Scholars International Journal of Chemistry and Material Sciences
Abbreviated key title: Sch. Int. J. Chem. Mater. Sci.
A Publication by "Scholars Middle East Publishers"
Dubai, United Arab Emirates

ISSN: 2616-8669 (Print)
ISSN: 2617-6556 (Online)

An Integrated Concept for Detoxification of Chromium (VI) Contamination in Water with Polyaniline/Micro-Crystalline Cellulose Fiber Composite

Javed Ahmed[*]
Department of Chemistry, Gauhati University, Jalukbari, Guwahati, Assam, India

Original Research Article

***Corresponding author**
Javed Ahmed

Article History
Received: 10.10.2018
Accepted: 15.10.2018
Published: 30.10.2018

DOI: 10.36348/sijcms.2018.v01i02.002

Abstract: In this short communication, an integrated process concept for detoxification of chromium (VI) contaminated water with Polyaniline/MCC composite is proposed. The preparation of composite involved in-situ oxidative polymerization of aniline in the presence of MCC (a bio-based material); the industrially favorable and cost effective oxidant ammonium persulphate (APS) was used. Under the conditions studied, the preliminary results reflected that the proposed concept was quite effective in the detoxification of the model solution. It is worth expecting that the use of PANI-engineered cellulose fibers prepared using low cost oxidant may serve as an interesting alternative for industrial water treatment.

Keywords: Detoxification, Chromium, Polyaniline, Cellulose.

INTRODUCTION

Water pollution by metal contamination

Water [1] is essential to life on our planet. A prerequisite of sustainable development must be to ensure uncontaminated streams, rivers, lakes and oceans. There is growing public concern about the condition of fresh water in the world. Heavy metals [2] are naturally occurring elements that have a high atomic weight and a density at least five times greater than that of water. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment.

Their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals. Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. Heavy metals occur in the earth's geological structures, and can therefore enter water resources through natural processes. For example, heavy rains or flowing water can leach heavy metals out of geological formations. Mining activity possess significant risks for heavy metal pollution and can lead to consequences such as acid mine drainage (AMD). Many industrial processes can generate heavy metal pollution, and in a large number of ways. For instance, electroplating industry, which can produce large volumes of metal-rich effluents will naturally be a more likely polluter than the food processing industry, heavy metal pollution is also contributed by coal-fired power generation etc. The importance of minimising heavy metal pollution for industrial organisations extends beyond simple compliance. The impacts of heavy metal pollution on living organisms are very serious. Heavy metals are bio-accumulative, toxic at high concentrations, have neurological impacts, and some are carcinogenic. They can also interfere with chemical processes by poisoning chemical catalysts and can impact on biochemical processes by interfering with enzyme action. There are hence serious environmental, economic and social impacts associated with heavy metal pollution.

CHROMIUM

Chromium (Cr) is the 17th most abundant element in the Earth's mantle [3]. It occurs naturally as chromite ($FeCr_2O_4$) in ultramafic and serpentine rocks or complexed with other metals like crocoite ($PbCrO_4$), bentorite $Ca_6 (Cr,Al)_2(SO_4)_3$, tarapacaite (K_2CrO_4) and vauquelinite ($CuPb_2CrO_4PO_4OH$).Chromium is an odourless and tasteless metallic element. Chromium is found naturally in rocks, plants, soil and volcanic dust, humans and animals. Chromium [4] is widely used in industry as plating, alloying, tanning of animal hides, inhibition of water corrosion, textile dyes and mordants, pigments, ceramic glazes, refractory bricks, and pressure-treated lumber. Due to this wide anthropogenic use of Cr, the consequent environmental contamination increased and has become an increasing concern in the last years. Chromium exists in several oxidation states, but the most stable and common forms are Cr (0), the trivalent Cr (III), and the hexavalent Cr (VI) species. Cr (0) is the metallic form, produced in industry and is a solid with high fusion point usually used for the manufacturing of steel and other alloys. Cr (VI) in the forms of chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), and CrO_3 is considered the most toxic forms of chromium, as it presents high oxidizing potential, high solubility, and mobility across the membranes in living organisms and in the environment [5].

