % removal. Similarly for the extraction of nickel from wastewater, composite (NF-polyamide) membrane was designed[50]. The % efficiency for nickel extraction in this case was 98%.

1.4.4Coagulation:

Coagulation plays a pivotal role in wastewater treatment whose foremost focus is particles of suspended nature and hydrophobic colloids. It neutralizes charge on the particles which keeps them at a distance. A variety of coagulants are extensively employed in the application of industrial wastewater like $FeSO_4$, Al and $FeCl_3$ which significantly extract the heavy metals.Two different coagulants (polyaluminium chloride and $FeCl_3$) may be employed for HM removal from sewerage water by applying the technique of coagulation[52].In cases where heavy metals are both insoluble and soluble then they may be separated out via coagulation. Grafting was carried out by means of sodiumxanthogenate upon PEI (polyethyleneimine)[53]. Subsequently, the coagulant formed was amphoteric which has pH dependent nature. At low pH, cations may not be extracted efficiently whereas anion colloidal particles may be coagulated. Likewise at high pH, coagulation of cations increases. .

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1.4.5 Flocculation:

Flocculation involves alignment of polymers in such a way so as to establish bridges and turned the particles into large clusters and agglomerates. Upon the formation of bulky agglomerates, they can be extracted via flotation or filtration. A variety of flocculants may be employed for wastewater treatment like PFS (polyferricsulphate), PAM (polyacrylamide) and PAC (polyaluminiumchloride). Nevertheless, it is pretty hard to completely extract HM with the help of flocculants. To cope with this, macromolecule flocculants (MF) are evolved which removed HM with great efficacy. For example MF-MAA chitosan may be synthesized by treating mercaptoacetic acid (MAA) with chitosan[54]

As coagulation and flocculation are unable to extract the heavy metals with much efficiency so usually both of them are simultaneously used along with other available strategies and techniques. For example, these techniques are simultaneously applied in the extraction of tungsten from wastewater using $FeCl_3$ where efficiency was around 98%[55]

1.4.6. Flotation

Flotation has widespread usage in wastewater treatment[56] This technique involves bubble attachment for the extraction of heavy metal from water. Many kinds of flotation procedures exist for HM extractionwhich are:

- Ion flotation
- Dissolved Air Flotation (DAF)
- Precipitation flotation

1.4.6.1 Ion flotation:

In ion flotation, metal ions are made hydrophobic by the application of surfactants and later on, these hydrophobic species are extracted via air bubbles. A biosurfactant which owes its origin from a plant, saponin was used for the extraction of lead, copper and cadmium by means of ion flotation. The % efficiency of Cu^{2+}, Pb^{2+} and Cd^{2+} was 81%, 89% and 71% in a ratio of 3:1[57]. Similarly, Polat and Erdogan (2007) extracted Zn^{2+}, Cr^{3+}, Cu^{2+} and Ag^{+} from wastewater using HDTMA(hexadecyltrimethylammoniumbromide)and SDS. % efficiency for HM extraction was 74% when pH was low while it was 90% when pH was high[27].

1.4.6.2 Dissolved Air Flotation (DAF):

DAF involves the formation of bulky agglomerates when micro-bubbles cling with the suspended particles that are present in the industrial wastewater. The agglomerates thus formed possess a density lower than that of water. Resultantly, they come upward and gradually amassing on the surface which may be separated out as sludge[58, 59]

1.4.6.3 Precipitation Flotation:

In precipitate flotation, precipitate is produced by means of metal hydroxide or anion salts (carbonate, phosphate or sulphideetc). The precipitate formed is separated out by clinging to air bubbles[60]. Studies show, Cr (III) was extracted using SDS and ethanol via technique of precipitate flotation. The % efficiency was 96% at pH 8[61].

1.4.7. Electrochemical treatment:

Electrochemical procedures involve electroplating of heavy metals over the surface of cathode and restoring them to their elemental form[62]. Many types of electrochemical techniques exist which involve:

- Electrocoagulation
- Electroflotation
- Electrodeposition

1.4.7.1 Electrocoagulation:

In electrocoagulation, coagulants are produced by electrochemical reactions on the corresponding electrodes (iron or aluminium). On anode, production of metal ion happens whereas hydrogen gas is produced at cathode. The liberated gas aids in removing the particles from water[63]. Many researchers have used electrocoagulation technique involving aluminium electrodes for the enhanced removal of Cu (II), Ag (I), Zn (II), Cr (VI) and Ni (II)[64]. Besides, electrodes of stainless steel were also employed for the extraction of zinc and nickel in wastewater treatment via electrocoagulation[65]

1.4.7.2 Electroflotation:

Electroflotation (EF) involves liberation of oxygen and hydrogen by electrolysis due to which pollutants come up and float on the water surface. Studies reflect EF is a procedure of chief significance regarding wastewater treatment. Different researchers employed different kinds of electrodes while employing electroflotation technique. When aluminium electrodes were used in EF for the extraction of Pb, Cu, Cd, Ni and Fe, the % efficiency was 99%[66]. Similarly, iron electrodes modified with UF and MF (ultrafiltration and microfiltration) were also used for nickel removal in the presence as well as absence of oxygen[67].

1.4.7.3 Electrodeposition:

One of the best techniques so far used for the HM extraction from wastewater is electrodeposition. Since permanent residues are absolutely absent hence it is often termed as a clean technique[68].Metal ions are extracted electrolytically using various chelating agents like nitrilotriacetic acid, EDTA and citrate in chambered cell. Minimum % efficiency was 40% which goes up to 90% for different metals[69].

Despite considered as the best method for wastewater treatment owing to its quick and credible results, electrothermal technique demands high electricity costs which limits their usage on a vast scale.

1.4.8 Adsorption

Adsorption is that protocol in which particles, gases or colloids cling to the surface (often termed as adsorbent) resulting in a thin film known as adsorbate.It is basically a surface phenomenon which happens because of the remaining unstable forces that are found on the surface.Such unstable forces will have the propensity to attract and hold the particles and species when on contact.

Adsorption is considered as cost-effective technique for wastewater treatment.Two different procedures may exist: one is physisorption(due to London forces) and the other one is chemisorption (due to chemical interactions and bonding). Adsorption techniques have an edge over other methods since it requires less energy and cost. More especially, it is preferred because there is no secondary pollution. Besides in adsorption procedures, regeneration of adsorbent is also possible via desorption mechanism which effectively aids in the separation of adsorbents from wastewater. Due to these reasons, adsorption systems play a pivotal role in the HM extraction from wastewater.

1.5 Adsorbents for Wastewater Treatment:

The selection of a right adsorbent is central to the benchmark of 100% HM removal from wastewater. The adsorbents usually employed involve activated carbon, silica, nanometal oxides, alumina which possesses fair % efficiency. Notwithstanding, they are pretty costly and cumbersome as well to be extracted from wastewater after their adsorption. Apart from the abundant and economical nature of agricultural waste, their stability is inadequate and adsorption capacity is worst. Adsorbent protocols are greatly affected by pore size dissemination, pores' nature and surface area more precisely the area which is internal. Besides, adsorbent should possess fair mechanical properties like damage resistance and the particles of adsorbent should have suitable shape and size. The adsorption capacity is also affected by chemical properties like functional groups' nature and extent of ionization. When the surface is modified with different kinds of functional groups i.e; chemisorption takes place which is entirely different from that of physisorption. Nowadays, growing focus is on the surface functionalization of adsorbents so as to boost the % efficiency. Various adsorbents are discussed as given below:

1.5.1. Activated carbon (AC):

Activated carbon, the adsorbent which is common and prevalently applied used in wastewater treatment[70].High surface area of AC is ascribed to its large pores (micro and meso-porous nature). Oxidized AC possesses lots of tiny sites which aids in extracting many organic and other particles which simply is not possible with normal filtration. (oxidized at high temperatures) containing millions of minute sites is an effective mean of adsorbing dissolved organic and other chemicals that cannot be removed by physical filtration. To boost their efficiency and cost-effectiveness, they may be modified or composites may be formed from it. Researchers have used additives like tannic acid, surfactants, magnesium, alginate and composites. All these adsorbents reflectedfair efficiency in HM extraction from wastewater. Extraction of AC from eucalyptus bark was also employed for the removal of Pb^{2+} and Cu^{2+}[71]Similarly AC may be synthesized from poultry litter to be used in wastewater treatment. A surprising efficiency was witnessed having % efficiency far greater than that of activated carbon of bituminous origin[72].

Owing to all above merits and features, activated carbon poses many drawbacks as well. Usually, it is not cost-effective involving lots of expenditures which limit AC's applicability.Besides, regeneration procedures of AC are pretty expensive, resulting in material losses. These reasons compelled the researchers to go for some effective and cheap adsorbents.

1.5.2. Carbon nanotubes:

Carbon nanotubes (CNTs) have established its worth as adsorbent in the HM extraction from wastewater.[73-75]Greater adsorption capacity is ascribed to its broad surface area and vast chemical interactions. CNTs when dissolved in watermake agglomerates (because of their hydrophobic nature) which lead to reduction in the area. Such agglomerates of CNT possess lots of minute spaces which serve as adsorption sites for HM extraction. Moreover, it contains micropores in enormous number which aids in the adsorption of giant organic species. Functional groups like -OH,-COOH and $-NH_2$ may interact resulting in hydrogen bond formation on the outer surface of CNTs. Besides, electrostatic interaction may also happen for the HM removal.

Heavy metals for instance chromium, copper, cadmium, nickel and lead are efficiently extracted from wastewater with the help of CNTs as reported in the literature[74, 76-79]. The adsorption mechanisms involved are quite complex. Notwithstanding, it may be ascribed to the chemisorption i.e; interaction between adsorbate and CNTs by chemical means or it may be because of electrostatic interaction or precipitation[75]. The pristine CNTs depict lower % efficiency but upon oxidation of CNTs with nitric acid or KMnO4, its efficiency instantaneously gets high. For example, MWCNTs were made acidified andwere used in the Pb(II) removal for which % efficiency comes out to be 75% [76]. Likewise, Pillay et al. (2009) employed different adsorbents like AC, MWCNTs (functionalized and non-functionalized) for the extraction of Cr (VI). The results depicted that non-functionalized MWCNTs possess greater % efficiency of 98% than activated carbon [72].Furthermore, oxidized CNTs reflect far more excellent adsorption capacity for HM extraction of Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} [73]. The groups present on the surface of CNTs attract metal ions via chemical interactions and electrostatic attraction.

Despite all these merits and CNTs having good efficiency, it poses many disadvantages as well. Firstly, when CNTs are applied as adsorbent on industrial level, its agitation with water in the presence of ultrasonic bath is technically not feasible (unless they are converted to oxides). Apart from this, it is quite cumbersome to entirely separate the CNTs powder from the water after adsorption without centrifugation. Also, their separation via filtration technique is pretty hard as the filter is obstructed by the CNTs. Besides, there are grave concerns of health and ecological threats by the toxic and poisonous nature of CNTs. When it adsorbs poisonous materials, its toxicity level may further be elevated resulting in environmental disturbances. All these reasons as mentioned restrict their applicability on a large scale.

1.5.3. Adsorbents (low-cost):

Number of studies has been carried out on adsorbents of low cost. The growing focus is to create such adsorbents which are not only cheap and cost-effective but also gives high efficiency of HM extraction. Industrial byproducts, natural materials and agricultural waste were considered as adsorbents in HM extraction from wastewater. Bhattacharyya andGupta (2008) studied HM adsorption upon raw and functionalized kaolinite and MMT (montmorillonite)[80]. Likewise, various researchers have employed plant wastes, industrial byproducts like diatomite, lignite, clino-pyrrhotite, aragonite shells, lignin, zeolites, kaolinite, peat and clay [81-89].

1.5.4. Bioadsorbents

The applicability of bioadsorbents in the HM extraction from wastewater is quite interesting and inexpensive. Biosorption is considered as a favorable process because it is cost-effective technique and the biosorbents exhibit exceptionally fair adsorption efficiency. Sources of bioadsorbents are: [86]

- Biomass from algae
- Biomass from microbial organisms (yeast, bacteria and fungi)
- Non-living biomass (shrimp, crab shell, lignin, bark, squidetc)

Researchers have applied variety of inexpensive biosorbents like seed shells, black husk, citrus peels, sawdust, coffee husks, egg shell and pectin gels in wastewater treatment[90-97]. Besides, algal biomass flourishes all across the world and is hence frequently been applied in the HM extraction because of its cheap nature, abundant availability and better efficiency. For example, Zn^{2+} and Cu^{2+} were used for HM removal using marine algae, Cr (VI) and Pb (II) by green algae. Similarly, Rhizopus biomass was also used. By using the technique of biosorption, extraction of biosorbent from treated water gets cumbersome.

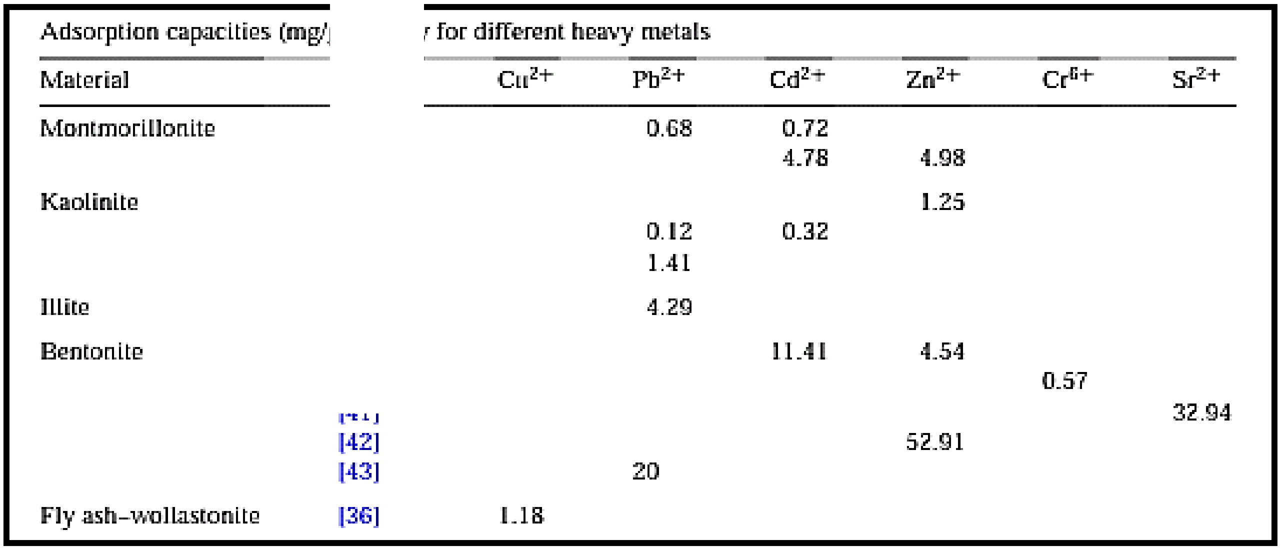
1.5.5 Clay materials:

Clay materials are considered as the most efficient adsorbent when it comes to the uptake of heavy metals from wastewater. This is because of their stacked formation, abundant availability, non-toxic and also it is cost-effective. Notwithstanding, adsorption capacity of clays are fairly low because of certain unapproachable sites in their structure. Their efficiency may be ameliorated by their modification with polymers.The composites of polymer and clay have shown their worth as the most likely adsorbent in HM extraction from wastewater.

Basically clays are classified into three groups: Smectites like MMT, micas and kaolinite. Among them, montmorillonite is inexpensive possessing greatest CEC (Cation Exchange Capacity). Due to these reasons, researchers have employed clays like MMT (montmorillonite) kaolinite, HNTs (halloysite nanotubes) for extraction of heavy metals like Cr (VI), Pb (II) from wastewater.