CHROMIUM IN WATER

Chromium may enter the natural waters by weathering of Cr-containing rocks, direct discharge from industrial operations, leaching of soils, among others. In the aquatic environment, Chromium may suffer reduction, oxidation, sorption, desorption, dissolution, and precipitation [6]. The aqueous solubility of Cr (III) is a function of the pH of the water. Under neutral to basic pH, Cr (III) precipitates and conversely under acidic pH it tends to solubilize. The forms of Cr (VI) chromate and dichromate are extremely soluble under all pH conditions, but they can precipitate with divalent cations.

TOXIC EFFECTS OF HEXAVALENT CHROMIUM

Most of hexavalent chromium compounds are irritating to the eyes, skin and mucous membranes, and chronic exposure to them can cause permanent eye damage if not properly cared for [7]. Ingestion of liquids containing chromium (VI) causes severe gastroenteritis with nausea, abdominal pain, vomiting and diarrhea. Hexavalent chromium is also a known genotoxic carcinogen to humans. Chromium (VI) induces both bulky DNA adducts oxidative DNA damage at adenines and guanines in the p53 gene of human lung cells, leading to an increase of lung carcinogenesis. Chromium may cause adverse health effects following inhalation, ingestion or dermal exposure. The toxicokinetics [8] of a given chromium compound depend on the valence state of the chromium atom and the nature of its ligands. In general, toxicity of chromium is mainly caused by hexavalent compounds as a result of a higher cellular uptake of chromium (VI) compounds than chromium (III). This is explained by the fact that the chromate anion ($CrO4^{2-}$) can enter the cells via facilitated diffusion through non-specific anion channels (similarly to phosphate and sulfate anions). Absorption of chromium (III) compounds is via passive diffusion and phagocytosis. Hexavalent chromium [9] is unstable in the body and is reduced intracellularly (by many substances including ascorbate and glutathione) providing very reactional pentavalent chromium and trivalent chromium. Both of these intermediates can alterate DNA.

COMPOSITE

A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure. Composites are formed by combining materials together to form an overall structure that is better than the sum of the individual components. Composite materials include metal composite, ceramic composite, fiber glass composite etc.

NANOCOMPOSITE

Nanocomposite [10] are a special class of materials originating from suitable combination of two or more nano sized objects in some suitable technique, resulting in materials having unique physical properties and wide application potential in diverse areas. Nanocomposites may be one-dimensional, two-dimensional, three dimensional and amorphous materials made of distinctly dissimilar components and mixed at the nanometer scale.

FORMATION OF NANOCOMPOSITES

Inorganic nanoparticles of different nature and size can be combined with the conducting polymers such as PANI, giving rise to a host of nanocomposites with interesting physical properties and important applications.

$$\text{Monomer} + \text{Inorganic particles} \rightarrow \text{Nanocomposite}$$

CLASSIFICATION OF NANOCOMPOSITES

Lamellar nanocomposites are divided into two distinct classes-

- Intercalated nanocomposite and
- Exfoliated nanocomposite

Intercalated Nanocomposite

The polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well-defined number of polymer layers in the intralamellar space.

Exfoliated nanocomposite

The number of polymer chains between the layers is almost continuously variable and the layers stand > 100 Å apart.

FORMATION OF INTERCALATED AND EXFOLIATED NANOCOMPOSITE

In the case of an intercalated, the organic component is inserted between the layers of the clay such that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other.

In an exfoliated structure, the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix.

CELLULOSE

Cellulose is the most abundant renewable polymer on earth. It is a linear polysaccharide with long chains, which consists of β-d-glucopyranose units joined by β-1,4-glycosidic linkages. Due to the absence of side chains or branching, cellulose chains can exist in an ordered structure. The structure of cellulose is semicrystalline and exists in amorphous and crystalline forms. The hydrogen bonding between the cellulose chains and van der Waals forces between the glucose units give rise to crystalline regions in cellulose [11]. Cellulose has many attractive physical and chemical properties like biocompatibility, biodegradability, hydrophilicity, stereoregularity, presence of reactive hydroxyl groups, and ability to form suprastructures [12]. The main sources of cellulose are wood, cotton, and aerobic bacteria. However, the most important source of commercial cellulose is wood pulp [13]. The cellulose content of cotton fiber is 90% and that of wood is 40%–50%. Wood pulp is utilized in making paper and cardboard. Cellulose derivatives, mainly esters and ethers, like ethyl cellulose, hydroxyethyl cellulose, hydroxyl propyl cellulose, methyl cellulose, carboxymethyl cellulose, and cyanoethyl cellulose [14] have been synthesized and found applications as fibers, films, coatings, laminates, optical films, and sorption media, as well as additives in building materials, pharmaceuticals, foodstuffs, and cosmetics.

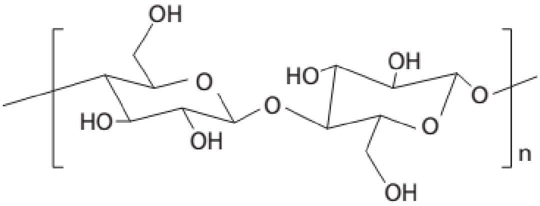

Fig-1: Structure of cellulose

MICROCRYSTALLINE CELLULOSE (MCC)

Microcrystalline cellulose (MCC) was discovered in 1955 by Battista and Smith. MCC is a purified, partially depolymerized cellulose prepared by treating α-cellulose obtained as a pulp from fibrous plant material, with mineral acids. Cellulose is the most abundant natural polymer on earth. Cellulose consists of linear chains of β-1,4-D anhydroglucopyranosyl units [15]. The most common source of pharmaceutical MCC is wood, in which cellulose chains are packed in layers held together by a cross-linking polymer (lignin) and strong hydrogen bonds. Cotton is also a possible cellulose source for MCC [16, 17]. Both softwoods (evergreen conifer) and hardwoods (deciduous broadleaf) can be used [18]. These woods differ considerably in chemical composition (proportions of cellulose, hemicelluloses and lignin) and structural organization i.e, regions which are relatively more crystalline or amorphous. The amorphous region are more prone to hydrolysis so partial depolymerization by acid hydrolysis results in shorter and more crystalline fragments called microcrystalline cellulose.

Structure of Microcrystalline cellulose:

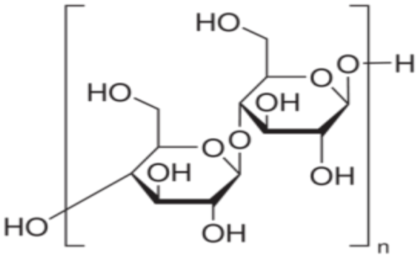

Fig-2: Structure of MCC

PROPERTIES OF MCC

- MCC has a very high intraparticle porosity with approximately 90–95% of the surface area being internal [19]. Therefore, surface area is not directly influenced by the nominal particle size.

- MCC is a stable though hygroscopic material [20], which can be attributed to the presence of abundant hydroxyl groups on cellulose chains and to the relatively large surface to volume ratio of micro fibrils due to their small size.
- Moisture within the pores [21] of MCC may act as an internal lubricant, reduce frictional forces, and facilitate slippage and plastic flow within the individual microcrystals .• Degree of crystallinity [22] for microcrystalline cellulose is about 60–80 %
- Attributes like strength, fibrous nature, stiffness, lightness, bio-degrability, water insolubility and renewability make MCC attractive for applications in diverse industrial fields [23].

FEW APPLICATIONS OF MCC

- MCC is used for the direct compression of tablets because of its tablet binding, low chemical reactivity and high compactibility [24].
- MCC/PANI composite acts as a good adsorbent for trapping toxic Cr (VI).
- MCC is also used as drug delivery vehicles as it triggers slow release of drugs from capsules and tablets.