Apart from this, the clay which carries peculiar significance is bentonite. Bentonite is composed of sand, clay and silt. It is considered as excellent clay in context of its efficiency and adsorption capacity. For example bentonite was applied in the HM extraction of Cd (II) and Zn (II) fromwater. The adsorption efficiency of various clays are given below in Table 1.4:

Table 1.4 Efficiency of Clays



Adsorption capacities (mg/ for different heavy metals

Material		Cu^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cr^{6+}	Sr^{2+}
Montmorillonite			0.68	0.72			
				4.78	4.98		
Kaolinite					1.25		
			0.12	0.32			
			1.41				
Illite			4.29				
Bentonite				11.41	4.54		
						0.57	
							32.94
	[42]				52.91		
	[43]		20				
Fly ash–wollastonite	[36]	1.18					

1.6 Halloysite nanotubes (HNTs):

Halloysite Nanotubes (HNTs) are unique nanomaterials (one dimension) which exist in the form of aluminosilicate sheets (rolled shape) having formula of $Al_2Si_2O_5(OH)_4.2H_2O$. This formula is quite same as that of kaolinite. The only exception is the existence of two water molecules in case of HNTs. The existence of interlayer water in HNT is a distinguishing feature that differentiates it from kaolinite.Besides, kaolinite possesses a stacked structure in contrast to HNTs which have rolled tubes shape. HNTs possess variation in its morphology like platy, tube-like or spheroidal forms and this variation is attributed to its crystallization and geographical presence. Nevertheless, the common shape in which it usually exists is elongated tubes, termed as halloysite nanotubes (HNTs).

The inner surface comprises of aluminol groups in octahedron pattern (Al-OH) while on external side, it comprises of siloxane groups in a pattern of tetrahedron (Si-O-Si). The mismatch between the adjacent octahedral aluminol, tetrahedral siloxane and the water molecules result in packing disruption which compel the sheets to transform into tubes. The possession of antagonistic surface and lumen chemistry consequently leads to the lumen being positively charged and the external surface being negatively charged. (Figure 1.1, 1.2)

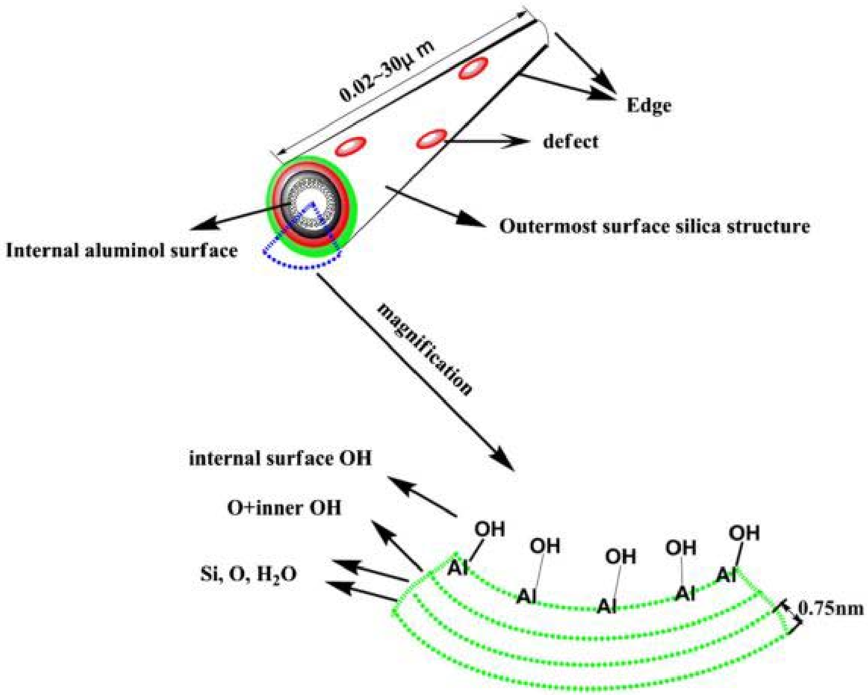


Figure 1.1 HNTs Structure

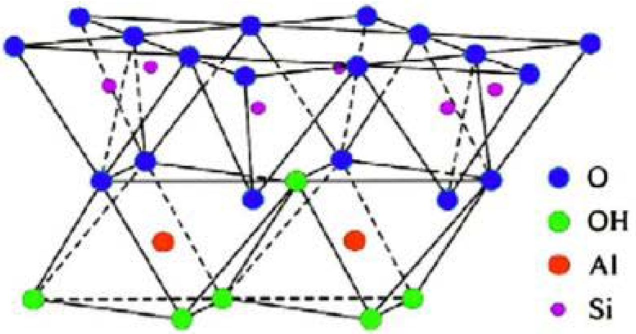


Figure 1.2HNTs Crystal Structure

Usually HNTs length, diameter of lumen and outer surface varies from 100-2000 nm, 10-30 nm and 50-100 nm respectively. Such special properties like tubular formation, unique surface chemistry leading to selective functionalization, superior mechanical strength, and cost-effectiveness results in extra-ordinary thermal, biological and mechanical features in HNTs-polymer NC. Consequently, HNTs may act as a substitute for expensive CNTs in the arena of polymer-NCs (nanocomposites). All these features made HNTs an emerging area of research and its applicability in various arenas is significantly increasing. An analysis of data gathered from SciFinder for the word "halloysite" reflects a growing trend for the publications in halloysite during the last 20 years is given in Figure 1.3:

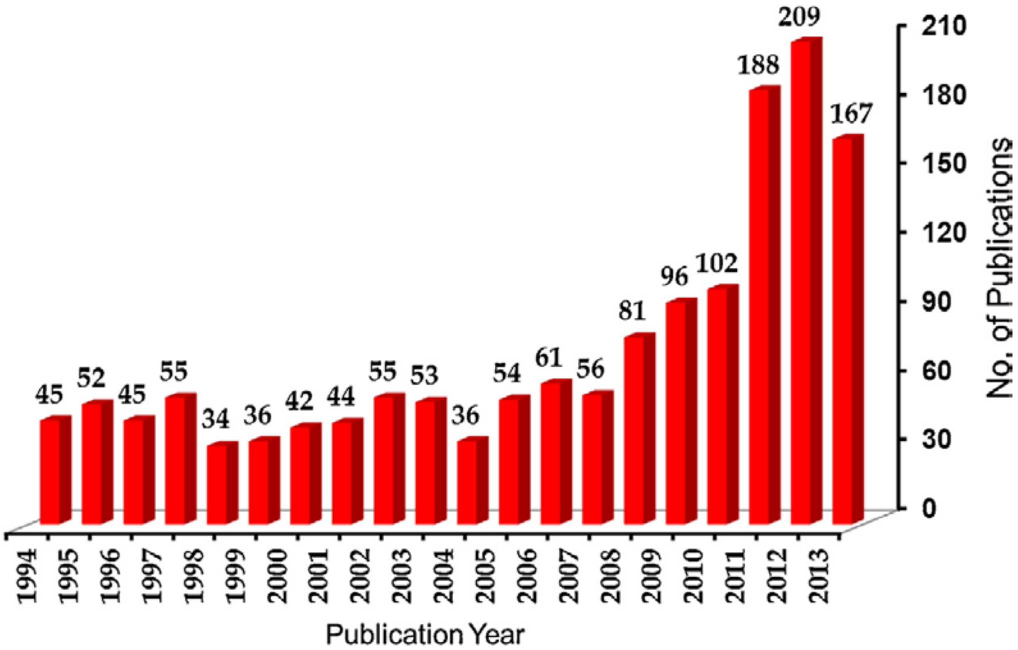


Figure 1.3 Number of Publications of HNTs in last 20 years [98]

Many exciting applications in the field of HNTs revolves around controlled release of medicines, 3-10, medical grafts 12-13, frameworks of tissue engineering, 16-19, cosmetics 11, use in cancer cells 14-15, nanotemplates 20-22 and adsorbent in HM extraction.

HNT is a biocompatible "green" material. Its simplicity in procedures along with its cost-effectiveness proved it an excellent adsorbent for the extraction of heavy metals. "Green" methodology is usually followed while treating wastewater. Green chemistry involves design, advancement and execution of chemical products so as to curtail the production of such materials which pose a threat to human well-being as well as ecology. Since they are "biocompatible" by nature, therefore they are not harmful to the atmosphere.

HNTs possess momentous applications in every field because it is quite cheap and having exuberant presence. Its deposits range in thousands of tons and may be obtainable from USA, France, China, Spain, New Zealand, Brazil etc. HNTs are considered as feasible alternatives in areas where cost makes an issue. The low cost coupled with high efficiency favors commercialization of HNT-polymer NCs. The tubules in HNTs do not interlock with one another which consequently lead to their better dispersion in polymers. Hence in comparison to CNTs, HNTs are cost-effective and environment-friendly material. Table 1.5 shows the inter-comparison of CNTs and HNTs:

Table 1.5 Inter-comparison of HNTs vs CNTs

Properties	**Halloysite Nanotubes**	**Carbon Nanotubes**
Inner diameter / length	15 nm × ca. 1000 nm	2 nm × ca. 1000 nm
Biocompatibility	Biocompatible	Toxic
Price*	$ 4 per kg	$ 500 per kg
Availability	Thousand tons	Grams
Exfoliation	Not required	Cumbersome exfoliation

*Average price

1.7 HNTs in Wastewater Treatment:

With rapid advancement and industrialization, there has been serious concern over scarcity of water and pollution issues. The major proportion of water pollution is ascribed to the presence of dyes, heavy metals and pollutants of organic nature. Various adsorbents of low cost are employed for wastewater treatment. Recently, halloysite nanotubes (HNTs) are extensively employed in water treatment. It serves as an excellent adsorbent in wastewater treatment because of its greater pore volume, greater surface area and the presence of hydroxyl groups in exuberant amounts.[99] Besides their applicability in HM extraction, they also possess good efficiency in dyes removal.

For HM adsorption, pristine HNTs show low % efficiency. Nevertheless, the adsorption efficiency may be substantially increased by modification. Various ways exist for the functionalization of HNTs. Many surfaces like lumen (inner surface), interlayer and external surface may be functionalized.

1.7.1Surface modification:

It involves the grafting of functional groups on the external surface of HNTs that may be achieved via physical or chemical modification.[100-103]Usually the outermost surface of HNTs possesses less reactivity due to which grafting is not possible. Nevertheless, because of negative potential in broader pH range, the outer surface can be functionalized by the adsorption of metal ions. Furthermore, the surface is exposed to the occurrence of surface defects which consequently leads to the availability of hydroxyl groups for surface functionalization.

1.7.2 Modification of interlayer:

The adsorption capacity is considerably ameliorated by modification via intercalation. For example, ten-fold rise in adsorption capacity was witnessed for Cd (II) than others chiefly because the $–NH_2$ of DEA (Diethanolamine) or TEA (Triethanolamine) that was introduced into the interlayer of HNTacted as an accessory position for adsorption. The metal ions were extracted by their slow diffusion into interlayer and their resultant attraction by $–NH_2$[104].

1.7.3 Modification of Inner lumen:

As discussed, HNTs have a tube-like shape so many materials may be loaded in the lumen (inner surface) via vacuum or by dipping in particular solution. Various drugs like NAD and tetracycline may be soaked in the presence of vacuum for drug loading in HNTs.[105-107]The internal aluminol (Al-OH) groups possess great affinity for variety of organic species like organosilanes. The functionalization of HNTs was achieved by covalent introduction of groups in HNTs lumen. For example, lumen was functionalized by introducing APTES (3-aminopropyltriethoxysilane) and groups of aminopropyl were grafted and embeddedvia covalent bonds [103].

HNTs as an adsorbent is preferred because of its following features:

- Larger pore volume
- Large surface area leading to high % efficiency
- Regeneration by desorption
- Abundant availability
- Biocompatibility
- Cost effectiveness
- Green material and environment friendly (non-toxic)
- Simple working protocols.

All properties as mentioned above make halloysite nanotubes (HNTs) an outstanding competitor for HM removal.

1.8 Literature Survey:

Numerous research papers were studied during the literature review process and their study reflects that halloysite nanotubes (HNTs) give extra-ordinary results in HM extraction which are:

Krawczyk*et al*.,(2016)developed an efficient way to analyzePb and Cd in water using dendrimer functionalized HNTs (HNTs-G3).HNTs-G3 was dissolved in samples of water containing heavy metals. These samples were isolated via centrifugation after adsorption. Afterwards, they were analyzed by atomic absorption (graphite furnace) for remaining concentration. The detection limits for Pb and Cd were 10 and 0.5 ngL^{-1} respectively. By using solid-phase extraction during preconcentration, coordination between adsorbent (HNTs-G3) and metal ions (Pd and Cd) has been considerably enhanced that actually reduced the duration of time for sample preparation. Resultantly, applicability of amine dendrimers f-HNTs provided a cost-effective way in contrast to preconcentration cost on graphene, carbon nanotubes, MWCNTs. The suggested method by Magdalena Krawczykand others was employed in the extraction of Pd and Cd in variety of water samples like river water, sea water, mine water, lake water, tap water and stream water.[108]

Farnaz S.F *et al*.,(2016)proposed the way by which amine dendrimers were grafted on the HNTs surface and functionalization was accomplished on the outer surface of HNTs. The prepared dendritic HNTs ameliorated the adsorption capacity regarding extraction of anionic dyes. For the preparation of HNTs-G3 (adsorbent), HCl was used to purify the pristine HNTs and amine functionalization was carried out with 3-aminopropyltriethoxysilane (APTES). Afterwards, methyl acrylate (MA) and ethylenediamine (EDA) was used for Michael addition and amidation respectively. Due to such successive reactions, dendrimer (branched tree like structure) was formed on the surface. Upon repeated steps, functionalized HNTs (HNTs-G3) were prepared. FT-IR, FESEM and EDX verified the successful modification on the outer surface. FESEM suggested that there was no distortion in HNTs morphology. The prepared adsorbent was assessed for the extraction of two dyes (acidic); AR1 and AR42. Various factors like pH, dye concentration, contact time and temperature were monitored to look for % efficiency. Maximum % efficiency of 93-94% was witnessed at pH 3 for both dyes while an efficiency of just 9-13% was shown by raw HNTs. Such functionalized HNTs (HNTs-G3) of high adsorption capacity may be employed in dyes removal from wastewater. [109]

.

Khelifa and coworkers(2011)developed intercalated HNTs by employing sodium acetate and the maximum adsorption capacity of 50 mg g^{-1} was noticed for the Cu (II) adsorption. The sodium acetate was introduced into the interlayer which was verified by FT-IR and XRD techniques. The intercalation was done by dissolving HNTs in sodium acetate and then shaked. Afterwards, excess liquid was separated and dried in oven. The inclusion of sodium acetate in HNTs interlayer remarkably ameliorated the % adsorption efficiency of Cu (II). High pH and minimal dosage of adsorbent lead to greater Cu (II) adsorption. This rise in adsorption capacity is dependent upon the proportion of COOH which is higher with the introduction of sodium acetate in HNTs interlayer. The optimum factors like contact time, dose, temperature and pH where the adsorption was maximum were 2 hours, 2.5 g/L, 25 °C and 6 respectively. Intercalated HNTs have adsorption capacity of 52.3 mg/g for the extraction of Cu (II) from wastewater[110]

Khelifa*et al.*, (2012) have used modified algerian HNTs as an adsorbent for Pb (II). They have functionalized Algerian HNTs (f-HNTs) with thermal treatment at various temperature ranges of 200-1000 °C with a gap of 200 °C. f-HNTs were characterized by XRD, TGA, FTIR, TEM and

DTA all of which verified successful modification. The modified HNTs were used for the extraction of Pb (II). The uptake by H1000 was least while the highest uptake was witnessed for H200. [111]

Samadiand M. Amjadi (2016) employed HNTs as adsorbent in solid-phase for the extraction of Fe (II). 2,2-bipyridine being a chelating agent make a complex with Fe (II). Consequently, the formed complex was adsorbed conveniently on the surface of HNTs. The pH where cationic complex was adsorbed with great efficacy was 3.5-6.0 and desorption happened with TCA (tricholoroacetic acid). For the confirmation, FTIR, SEM, EDX and UV-Vis techniques were employed. The absorption band for complex appeared at 520 nm from which Fe (II) concentration was found out. When conditions were optimized, detection limit was 1.3 μg/L. The protocol was successfully utilized for Fe (II) concentration in many samples of food and water. [112]

Matusik*et al. (2014)* reported grafting of HNTs interlayer involving aminoalcohols (diethanolamine and triethanolamine). The grafted HNTs were verified by characterization like FTIR and XRD techniques. Intercalation took place when HNTs were treated with DEA or TEA in the presence of DMSO. Later on, centrifugation and washing were carried out. This functionalization by intercalation considerably ameliorated the adsorption efficiency of Zn (II), Pb (II), Cu (II) and Cd (II). First metals slowly diffused in the interlayer and later on, grafted aminoalcohol binds these metal ions. Especially, Cu (II) extraction was more feasible as they make complex with ligands that are N-donor. The HM extraction by pristine HNTs had comparatively low efficiency while HNTs modified with diethanolamine or triethanolamine showed considerably higher efficiency. This amelioration was attributed to their distribution in interlayer and their ensuing binding by nitrogen of amine [104].

Luo*et al.* (2011)have modified pristine HNTs with organosilane (KH-792) that leads to the generation of an excellent adsorbent for extraction of Cr (VI). The adsorbent was verified by various techniques of characterization like TEM, TGA and FTIR that authenticated functionalization. The results of adsorption suggested that extraction of Cr (VI) by f-HNTs was greatly affected by pH, contact time and temperature. Their results depicts that the adsorption burst took place in just 5 minutes with % efficiency of 95%. The adsorption capacity witnessed for Cr (VI) was 37.25 mg/g and duration of 30 minutes was needed to attain equilibrium. Moreover, low temperature promoted Cr (VI) extraction by f-HNTs while it decreased considerably when the pH is increased[113].

In another study, **Mishra *et al.* (2014)**madenanocomposite (NC) of HNTs with polypyrrole (PPy) through simultaneous polymerization of pyrrole (Py). These NC were used as prospective adsorbent for Cr (VI) extraction from wastewater and polluted groundwater. Various characterization techniques like FTIR and XRD verified the formation of nanocomposite(NC). Besides, morphology of SEM and TEM snaps reflected that polypyrrole (PPy) was coated upon HNTs. Also, XPS analysis suggested that Cr (VI) was adsorbed upon nanocomposite (NC) and some of metal ion was converted to Cr (III). Parameters like time, pH, temperature and Cr (VI) concentration that considerably affect the adsorption process were studied. The optimized conditions for adsorption capacity of Cr (VI) were 149.25 mg/g when pH was 2. Furthermore, NC was also regenerated by desorption which suggests its again usage for atleast three times[114].

Y. Lvov *et al.* (2013)studied the adsorption properties of HNTs upon cationic and anionic dyes (Rhodamine and Chrome azurol) and its evaluation with kaolinite. The adsorption efficiency for HNTs was much greater than kaolinite and others. The adsorption capacity for Rhodamine was 43.6 mg/g while for Chrome azurol, it was 38.7 mg/g. The optimized pH was in acidic range for Chrome azurol while for Rhodamine, pH fall in basic range 8-9. Nevertheless when adsorbed dyes were burnt, 50 % of HNTs were regenerated. % efficiency for dyes was more than 95-99.99%[115]

Zhang *et al.* (2011) employed HNTs for the extraction of methyl violet (cationic dye) from wastewater. The adsorbent efficiency varies with time, dose, temperature and pH. Good adsorption capacity was witnessed for MV i.e; 113.64 mg/g[116]. Likewise, another cationic dye named, Neutral Red was also tested by the same researcher Zhang in which HNTs were verified by TEM, XRD, BET and FTIR. For adsorption capacity, factors were optimized and good efficiency was witnessed[117].Furthermore, Zhang also prepared Fe_3O_4-HNTs composite which was verified by techniques like TEM, XRD, BET and VSM. These techniques reflect that particles of Fe_3O_4 were fairly distributed on HNTs surface that confirmed formation of composite. This composite was applied in methyl violet (MV) extraction which showed fair % removal. All these results and researches testify HNTs as extra-ordinary adsorbents in dyes extraction from wastewater[118].

Wang *et al.* (2017) reported HNTs-Fe3O4 composite which were used for Cr (VI) and Sb (V) removal. The composites synthesized were verified by XRD, FTIR, TGA, BET and TEM. These techiques reflect that organosilanes were attached on the outer surface while Fe_3O_4 were introduced into the inner surface (lumen). The organosilane (KH-42) used in composite preparation displayed the greatest adsorption capacity for Sb (V) and Cr (VI). The % removal of 67% to 99% was witnessed for both Sb (V) and Cr (VI) by the composite which reflected their usage in wastewater treatment[119].

Tian*et al.* (2016) have synthesized magnetic HNTs-Fe_3O_4nanohybrid and used it for uptake of Cr (VI). The prepared nanohybrid was verified by characterization techniques like XPS, XRD, TEM, VSM and FTIR. The results depict the dispersal of Fe3O4 upon HNTs surface. Furthermore, XPS depicts the adsorption of Cr (VI) upon HNTs by their transformation to Cr (III). The nanohybrid manifested significant removal of 132 mg/L, almost 100 times greater as compared to pristine HNTs [120].

Yang *et al.* (2015) functionalized the HNTs surface with PEI (polyethyleneimine) and noticed that it possesses excellent efficiency for Cr (VI) extraction. PEI-HNTs exhibited 64 times greater % removal as compared to raw HNTs having capacity of 102 mg/g. Moreover, XPS analysis signifies that PEI-HNTs may be used both for Cr (VI) reduction as well as immobilization[121].

Zhang *et al.* (2010) reported functionalization of HNTs outer surface with surfactant named as hexadecyltrimethylammonium bromide (HDTMA). The confirmation of this adsorbent (functionalized HNTs) was verified by characterization techniques of TGA, FTIR and TEM, all of which testified successful functionalization. Within a short span of 5 minutes, % removal of 90% was witnessed. This efficiency was affected by ionic strength and pH. As the pH and ionic strength is getting higher, the adsorption capacity considerably falls. The synthesized adsorbent was regenerated by desorption[122]

.

Chang *et al.* (2013) have modified the HNTs with 2-hydroxybenzoic acid for Fe (III) removal. HNTs when functionalized were attested by TEM and FTIR which depicted successful modification. Various factors like pH, flow rate, shaking time and sample volume were optimized. The preconcentration was calculated using ICP-AES. The maximum % adsorption for Fe (III) was 45.54 mg/g at optimized parameters [123]

Similarly, **Qun He *et al.* (2013)** developed HNTs-PSA (adsorbent) by modification of HNTs surface with N-2-Pyridylsuccinamicacid (PSA). The modified HNTs were used for Pb (II) uptake. Characterization techniques TGA, FTIR and TEM reflect that the HNTs surface has been functionalized with PSA. 3.5% of PSA was grafted upon HNTs. Parameters were optimized with a pH of 5 and Pb (II) was calculated by ICP-AES. The adsorption capacity was 23.58 mg/g and % efficiency for Pb (II) was in between 95%-102%. The technique was authenticated from RM (Reference Material which was Peach leaf GBW 08501) via column protocol. Since the determined value (0.96) was quite close to the referenced value (0.99), hence may be used for Pb (II) uptake[124].

Chang *et al.* (2012) reported HNTs modified with murexide to form functionalized murexide-HNTs. The adsorbent (HNTs-murexide) was tested for Pd (II) extraction. The synthesis of adsorbent was verified by SEM, TEM, XRD, FTIR and N_2 isotherm. Before measurement by ICP-AES, parameters for preconcentration were inspected and optimized. In optimized settings, when pH was 1 then adsorption capacity was 43 mg/g. The % efficiency was more than 95% in case of Pd (II)[125].

Zhang *et al.* (2014) developed hybrid beads by the combination of alginate and HNTs. These beads were used for Cu (II) extraction by a fixed column. Parameters like flow rate, bed height etc were evaluated. When flow rate and bed height was 3 mL/min and 12 cm respectively then adsorption capacity was 74.13 mg/g. Moreover, HNTs-murexide was also regenerated and the % efficiency for Cu (II) extraction from wastewater was extra-ordinary[126].

Subhra Jana *et al.*,(2018) prepared two different amine-functionalized NCs (nanocomposites) of HNTs and their application for Hg (II) uptake. The % efficiency varied with pH that it rises up to pH 7 and afterwards it declines. Both adsorbents displayed extra-ordinary efficiency of adsorption; nevertheless, greatest efficiency for Hg (II) was witnessed for P-HNTs. The synthesized nanocomposites may be used for heavy metal extraction [127].

1.9Aims and Objectives:

- To functionalize the outer surface of HNTs by various groups like amidoxime, hydrazine, EDA (ethylenediamine) and DETA (Diethylenetriamine).
- To characterize the four different functionalized HNTs (f-HNTs) H1, H2, H3 and H4 with FTIR, XRD, SEM and EDX.
- To apply f-HNTs in HM uptake of Cr (VI) present in wastewater.

Chapter 2: Experimental Section

2.1 List of Chemicals:

No.	Chemical Name	Formula
1	Deionized water	H_2O
2	Diethylenetriamine	$HN(CH_2CH_2NH_2)_2$
3	Dry toluene	$C_6H_5\text{-}CH_3$
4	Ethanol	C_2H_5OH
5	Ethylenediamine	$NH_2CH_2CH_2NH_2$
6	Halloysite Nanotubes (HNTs)	$Al_2Si_2O_5(OH)_4.2H_2O$
7	Hydrazine	NH_2NH_2
8	Hydroxylamine	NH_2OH
9	*N*-Methylpyrrolidone (NMP)	C_5H_9NO
10	4-Nitrophthalonitrile	$C_8H_3N_3O_2$
11	Potassium carbonate	K_2CO_3
12	Potassium chromate	K_2CrO_4
13	Tetrahydrofuran(THF)	C_4H_8O

2.2 Glassware and Apparatus

2.2.1 Glassware

Three neck round bottom flask, Condenser,Dean-Stark trap, Beakers, Conical flasks, Spatula, Sample bottles, Thermometer, Pipettes, Graduated cylinder, Volumetric flasks (100 mL, 500 mL), Funnel, Syringes, Magnetic Bar, Oil bath etc.

2.2.2 Apparatus

Hot plate, Ultrasonic bath, Nitrogen gas cylinder, UV lamp, Centrifuge, Weighing balance, Stands, Orbital shaker, TLC plates and Vacuum oven.

2.3 Synthesis of functionalized halloysite nanotubes (f-HNTs):

For the surface modification of halloysite nanotubes (f-HNTs), reaction was performed in nitrogen gas atmosphere. A 250 mL three-neck round bottom flask was used which was equipped with a magnetic stirrer, Dean Stark trap, condenser and a nitrogen inlet.A calcium chloride drying tube attached on the top of condenser served the purpose of dry environment. At first, 50 mL of NMP was added to the 500 mL three-neck round bottom flask through syringe and then HNTs (7g, 0.027 moles) and potassium carbonate (5.53g, 0.040 moles) were mixed to it. Besides, 10 mL of dry toluene was used as an azeotropic agent. Afterwards, the reaction mixture was heated to 140 °C for 3 hours so that it is dehydrated and then the temperature was raised up till 190 °C. At 190 °C, 4-Nitrophthalonitrile(4.7g, 0.027 moles)was added to the flask and the reaction mixture was refluxed for 18 hours at 190 °C.The formation of product was confirmed by TLC. Afterwards when the solution was cooled down, dark brownish-black colored product was diluted with 50 mL of tetrahydrofuran then washed many times with THF and methanol/water (80/20), filtered, and dried overnight at 80°C in vacuum oven.

The product formed from 1st step (abbreviated as f-HNTs) was treated with different species which resulted in four different kinds of functionalized halloysite nanotubes (f-HNTs) which are:

2.3.1 Amidoxime modified f-HNTs:

The synthesis of amidoxime modified HNTs involved dissolution of modified HNTs (2 g) in ethanol in a 250 mL round bottom flask and then hydroxylamine solution (50 wt. % in H_2O) (0.15 mL) was added with continuous agitation at 70 °C for the duration of 3 hours. With the passage of time, dark brown colored precipitates were formed. The reaction was checked with TLC plate from time to time till the reactant was completely consumed. Later on, centrifugation was carried out to separate the precipitates,washed and dried under vacuum.

2.3.2 Hydrazine modified f-HNTs:

In a 250 mL three necked round bottom flask, 2 g of modified HNTs were taken and dissolved in ethanol, followed by the addition of hydrazine solution (0.17 mL). The reaction mixture was stirred for the duration of three hours at 70 °C. As the reaction proceeds, the color of solution gets darker and dark brown precipitates appeared which was checked by TLC. For the isolation of product, reaction mixture was centrifuged which were then washed with ethanol and dried under vacuum [128].

2.3.3 Ethylenediamine modified f-HNTs:

Modified HNTs (2 g) were dispersed in ethanol in a round bottom flask followed by the addition of ethylenediamine (0.35 mL) with constant stirring at 70 °C for 3 hours. As the reaction advances, precipitates were formed. The verification of product was done by TLC so that no reactant is left behind. Afterwards, centrifugation was performed on the contents of flask for the isolation of precipitates. The dark brown colored product was washed with ethanol and then dried overnight in vacuum oven.

2.3.4 Diethylenetriamine modified f-HNTs

The synthesis of diethylenetriamine modified HNTs was initiated by dissolving 2 g of modified HNTs in ethanol in a 250 mL round bottom flask, followed by theaddition of diethylenetriamine (0.56 mL) with non-stop stirring for the period of 3 hours at 70 °C. As the reaction goes on, precipitates were formed. The completion of the reaction was tested by TLC which showed successful formation of product. Subsequently, the reaction mixture was centrifuged at 4500 rpm for the separation of precipitates, washed and dried overnight in vacuum oven at 60 °C.

2.4 Reaction Scheme:

Chapter 3: Results & Discussion

3.1 Characterization Techniques:

The pristine and functionalized halloysite nanotubes (HNTs) are verified by various characterization techniques which are given as under:

1. Fourier Transform Infrared Spectroscopy (FTIR)
2. X-ray Diffraction Technique (XRD)
3. Scanning Electron Microscopy (SEM)
4. Energy Dispersive X-ray Spectroscopy (EDX or EDS)

3.2 Fourier Transform Infrared Spectroscopy (FTIR):

Principle

The core idea of infra-red spectroscopy revolves around the vibrational motion which the molecules possess. Those molecules display IR bands whose dipole moment varies.

Mechanism

In FTIR (Figure 3.1), sample is being stroked by light radiation having frequencies in extensive range. The detector signal corresponds to that particular frequency which the molecule absorbed. The resultant IR band gives us data and properties about unknown structure. FTIR involves measurement of intensity change corresponding to a peculiar frequency when it interacts with a specific sample. Besides, intensity ratio may also be determined using this technique. By plotting the intensity ratio against frequency, infrared spectrum is generated. FTIR range falls between 4000 cm^{-1} to 400 cm^{-1}. It is a non-destructive procedure from which unknown information about molecule may be gathered from fingerprint region.