ANILINE

Aniline is a toxic organic compound with the molecular formula **$C_6H_5NH_2$**. It consists of a phenyl group attached to an amino group. Aniline is the prototypical aromatic amine. Like most volatile amines, it possesses the odour of rotten fish. It ignites readily, burning with a smoky flame characteristic of aromatic compounds. Industrial aniline production involves two steps. First, benzene is nitrated with a concentrated mixture of nitric acid and sulfuric acid at 50 to 60 °C to yield nitrobenzene. The nitrobenzene is then hydrogenated (typically at 200–300 °C) in the presence of metal catalysts.

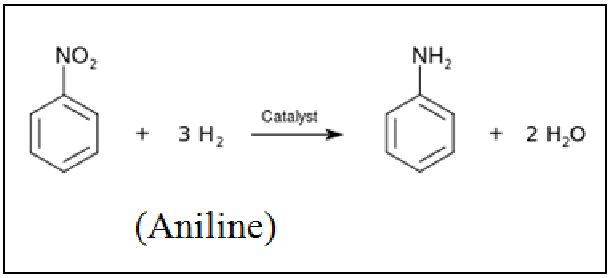

Fig-3: Synthesis of aniline

The reduction of nitrobenzene to aniline was first performed by Nikolay Zinin in 1842 using inorganic sulfide as a reductant. Aniline can alternatively be prepared from ammonia and phenol derived from the cumene [25] process. Like phenols, aniline derivatives are highly susceptible to electrophilic substitution reactions. Its high reactivity reflects that it is an enamine, which enhances the electron-donating ability of the ring. For example, reaction of aniline with sulfuric acid at 180 °C produces sulfanilic acid, $H_2NC_6H_4SO_3H$. If bromine water is added to aniline, the bromine water gets decolourised and a white precipitate of 2,4,6-tribromophenylamine is formed. The largest scale industrial reaction of aniline involves its alkylation with formaldehyde. . An idealized equation is shown below:

$$2\ C_6H_5NH_2 + CH_2O \rightarrow CH_2(C_6H_4NH_2)_2 + H_2O$$

REACTIONS OF ANILINE

- Aniline undergoes diazotization reaction to produce diazonium salts.
- Aniline undergoes acylation reaction to give amides.
- Aniline undergoes N-alkylation reactions to give N-methylaniline and dimethylaniline.

USES OF ANILINE

- Aniline is used for the preparation of methylene dianiline and related compounds by condensation with formaldehyde.
- Aniline derivatives such as phenylenediamines and diphenylamine are used as additives to rubber.
- Aniline is used as a precursor to indigo, the blue of blue jeans in dye industry.
- Aniline is also used at a smaller scale in the production of the intrinsically conducting polymer, polyaniline.

POLYANILINE (PANI)

Polyaniline belongs to the class of intrinsically conducting polymer (ICP). It is a phenyl based polymer having a chemically flexible –NH- group in polymer chain flanked either side by phenylene ring. The polyanilines are formed by the chemical or electrochemical oxidative polymerization of aniline or its derivatives. Electronic conduction in polyaniline involves the ingress of protons and is also accompanied by the ingress of anions to maintain the charge neutrality. The electrochemical stability of polyaniline depends on the conditions of p^H as well as on the counter ion of the bronsted acid used for doping. Lewis acids can also be used for doping. Doping of PANI with Bronsted-acid is often called protonation [26].

The structure of polyaniline can be represented by the general formula as:

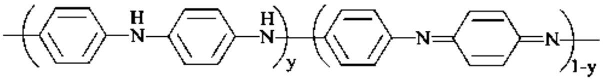

Fig-4: Polyaniline general formula

In the general formula, 1-y represents the oxidation state, which can be varied from 0.0 to 1.0

A large variety of derivatives can be prepared through substitution in the ring or on the N atoms. Polyaniline exists in three different, isolable oxidation states at the molecular level. They are the leucoemeraldine oxidation state, the emeraldine oxidation state, and the pernigraniline oxidation state. Other oxidation states are the result of physical mixture of these oxidation states.

(i) Leucoemeraldine Base: It is the fully reduced form of non-doped polyaniline [27]. It is composed solely of reduced units as shown below:

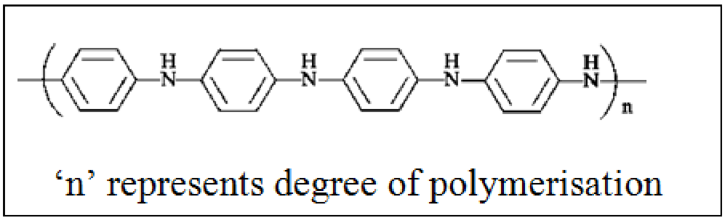

Fig-5: Leucoemeraldine Base

(ii) Pernigraniline Base: Is is the fully oxidized form of non-doped polyaniline. It is composed solely of oxidized base unites as shown below:

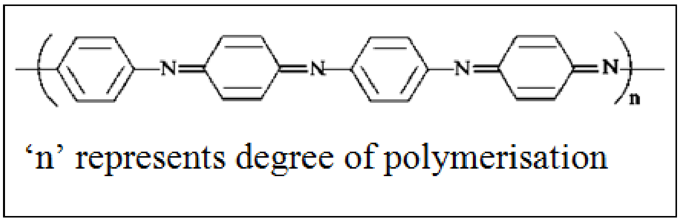

Fig-6: Pernigraniline Base

(iii) Emeraldine Base: It is the intermediate oxidation state of polyaniline [28]. It is composed of equal amounts of alternating reduced base and oxidized base units as shown below:

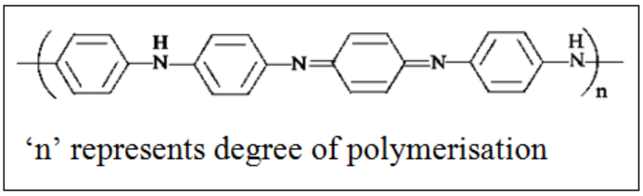

Fig-7: Emeraldine Base

SYNTHESIS OF POLYANILINE

One method of synthesis of polyaniline involves mixing of aqueous solutions of aniline hydrochloride and ammonium peroxydisulphate at room temperature followed by separation of PANI hydrochloride precipitate by filtration and drying [29]. The polymerization is completed within 10 min at room temperature and within 1 hour at 0-2˚C. The oxidation of aniline is exothermic and so the temperature of the reaction mixture can be used to monitor the progress of the reaction [30].

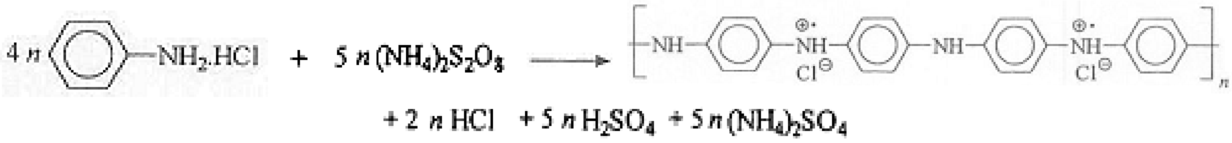

Fig-8: Oxidation of aniline hydrochloride with ammonium peroxydisulphate yields polyaniline (emeraldine) hydrochloride

PROPERTIES OF POLYANILINE

- Electrical properties of polyaniline can be reversibly controlled by charge-transfer doping and protonation.
- Polyaniline is environmentally stable and inert (noble) where stainless steel is corroded.
- Polyaniline is applicable to electrical, electrochemical, and optical applications.
- Polyaniline is currently used in cell phones and calculators and other LCD technology etc.