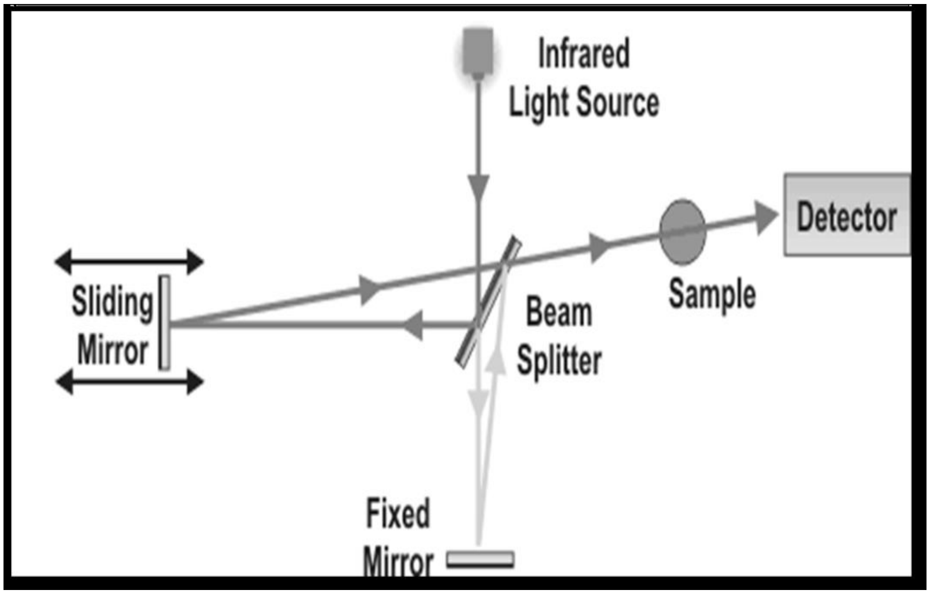


Figure 3.1 Operational working of FT-IR

ATR-FTIR spectra of pristine and functionalized HNTs are given in Figure 3.2 below:

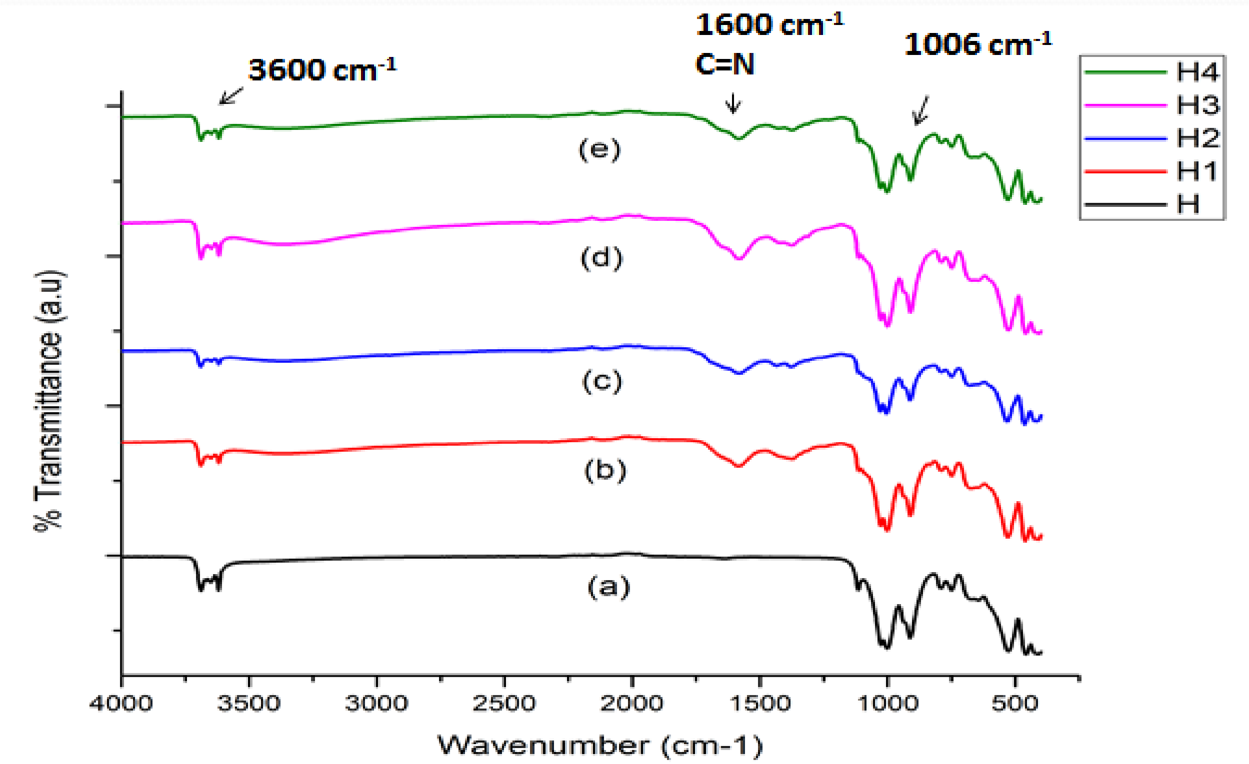


Figure 3.2FTIR spectra of (a) H (b) H1 (c) H2 (d) H3 and (e) H4

As shown in figure 3.2,before functionalization, absorption bands at 3696 cm^{-1}and 3656 cm^{-1}are ascribed to the vibrations of inner surfaceO-H groups of aluminol (Al-O-H).Bands of OH, Si–O–Si and Al–O–H fall in the region 1000 cm^{-1} and 400 cm^{-1}. Bending vibration at 1631/1593 cm^{-1}exhibits interlayer water while its stretching vibration is observed at 3531 cm^{-1}. Likewise, a prominent absorption band at 1006 cm^{-1}reflects the presence of Si-O-Si present on the outer surface of HNTs. As seen in the figure, bending vibration of Al–OH is present at 910 cm^{-1}whereas stretching and bending vibration for Si-O are shown in the region 1000-1100 cm^{-1}and 450-550 cm^{-1}respectively.

After functionalization of HNTs, various new bands are observed as shown in figure. Stretching vibration of C=N is observed at 1687 cm^{-1} whereas prominent aromatic C=C stretch is witnessed at 1600 cm^{-1} and 1435 cm^{-1}. Similarly, absorption band at 2950 cm^{-1} and 3000 cm^{-1} are ascribed to the CH_2 vibrations (symmetric and asymmetric). N-H stretching was also observed in the region 3500-3600 cm^{-1}which might be overlapped with the O-H stretch of inner surface hydroxyl groups of HNTs. This may result in the absorption band of lower intensity in 3500-3600 cm^{-1} region. Besides, N-H bending is observed at 1556 cm^{-1}. It is to be noted over here that absorption bands in the region around 3350 and 3080 cm^{-1} in f-HNTs are seen which may be ascribed to stretching vibrations of N−H and C−H respectively.The absorption band of C-N appears at 1304 cm^{-1}. These results reflect that the functionalization is successfully being done on the surface of HNTs resulting in four different kinds of functionalized HNTs like H1, H2, H3, H4 as shown in figure3.3:

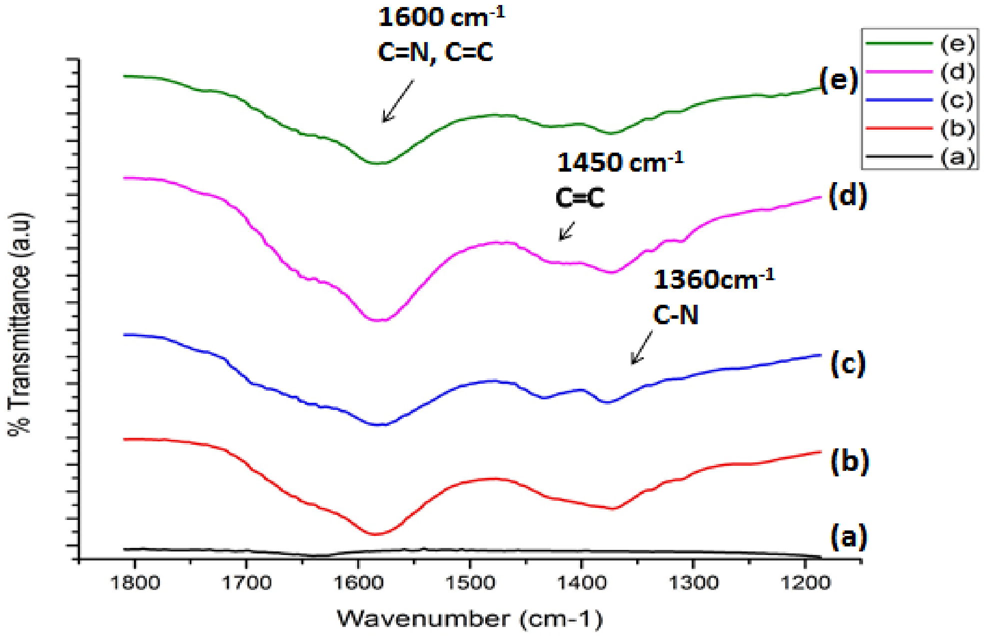


Figure 3.3FTIR spectra of (a) H (b) H1 (c) H2 (d) H3 and (e) H4

Infrared spectroscopy method was used to determine whether the functional groups had been grafted onto the surface of nanotubes. It is evident from figure 3.3 that surface of halloysite nanotubes (HNTs) are successfully functionalized. The characteristic bands of functionalized HNTs (f-HNTs) are given in the following Table 1.6:

Table 1.6 IR bands of f-HNTs

No.	Functional Groups	Absorption bands
1	O-H stretching of inner surface hydroxyl groups	3696, 3656 cm^{-1}
2	O-H stretching of water	3450 cm^{-1}
3	Asymmetric stretching of N-H	3500 cm^{-1}

4	Symmetric stretching of N-H	3400 cm^{-1}
5	C-H stretching	2950-3000 cm^{-1}
6	Symmetric stretching of Si-O-Si	1100 cm^{-1}
7	C=N stretch	1650 cm^{-1}
8	C=C stretch of benzene	1650, 1435 cm^{-1}

3.3 X-ray Diffraction (XRD):

XRD gives in-depth information about the sample. XRD involves striking of X-ray beam upon a material that is actually placed at angle θ. Some of the rays get through while the rest undergo deflection or diffraction (bending). Figure 3.4 below depicts that path difference exist between plane 1 and 2. If this path difference is equal to or a multiple of wavelength, rays overlap and support one another to produce constructive interference ($2d \sin\theta = n\lambda$). In this way, various properties of that particular sample like cell volume, crystalline structure, lattice parameters or crystallographic dimensions, phase and crystallite size may be unleashed[129].

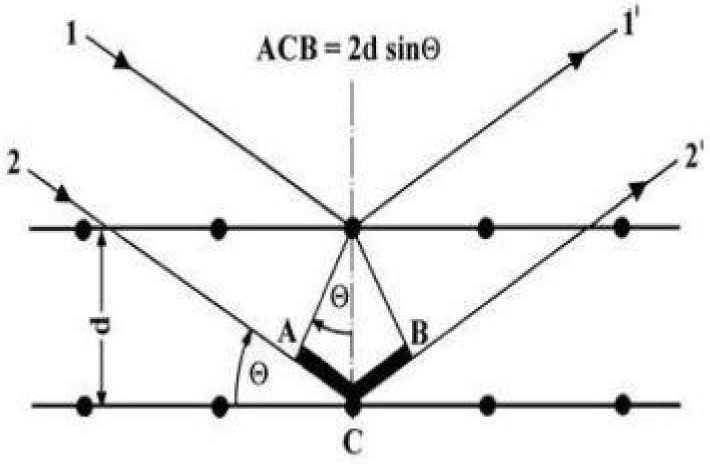


Figure 3.4 X-ray Diffraction Phenomena

X-ray diffraction (XRD) was performed with a Rigakudiffractometer having incident wavelength of Cu Kα (λ = 1.542Å) [130].

Crystallite size of halloysite nanotubes was determined from FWHM by Scherer's formula as given below:

$$\boldsymbol{D = \frac{k\lambda}{\beta cos\theta}}$$

Where,

D = Diameter of crystallite size

k = 0.89 (shape factor)

λ = Wavelength of Cu Kα (1.542Å)

β = Full Width at Half Maximum(FWHM)

θ = Bragg's angle in degrees [131]

X-ray diffraction method was employed to study the crystalline phase. XRD plots as shown in figure 3.5 represent peak position at 12.00°, 20.14°, 24.85°,35.09°, 45°, 55° and 62° that correspond to (001), (020), (002) hkl values. These values are in line with the Joint Committee on Powder Diffraction Standards, JCPDS Card # 29-1487. The XRD patterns of pristine and functionalized HNTs are given in figure 3.5.

The diffraction peak at 12.00 ° shows the presence of (0 0 1) plane in raw HNTs (H). This plane reflects the tubular shape of halloysite nanotubes. Furthermore in XRD plot H, a sharp reflection at 20.14° and 24.85° which correspond to second order (0 2 0) and (0 0 2) planes.The d values of 0.733 nm, 0.411 nm, 0.358 nm, and 0.254 nm were determined from their respective peaks at 12.00°, 20.14°, 24.85°, and 35.09° respectively, that belongs to HNTs. (Figure 3.5)

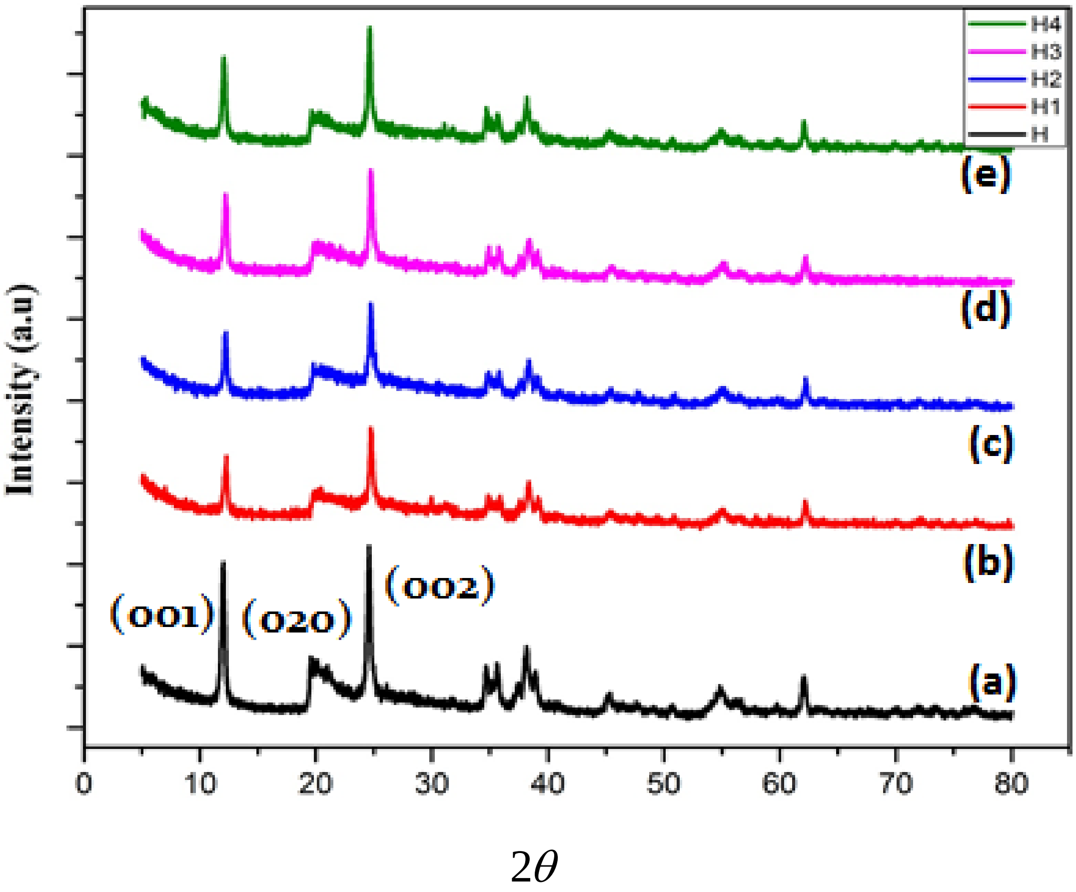


Figure 3.5XRD patterns of (a) H (b) H1 (c) H2 (d) H3 and (e) H4

As shown in figure 3.5, crystalline phase of pristine and functionalized HNTs are retained and there is no shift in diffraction peaks. This suggests that the basic structure of nanotubes remain same after functionalization of its surface. Moreover, reduction in peak intensity in H1, H2, H3 and H4 as compared to H may reflect the successful modification of outer surface of halloysite nanotubes.Nevertheless, it is clear from figure 3.5 that no peak shift has been taken place along (001) and other planes which may indicate that no intercalation has been observed. Rather no peak shift in XRD patterns reflects that the central mechanism of chromium removal is adsorption of chromium on the external surface of HNTs instead of intercalation.