OBJECTIVES

The objective of the present work was to-

- Preparation of microcrystalline cellulose
- Preparation of polyaniline
- Preparation of polyaniline/microcrystalline cellulose composites
- Investigate the ability of detoxification of Cr (VI) contaminated water by the prepared composites

LITERATURE REVIEW

Liu *et al*., [31] engineered cellulose fibers by in situ oxidative polymerization of aniline using ammonium persulfate as oxidant/initiator. The polyaniline/cellulose fiber composite was used for the treatment of Cr(VI)-contaminated water, and its effect was evaluated. Under the conditions studied, the composite exhibited very high water detoxification efficiency, as a result of reduction of Cr(VI) to Cr(III) in combination with adsorption of the Cr(III) onto the cellulosic substrate. Cellulose fibers used in the study served tw purposes simultaneously, i.e., carrier of polyaniline and the adsorbent for Cr(III). The complexation of polyaniline with cellulose fibers provided synergistic effects on Cr(VI)-detoxification.

The demonstration of a new integrated process concept involving the use of a bio-based material for detoxification of Cr (VI)-contaminated water was presented by *Liu et al*., [32]. Specifically, the biobased material is a polyaniline/cellulose fiber composite prepared by in situ polymerization of aniline in the presence of cellulose fibers, using the industrially favorable hydrogen peroxide (instead of costly oxidants such as ammonium persulfate) as the oxidant. Ferric chloride was used to catalyze the polymerization reaction. The process conditions for the preparation of the composite were preliminarily coptimized, and the proposed concept was demonstrated. Under the conditions studied, the use of the composite was quite effective in the detoxification of the model solution. The proposed concept served as an alternative approach for water treatment using renewable materials.

An alternative process for detoxification of Cr(VI)-contaminated water with polypyrrole-engineered pulp fibers prepared using low cost hydrogen peroxide as oxidant was proposed by Lei *et al*., [33] The process conditions in preparation of the engineered fibers as well as the water treatment conditions were optimized, and the behavior of Cr desorption from the engineered fibers was evaluated. The results showed that the proposed process was highly efficient in Cr(VI)-detoxification via the integration of adsorption with reduction.

Camacho *et al.,* [34] studied fabrication of a composite material consisting of Cladophora cellulose and polyaniline (PANI).Cellulose extracted from environmentally polluting green algae *Cladophora rupestris* was used as a matrix and conducting polyaniline coating was applied on its surface. The characterization of the composite revealed the presence of a nano-layer of PANI coating on the cellulose fibers, thus preserving the high surface area of the cellulose. The cellulose/PANI composite was used effectively as a reducing agent in the remediation of toxic hexavalent chromium. The efficiency of the reduction activity of metals can be attributed to the high surface area of the cellulose/PANI composite. This study provided alternative ways to solve an environmental issue and maximize the use readily available resources.

MATERIALS AND METHODS

Materials

The list of chemicals used in the experiment is enlisted in the Table-1.

Sl No.	CHEMICALS	BRAND	CONDITION
01	Aniline	MERCK	*Distilled and used
02	Hydrogen peroxide	MERCK	Used as received
03	Sodium hypochlorite	MERCK	Do
04	Ammonium persulphate	MERCK	Do
05	Potassium dichromate	QUALIGENS	Do
06	Sodium hydroxide	FISCHER SCIENTIFIC	Do
07	Hydrogen chloride (conc.)	MERCK(E)	Do
08	Ammonium hydroxide	HIMEDIA	Do

*Purification of Aniline

Aniline (MERCK) was purified by distillation under reduced pressure. The distilled aniline was almost colourless and was kept in dark bottles under air tight condition to prevent oxidation by atmospheric oxygen and light.

- Cellulose fibers (fully bleached) derived from fodder grass (*Imperata cylindrica),* obtained from BioTech Park, Gauhati University was used in the experiment.