3.4 Scanning Electron Microscopy (SEM):

In SEM when electron beam is focused upon sample and surface is scanned, images are produced. Upon interaction, ranges of signals are generated that gives data about material like surface morphology, crystal structure, material orientation and its composition. Most of the time, data collection is carried out over a particular area which results in the making of 2D image. Scanning of electron beam takes place in a raster scan pattern and signal overlaps with beam position to generate an image. A high vacuum is a mandatory requirement in SEM and samples must be in dry form.Usually SEM can easily reach a resolution of 1 nm.

As discussed, diverse forms of signals are produced in SEM which may be:

- Back-scattered electrons (BSE)
- Secondary electrons (SE)
- Specimen current
- Cathodoluminescence (CL)
- Transmitted electrons

Figure 3.6 shows that secondary electrons are released quite close to the surface of sample. Resultantly, minute details are unleashed even less than 1 nm leading to images of high quality resolution. BSE are electrons arising from deep down the sample through elastic scattering. Consequently, their resolution is smaller as compared to SE.SE and BSE are usually employed in imaging. SE tells the surface morphology of samples while BSE are pivotal in multiphase samples where composition is find out by looking on contrasts. BSE gives an idea about distribution of these multiphase samples rather than their identity.

SEM images possess an enormous depth of field because of fine electron beam. Resultantly, a 3-D image is generated that tells properties about surface. Broad number of magnifications exist in SEM from 10 X to greater than 500,000 X [132][133].

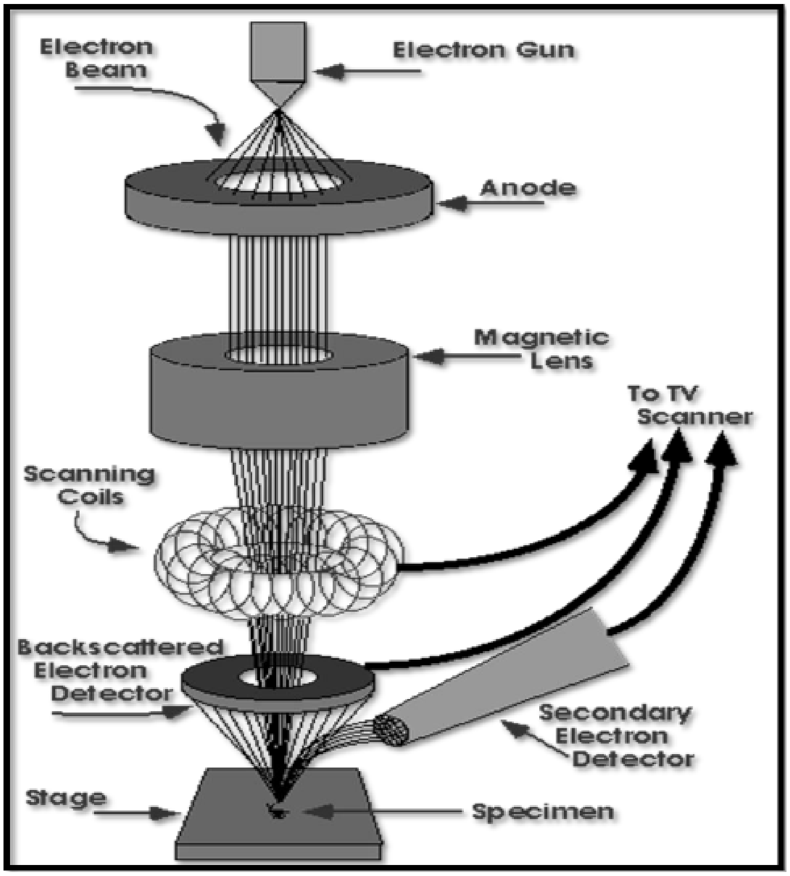


Figure3.6 Working of SEM

Scanning Electron Microscopy (SEM) was employed to determine the morphological characteristics of pristine HNTs (H) and functionalized HNTs.(H1, H2, H3, H4)as shown in Figure 3.7 (a to e). The SEM images suggest that the H, H1, H2, H3, H4 are made up of rod shaped tubes whose lumen (inner diameter) is 15-20 nm, length of 0.5 - 2 mm and an external diameter of 50-100 nm.The specific surface area of pristine HNTs is 64.21m^2/g and owing to its greater surface area, it provides lot of adsorption sites which may be used for heavy metal extraction. The tubular form of HNTs is well conserved before and after functionalization which shows that modification has been done on the external surface rather than the lumen.Moreover as shown in figure 3.7, the surface of halloysite nanotubes in f-HNTs become cloudy, coarser andthicker as we progresses from H1 to H4.This reflects the successful functionalization over the surface of halloysite nanotubes (HNTs).Besides, pristine and functionalized HNTs (H, H1, H2, H3, H4) are linear and their ends are open.Such morphology aids well in heavy metal ion extraction through adsorption on surface.

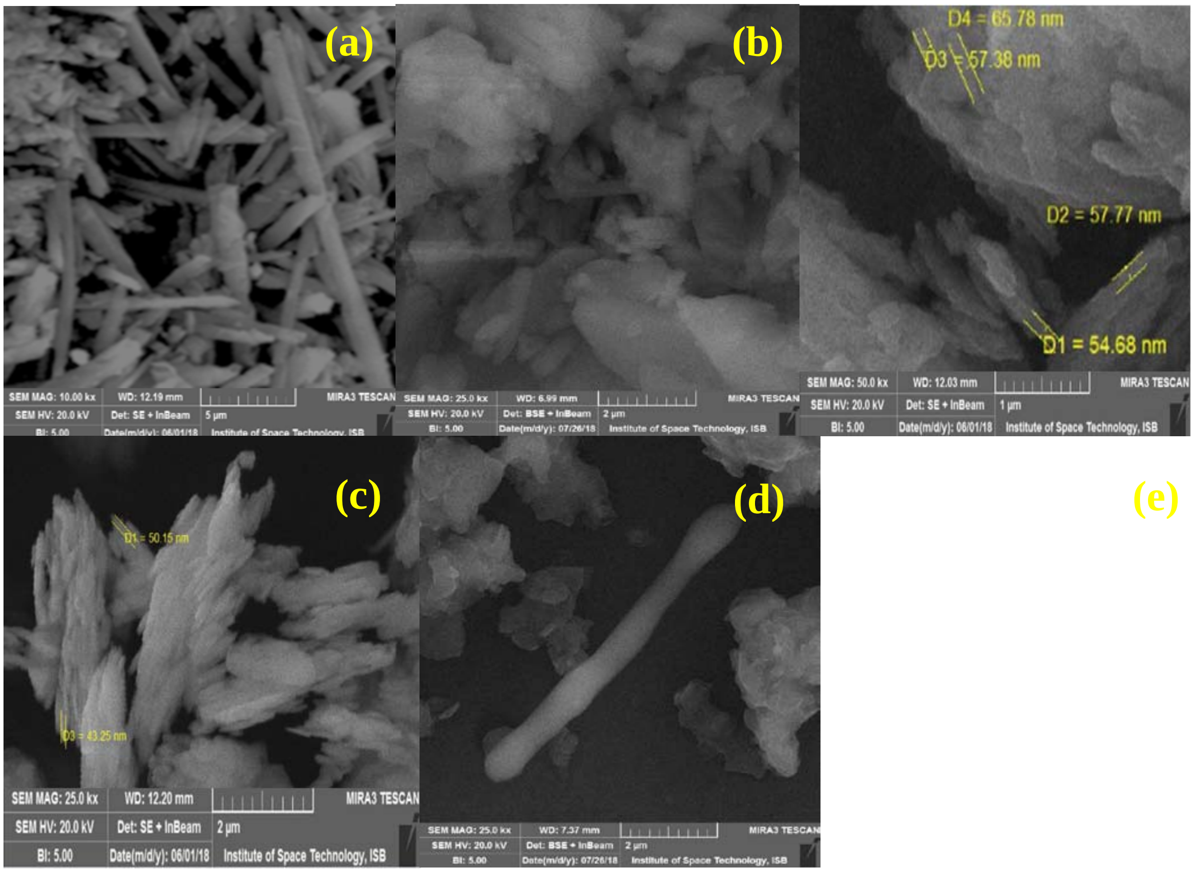


Fig3.7 SEM images of (a) H, (b) H1, (c) H2, (d) H3, (e) H4

3.5 Energy Dispersive X-ray Spectroscopy (EDS or EDX):

Principle:

The main principle of EDS is that every element possesses an exclusive structure of atoms which permits an exclusive group of peaks for its corresponding emission spectrum.

Mechanism:

When a beam of peculiar energy strikes the sample containing electrons in ground state, an inner electron is excited and gets knocked out. After its expulsion, a hole is produced and to fill that space, an electron from adjacent cell falls into inner shell (Figure 3.8). Because of this energy difference between shells, X-rays are emitted whose energy may be determined from the energy dispersive spectroscopy. Since every element possesses specific energy, this helps in finding the elemental composition of concerned substance.[134].

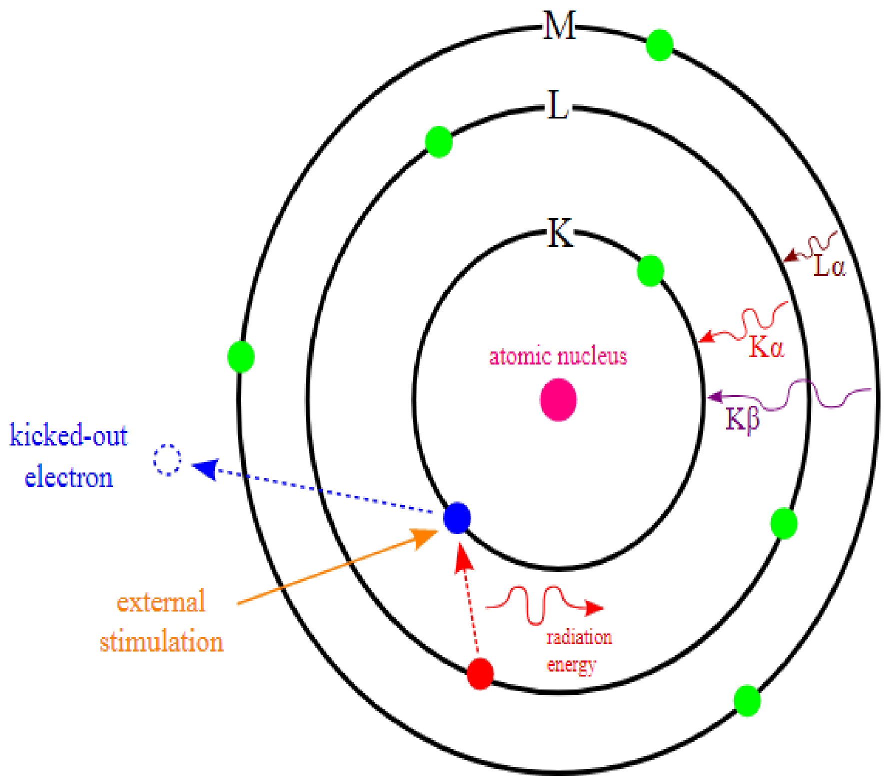
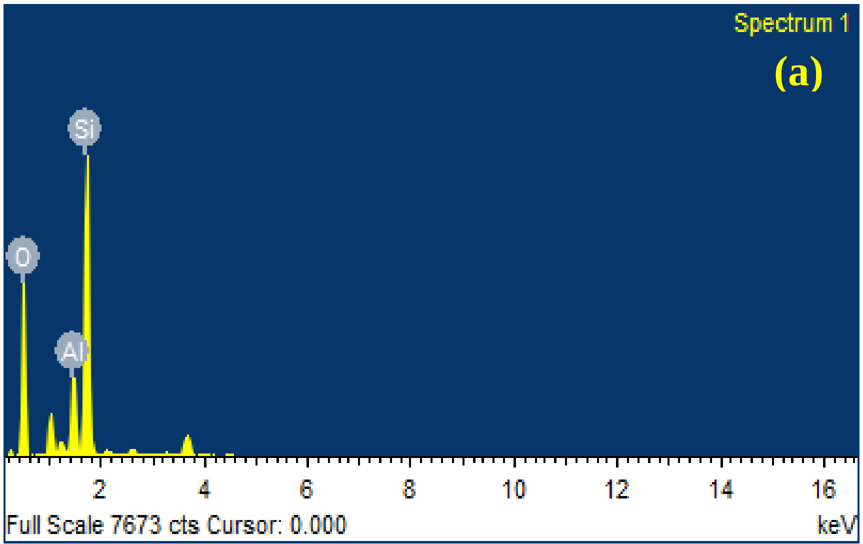
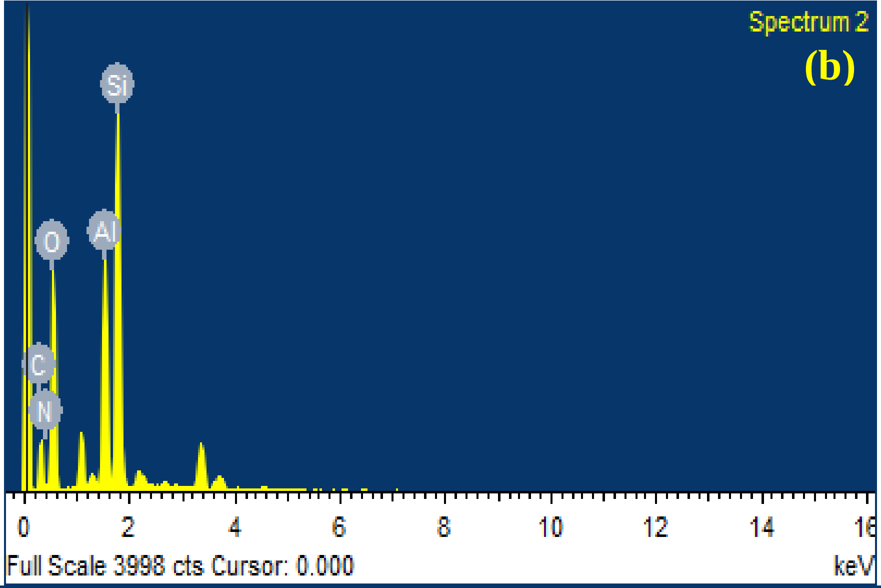
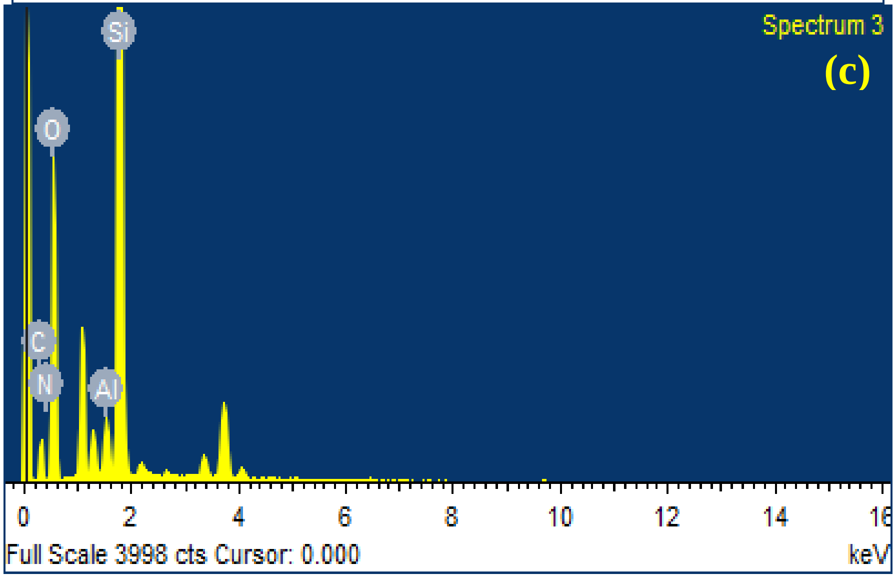


Figure3.8 EDS Mechanism

EDS may be used to assess the elemental composition of a particular substance, their distribution maps, % purity and relative abundance. The accuracy of all these depend upon factors like samples' nature and likewise. EDSspectra of HNTs and f-HNTs are shown in figure 3.9 (a to e):


Spectrum 1
(a)
Si
O
Al
2
4
6
8
10
12
14
16
Full Scale 7673 cts Cursor: 0.000
keV


Spectrum 2
(b)
Si
O
Al
C
N
0
2
4
6
8
10
12
14
16
Full Scale 3998 cts Cursor: 0.000
keV


Spectrum 3
(c)
Si
O
C
N
Al
0
2
4
6
8
10
12
14
16
Full Scale 3998 cts Cursor: 0.000
keV

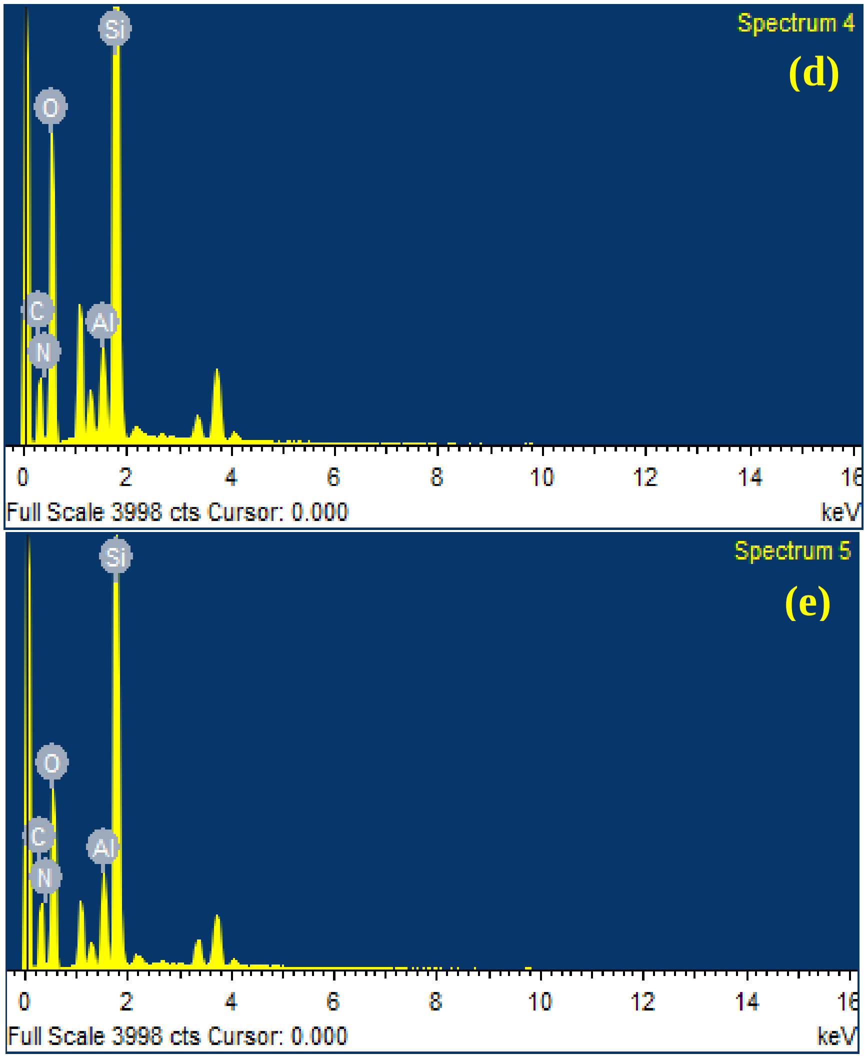


Fig3.9 EDX spectra of (a) H, (b) H1, (c) H2, (d) H3, (e) H4

Fig. 3.9 (a) suggests that in pure HNTs, aluminium, silicon and oxygen is present only. While in case of (b), (c), (d) and (e), additional peaks of carbon and nitrogen are also observed inaddition to aluminium, silicon and oxygen. This confirms the successful functionalization of outer surface of halloysite nanotubes (HNTs).In figure 3.9(a), elemental composition reveals the presence of aluminium and silicon with 19.17 and 20.44 weight percent, respectively.

3.6 Heavy Metal Extraction Study:

The efficacyof prepared f-HNTs was tested by utilizing them for the extraction of Cr (VI) ions present in wastewater. Parameters like pH, contact time,metal concentration directly affects the HM adsorption. So series of experiments were performed in batches so as to optimize these parameters to get maximum adsorption. Time was witnessed from 10 minutes to anhour, pH range was kept from 2-10 while metal concentration was taken from 10 ppm to 150 ppm. Adsorption isotherm (Langmuir) study was also carried out to assess the favorability of adsorption.

% removal of all four f-HNTs were determined using equation below:

$$\%\ \mathbf{Removal} = \frac{\mathbf{C_i - C_e}}{\mathbf{C_i}} * \mathbf{100}$$

Where,

C_i = initial concentration

C_e = equilibrium concentration

3.6.1 Contact time effect:

In order to optimize the contact time, batch experiments were carried out. 10 mL of 10 ppm Cr (VI) solution was taken and afterwards, 10 mg of f-HNTs (H1) was added to Cr (VI) solution at various time durations from 10 minutes till one hour on a shaker at the rate of 125 rpm.Later on, samples were centrifuged and filtered. The filtrate was checked for Cr (VI) concentration by AAS (Atomic Absorption Spectroscopy).

It was observed that adsorption took place within 10 minutes at an exponential rate and contact time of 30 minutes was enough to establish equilibrium. Fig. 3.10 (a) shows that the percentage efficiency for chromium removal was 91 % with the amidoxime modified f-HNTs (H1).

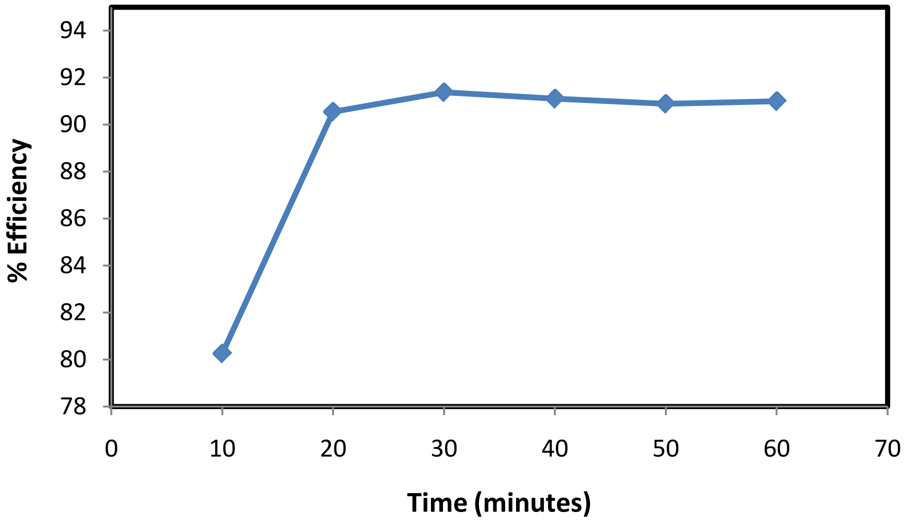


Figure3.10 (a) Trend of chromium extraction using f-HNTs (H1)

Similarly, contact time was also assessed for other adsorbents as well like hydrazine modified f-HNTs (H2), EDA modified f-HNTs (H3) and DETA modified f-HNTs (H4) using same protocol. Fig. 3.10 (b), (c) and (d) shows that the % efficiency for chromium removal in case of H2, H3 and H4 are 94%, 66% and 58% respectively. The equilibrium was achieved in 30 minutes.

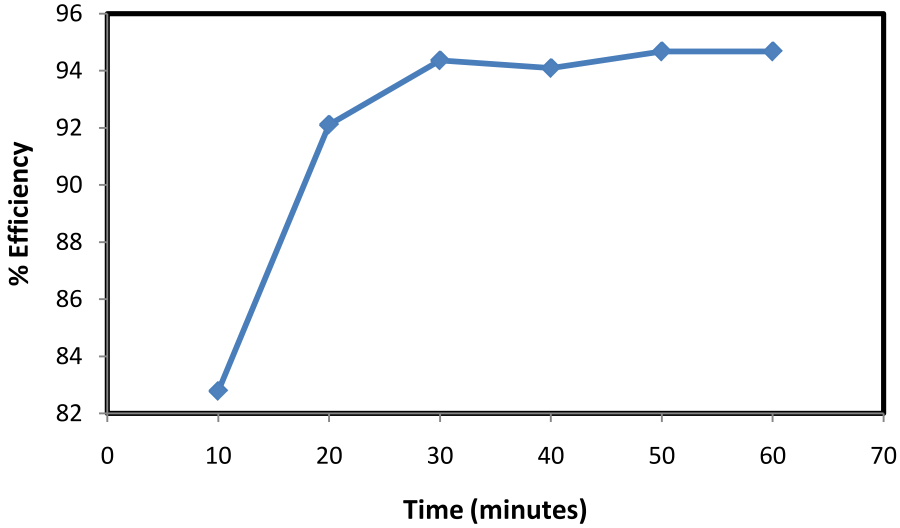


Figure 3.10 (b). Trend of chromium extraction using f-HNTs (H2)

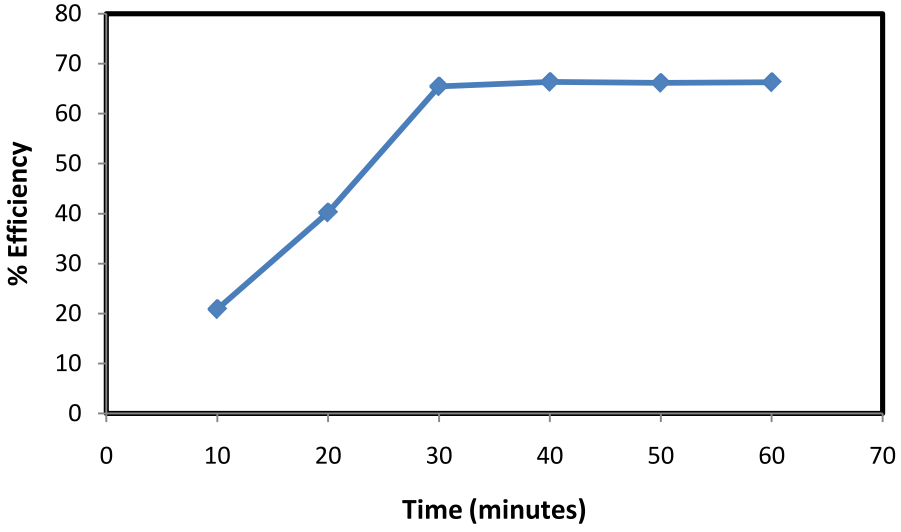


Figure 3.10 (c). Trend of chromium extraction using f-HNTs (H3)

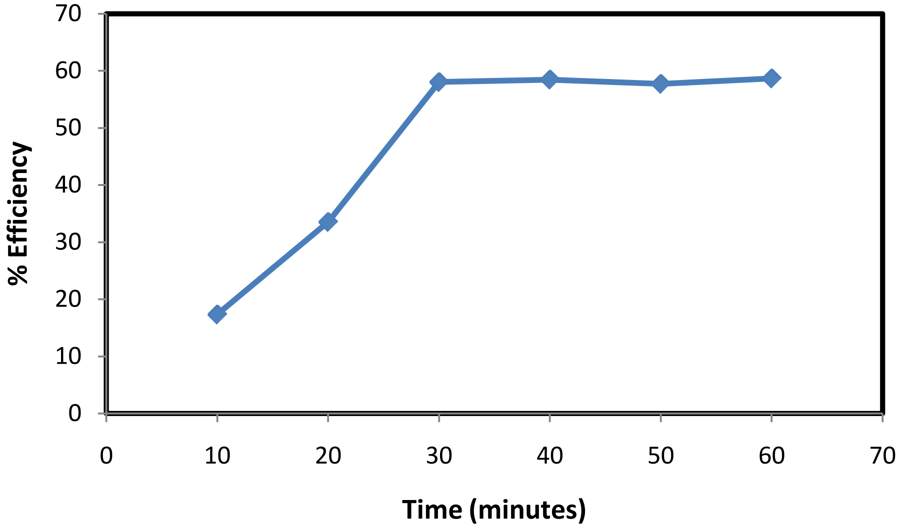


Figure 3.10 (d). Trend of chromium extraction using f-HNTs (H4)

Figure 3.11 given below provides a comparison of adsorption efficiency shown by four different f-HNTs (H1, H2, H3 and H4):

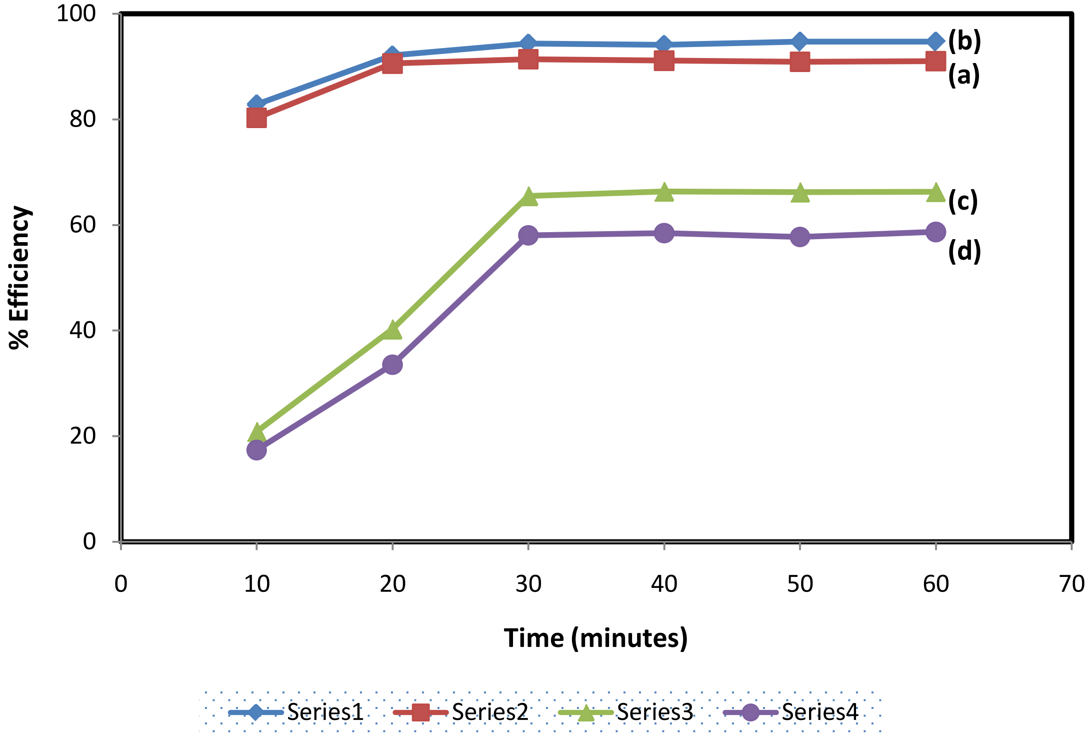


Fig. 3.11 Comparison of % removal of f-HNTs (a) H1 (b) H2 (c) H3 and (d) H4vs time

3.6.2Effect of pH:

pH is an essential constraint that significantly alters the adsorption of heavy metal ions. To study the effect of pH upon the adsorption of Cr (VI), 10 mg of f-HNTsis dissolved in 10 mL of 10 ppm solution of Cr (VI). Afterwards, 3-4 mL of already prepared buffer solution of various pH values (2–10)were separately added in respective glass bottles. The respective samples were kept in a water bath for shaking at an optimized time of 30 minutes. Later on, centrifugation was performed on the samples and then filtered. The left-over chromium in the filtrate was assessed by AAS.