METHODS

PREPARATION OF MICROCRYSTALLINE CELLULOSE (MCC)

The grass samples were first washed thoroughly with water, dried under sunlight and cut into small pieces. The dried samples were treated with NaOH (4%) and boiled at 80˚C in water bath for 4 hours. The samples were washed with distilled water until neutral pH and then bleached with a solution of sodium hypochlorite and hydrogen peroxide in 1:1 ratio for 40 minutes at 100˚C. The samples were rewashed with distilled water until neutral pH yielding the α-cellulose fibers. For extraction of MCC, 10 g of the α-cellulose was acid hydrolysed using HCl (2.5N) at 100˚C for 30 minutes. The extracted MCC was washed thoroughly with distilled water for complete removal of HCl.

PREPARATION OF POLYANILINE/MICROCRYSTALLINE CELLULOSE COMPOSITE

For preparation of the composite, molar ratio of aniline:persulphate is taken as 1:1,1 M conc. HCl, 6 gram of dry microcrystalline cellulose powder (cellulose powder is kept in a desiccator before weighing) are used. The reaction is carried out for 2 hours at room temperature.

Actual amount of aniline (X gram) = Ammonium persulphate (Y gram)

Three samples of composites are prepared:-

Sample 1:-	Sample 2:-	Sample 3:-
MCC-PANI$_1$ (1 ml)	MCC-PANI$_2$ (1.5ml)	MCC-PANI$_3$ (2 ml)

Transfer 3 gram dry microcrystalline cellulose powder into a 250 ml dry beaker. Add 30 ml 1 M HCl into it and stir for 30 minutes at 350 rpm. Add X ml aniline dissolved in 20 ml 1M HCl into under constant stirring for 10 minutes. Cool the mixture in an ice-bath. Dissolve Y gram of ammonium persulphate (APS) in 50 ml of 1 M HCl and cool in an ice-bath. Add APS solution slowly to aniline solution with dispersed cellulose under constant agitation. Continue the agitation for 2 hours. Filter the product under suction, wash with large amount of distilled water and dry in an oven at 60˚C till it is completely dry. Store in a desiccator.

TREATMENT OF Cr (VI) CONTAMINATED WATER

Add Polyaniline/microcrystalline cellulose composite of drug weight 1 gram to 100 ml of 100mg/L Cr(VI) solution (stock solution) with pH= 4.8 and stir the mixture at 350 rpm for 2 hours. After the treatment filter it through a Whatman no. 41 filter paper. Then collect the filtrate i.e treated water for UV-VIS studies.

SYNTHESIS OF PANI EMERALDINE SALT

An aqueous solution (200 mL) of 1 M HCl was prepared. 9.12 g ammonium persulphate (APS) was dissolved in 60 mL of 1M HCl and then cooled. 3.64 mL aniline was dissolved in the remaining 140 ml of 1 M HCl under ice-cold condition. The APS solution was added slowly into aniline over 30 minutes under constant stirring and the stirring was continued for another 2 hours. It was then filtered, washed with dilute HCl and thereafter with distilled water and dried in vaccum oven for 6 hours at 60 ˚C. This is HCL doped PANI or emeraldine salt (ES-PANI).

SYNTHESIS OF PANI EMERALDINE BASE

The emeraldine base form of PANI (EB-PANI) was prepared by treating ES-PANI with 1 M NH_4OH solution and agitated for 6 hours. The products were then filtered and dried in vacuum at 60˚C for 6 hours.

PREPARATION OF STANDARD CALIBRATION CURVE FOR Cr(VI)

The concentration of Cr (VI) in the treated water was determined by spectrophotometry. A UV-VIS spectrophotometer (SHIMAZDU) was used. The concentration of Cr (VI) was measured at 375 nm. The standard working curve (y=3.4982x + 0.0254) with correlation coefficient of 0.9814 was prepared by plotting absorbance against concentration of Cr (VI) in the concentration range 0.03-1.16 mg/L (Fig-10).

For the determination of total Cr concentration of the treated water, oxidise the water by APS for 10 minutes under acidic and boiling conditions. Then cool the mixture and measure the total chromium concentration according to the same procedure as Cr (VI) determination described above.