The results of % removal of Cr (VI) vs pH are given in figure 3.12 below. It was observed that adsorption efficiency is greatly affected by the pH and hence a pH dependent parameter. The figure 3.12 shows that there is a rapid surge inadsorption efficiency as we move from pH 2 to pH 3. Afterwards, it showed a constant behavior as we move from pH 3 to pH 5. This is the point where maximum Cr (VI) was adsorbed on the surface of functionalized HNTs. From pH 6 onwards, a significant fall was noticed till pH 8. A slight decrease or more or less constant trend was witnessed in adsorption efficiency as we move from pH 8 to pH 10.The optimized pH for maximum Cr (VI) extraction was in range of pH 3 to 5.

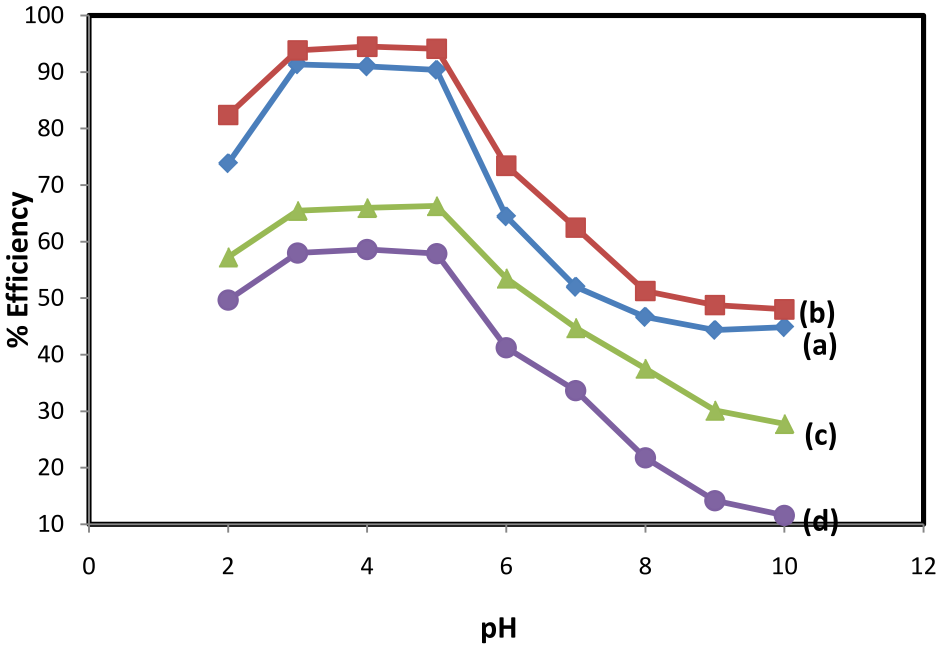


Fig. 3.12: Comparison of % removal of f-HNTs (a) H1 (b) H2 (c) H3 and (d) H4 vs pH

Figure3.13 (a) as given below shows the % removal of chromium by amidoxime modified f-HNTs (H1). It was noticed that the % adsorption was 91% in the pH range 3-5. At low pH, Cr (VI) exists in the state of $HCrO_4^-$ and $Cr_2O_4^{2-}$in the pH range 2.0-6.0 while CrO_4^{2-} is the prevailing form when pH is greater than 6. Under acidic conditions, NH_2 groups present on the surface of functionalized HNTs abstracts a proton from chromate anion $HCrO_4^-$ resulting in the formation of $NH_3^+$and subsequently, high adsorption efficiency, as shown in the figure 3.13 (a), is achieved by electrostatic attraction between negatively charged chromate anion and positively charged NH_3^+ groups.

$$-NH_3^+ \quad + \quad HCrO_4^- \quad \text{----}\rightarrow \quad -NH_3^+ \ldots\ldots HCrO_4^-$$

As the pH rises, the capability of amine groups to protonate falls leading to drop in Cr (VI) uptake. Besides, it may also be possible that Cr (VI) is converted into Cr (III) by the formation of $Cr(OH)_3$ which resulted in enhanced removal of chromium.

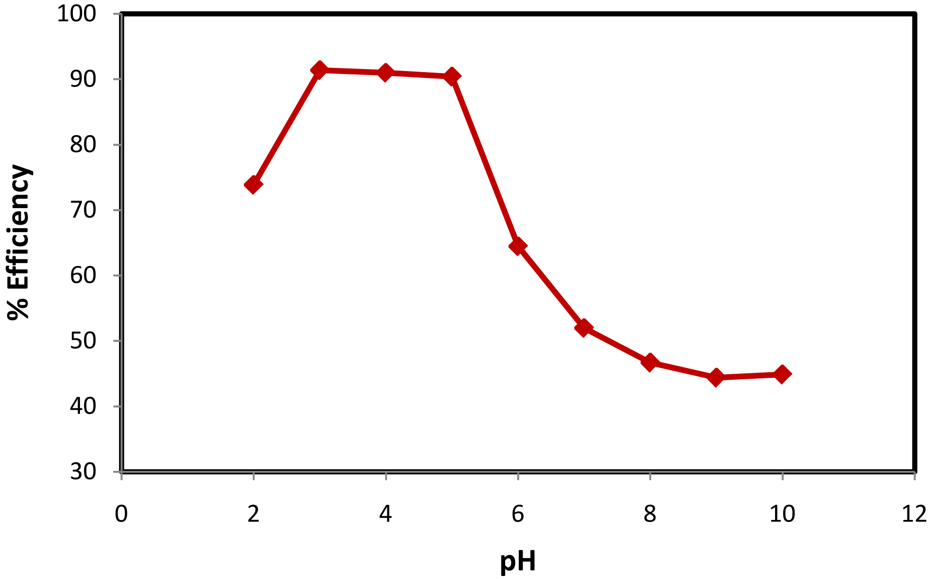


Figure. 3.13 (a) % efficiency of amidoxime f-HNTs (H1)vs pH

Similarly, pH effects were also observed for other adsorbents. Figure 3.13 (b) shows the adsorption efficiency by hydrazine modified f-HNTs (H2) as given below:

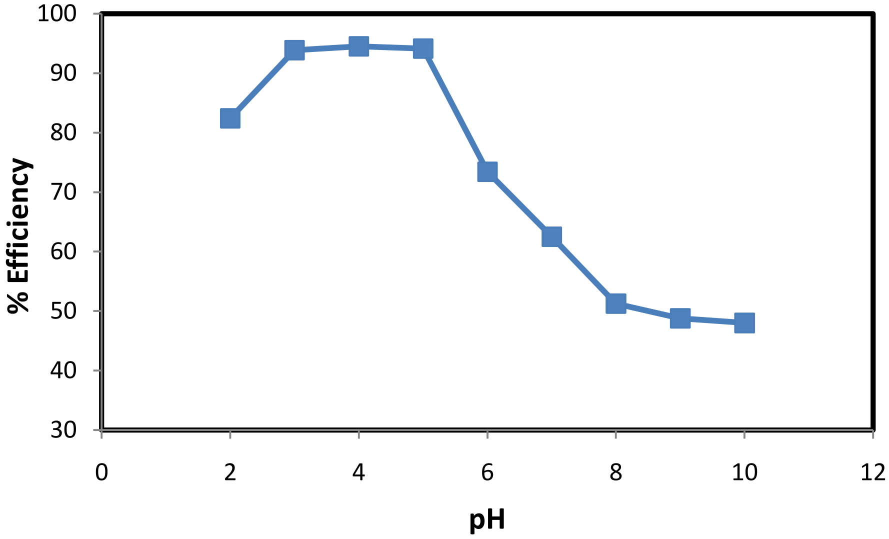


Figure. 3.13 (b) % efficiency of hydrazine modified f-HNTs (H2)vs pH

The adsorption efficiency reaches a record high of 94% in case of adsorption by hydrazine modified f-HNTs within 30 minutes in a wide pH range of 3-5. This may be ascribed to the presence of greater amino groups in H2 as compared to that of H1. The NH_2 groups are easily protonated at low pH to form NH_3^+ which will adsorb chromium anion by electrostatic attraction. As the graph shows that adsorption efficiency is decreasing gradually as we move from pH 6 onwards. That may be due to the reason that concentration of OH^- ions increases with the increase in pH which caused repulsion between metal ion and adsorbent leading to decrease in adsorption efficiency.

Likewise, % removal of Cr (VI) by EDA modified f-HNTs (H3) was also assessed by using 10 mg of H3 in 10 ppm Cr (VI) solution with a pH range from 2 to 10 in an optimized time of 30 minutes.

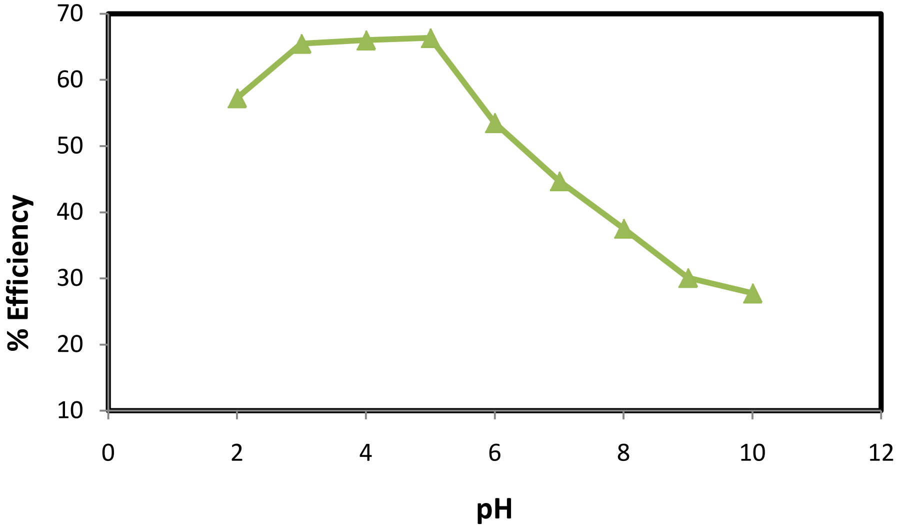


Figure.3.13 (c)% efficiency of EDA modified f-HNTs (H3) vs pH

Fig. 3.13 (c) shows that the adsorption efficiency achieved by EDA modified f-HNTs (H3) was 66% which is comparatively lesser than that of H1 and H2. The NH_2 groups of EDA will be protonated in the same way as discussed in the case of H1 and H2. Nevertheless, ethylenediamine (EDA) being a bidentate molecule having chelating nature, should have shown greater efficiency but due to the hindrance between the molecules, the efficacy with which the EDA would adsorb the chromium, is affected resulting in adsorption efficiency of 66%.

The adsorption efficiency of DETA modified f-HNTs (H4) were also analyzed under optimized conditions at various pH values from 2 to 10 as shown in figure 3.13 (d).

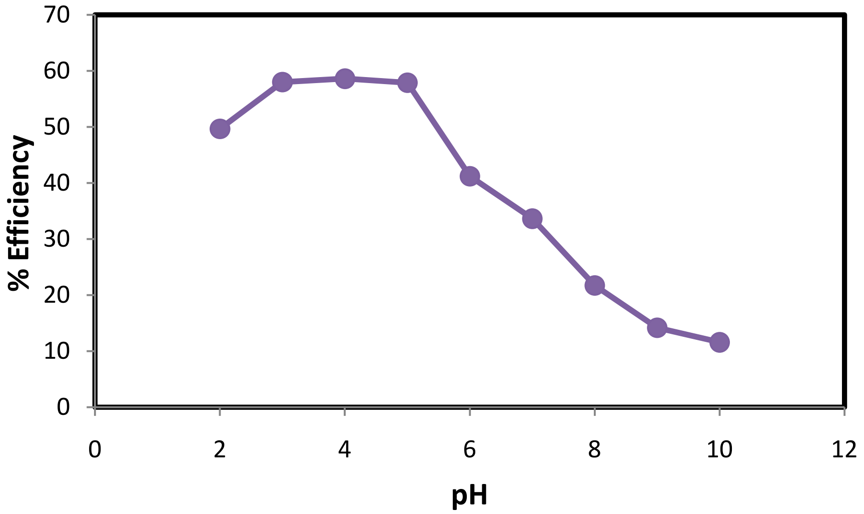


Figure.3.13 (d) % efficiency of DETA modified f-HNTs (H4) vs pH

Figure.3.13 (d) shows that the adsorption efficiency in case of DETA modified f-HNTs (H4) was found to be 58% which is relatively lesser than that of H1, H2 and H3. NH_2 groups of DETA are protonated when the pH is low, forming NH_3^+ which adsorbs chromate anions by electrostatic attraction. Nevertheless, DETA being a tridentate ligand, may have generated greater steric hindrance between the ions which results in significant fall in adsorption efficiency Besides,as shown in figure 3.13 (d), deprotonation take place at high pH from 8 to 10 and the adsorption efficiency in case of DETA modified f-HNTs (H4) reached a drop low of 12 %.

3.6.3 Effect of Metal Concentration:

The change of metal concentration upon the adsorption efficiency of Cr (VI) was examined using metal concentration from 10-150 ppm with a pH of 3. This effect of various metal ion concentration upon the adsorption efficiency and adsorption capacity by four different kinds of adsorbents (H1, H2, H3 and H4) is shown in figure 3.14 below:

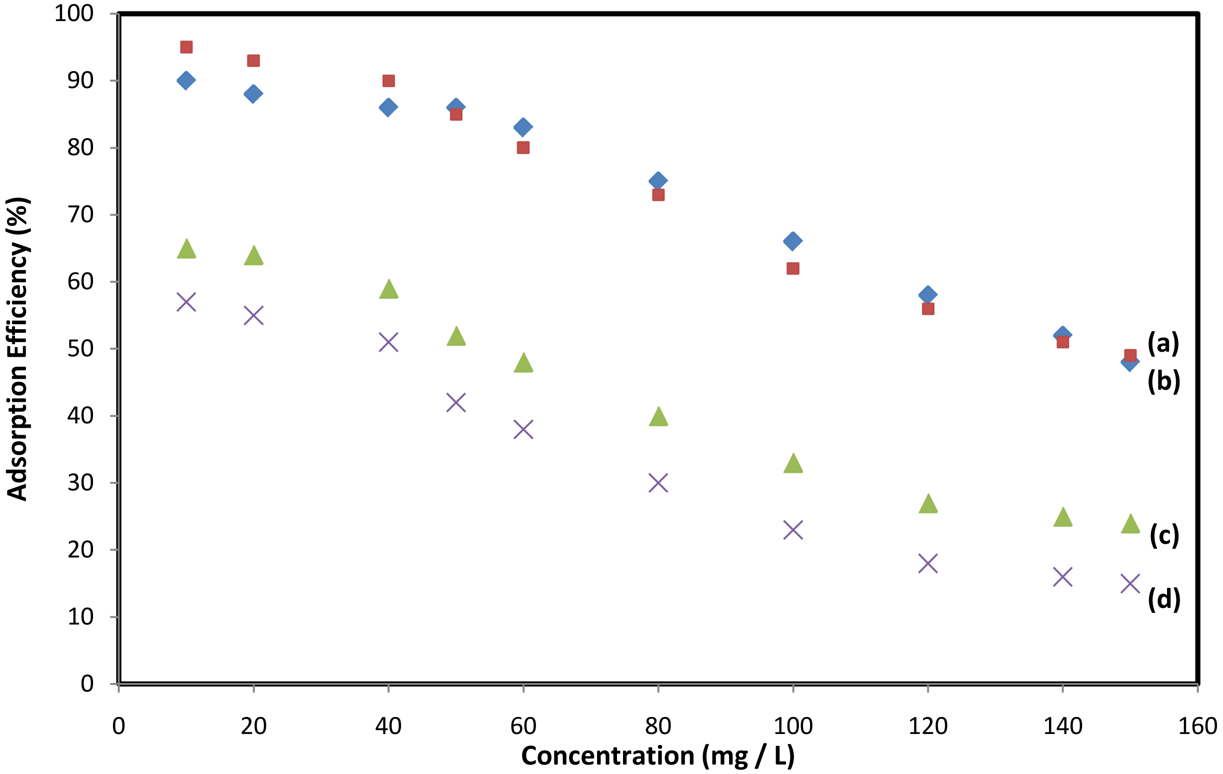


Figure.3.14 Effect on adsorption efficiency vs Metal ion concentration (a) H1 (b) H2 (c) H3 (d) H4

Figure 3.14 reflects that as the concentration of metal ion is increasing from 10 to 150 mg/L, there is decrease in the adsorption efficiency. Maximum adsorption took place at 10 and 20 ppm in all adsorbents while a drop low of 15-25% was witnessed around 150 ppm. This decrease may be attributed to the reason that the available sites for adsorption are less which are already occupied and with the increase in metal concentration, the adsorption efficiency is reduced.

3.7 Adsorption Isotherm Study:

To assess the favorability of adsorption protocol, Langmuir adsorption isotherm was employed.

3.7.1 Langmuir adsorption isotherm

This model is usually employed when the gas phase is being adsorbed on adsorbent's surface (solid). According to this isotherm, adsorption protocols are treated as monolayered since the active sites of homogeneous nature upon adsorbent's surface are quite inadequate. There is only one site for one metal ion. If that is filled, adsorption will stop. Graphically, constant R_L is employed which is often termed as a "separation factor". Separation factor (R_L) is a pivotal constant which tell us the favorability of adsorption to occur or not. If R_L value is greater than 1 then adsorption is highly unfavorable while if it is equal to 1 then it reflects linear process. Nevertheless, if separation factor falls between 0 and 1 then it is favorable.

$$R_L = 1 / (1 + K_L C_o)$$

Langmuir equation is given as:

$$C_e / q_e = 1/ q_m K_L + C_e 1/ q_m$$

Where,

C_o= initial metal concentration
C_e = equilibrium concentration
K_L= Langmuir constant
R_L = Separation factor [74].

By plotting Ce/qe vs. Ce, all above parameters may be determined. $1/ q_m K_L$ gives intercept while $1/ q_m$gives slope from the plot. Graphical plots of Langmuir isotherm for all four f-HNTs (H1, H2, H3 and H4) are given in following figures 3.15 (a to d):

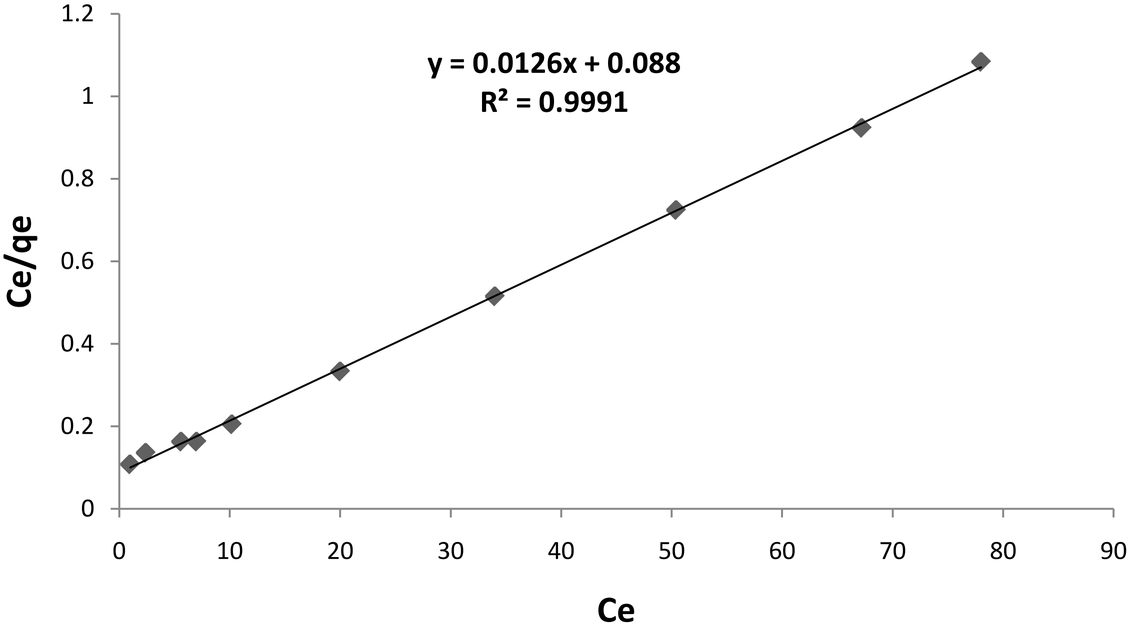


Fig. 3.15 (a)Langmuir adsorption isotherm of H1

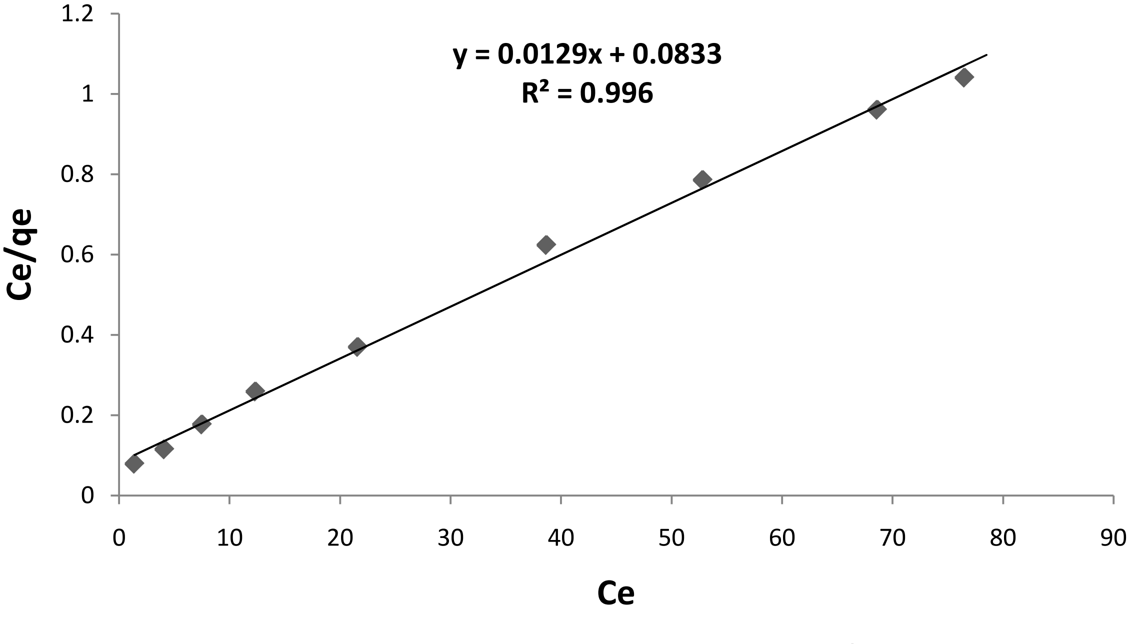


Fig. 3.15 (b) Langmuir adsorption isotherm of H2

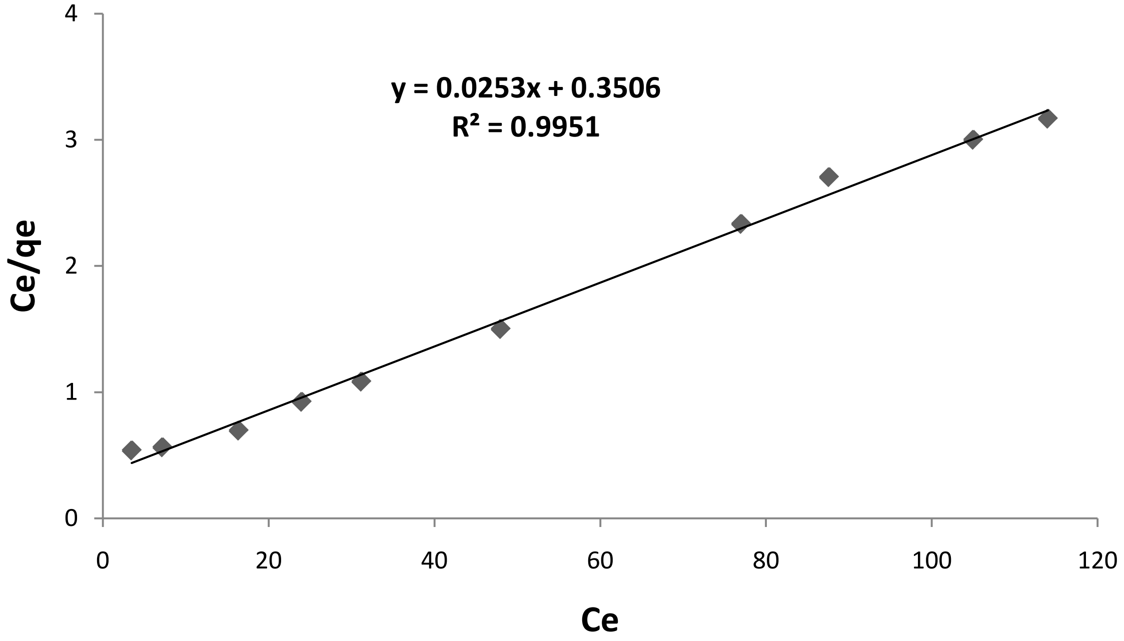


Fig. 3.15 (c) Langmuir adsorption isotherm of H3

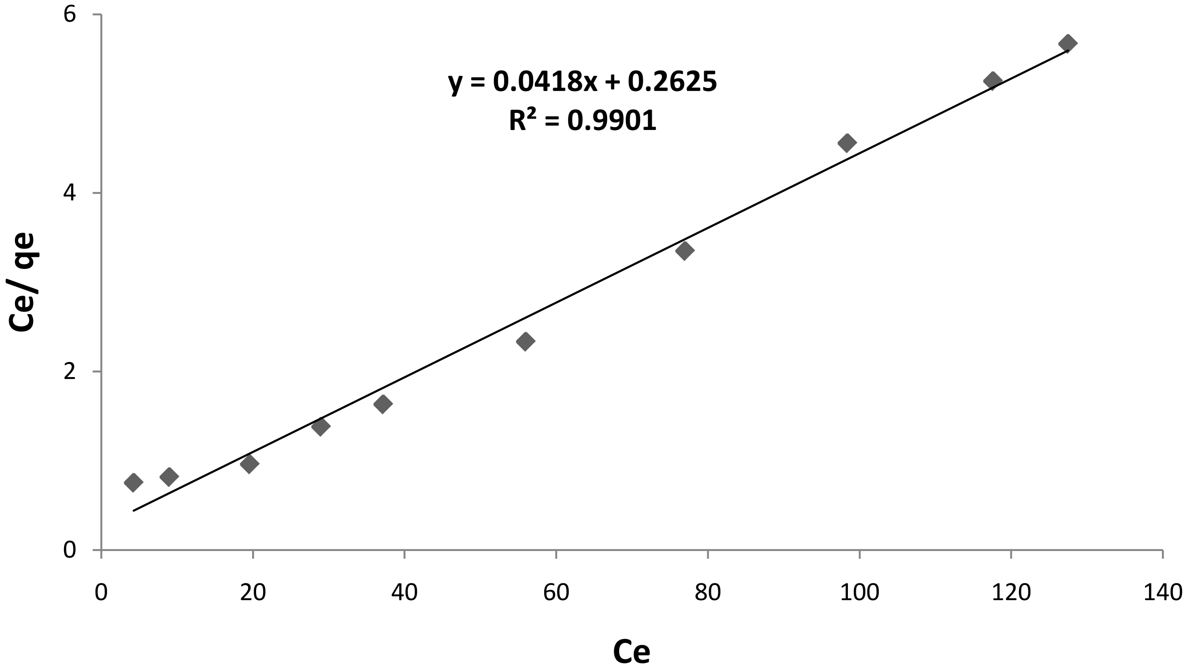


Fig. 3.15 (d) Langmuir adsorption isotherm of H4

All parameters and constants for Langmuir equation are tabulated in Table 3.2:

Table 3.2 Langmuir parameters for the extraction of Cr (VI) ions on f-HNTs

Adsorbents	**q_m**	**K_L**	**R^2**	**R_L**
H1	79.36	0.143	0.9991	0.411
H2	77.52	0.155	0.996	0.39
H3	39.52	0.072	0.9951	0.58
H4	23.92	0.159	0.9901	0.38

Figures 3.15 (a),(b),(c),(d) and Table 3.2 reflects that the adsorption process was favorable since the R_L value falls within the range of 0 to 1. Besides, straight linear fit of plots indicates the monolayer adsorption of Cr (VI) ions by f-HNTs hence following the model of Langmuir isotherm.

Chapter No 4: Conclusions

- ✓ Four different kinds of functionalized halloysite nanotubes (H1, H2, H3 and H4) were successfully synthesized.
- ✓ These f-HNTs were characterized by various techniques like FTIR, EDX, XRD and SEM that verified successful functionalization on its outer surface.
- ✓ f-HNTs were applied in the HM uptake of Cr (VI) and the results revealed excellent adsorption of >90% within first 10 minutes in case of H1 and H2 and 66% and 58% in case of H3 and H4 respectively.
- ✓ High adsorption was achieved in wider pH range i.e; 3 – 5.
- ✓ Langmuir adsorption isotherm also suggests that the adsorption process was favorable (R_L value between 0 and 1)
- ✓ The synthesized f-HNTs may be applied in the wastewater treatment plants for HM extraction.

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