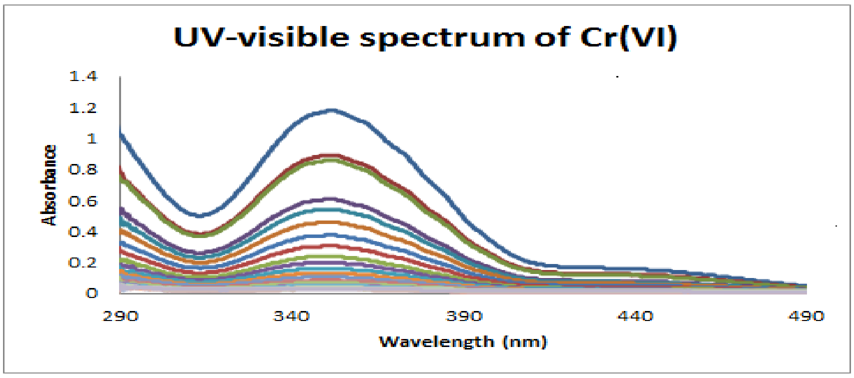

Fig-9: UV-VIS spectrum of Cr (VI)

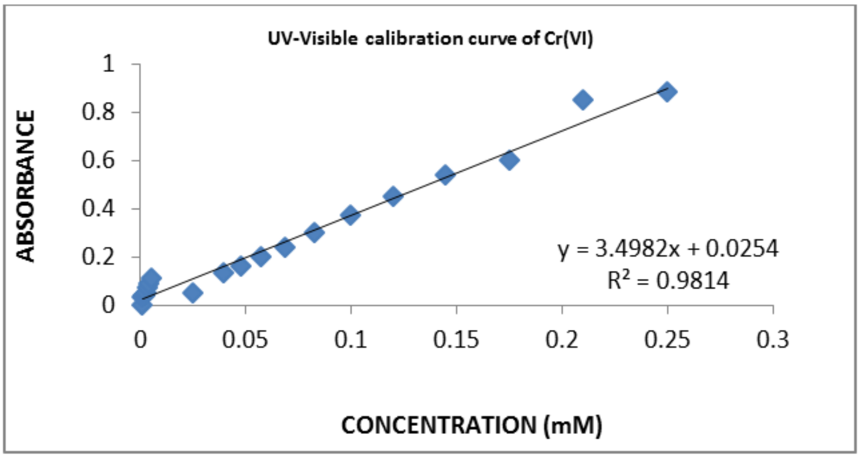

Fig-10: Calibration curve of Cr (VI)

TOOLS AND TECHNIQUE FOR CHARACTERISATION

FTIR Spectroscopic studies

The FTIR spectra of different samples were recorded by SHIMAZDU IR-AFFINITY-1 spectrophotometer using KBr pellets of solid samples within the scanning range of 4000-500 cm^{-1} and all the data were taken in the transmittance mode.

UV-Visible Spectral analysis

A UV spectrum obtained directly from an instrument is the plot of wavelength (or frequency) of absorption versus the absorption intensity (absorption or transmission). UV-Visible spectra of different samples were recorded by SHIMAZDU (Japan) 1800 UV-VIS Spectrophotometer in the range 200-800 nm.

Thermal analysis

The thermal stability of the samples was studied by TGA method by measuring the % weight loss with temperature. TGA were recorded at METLER TOLLEDO.

Powder-XRD analysis

The powder X-Ray Diffraction pattern were recorded in the scan range from 2ϴ = 4 to 50˚ on a Bruker DS Advanced X-Ray Diffraction measurement system with CuKα radiation (40 kV, λ=1.5414 Å)

RESULTS AND DISCUSSION

UV-VISIBLE STUDIES OF SAMPLES

UV-VISIBLE STUDIES FOR THE FOLLOWING ADSORBENTS WERE DONE FROM THEIR RESPECTIVE SPECTRAS

- PANI/MCC Composite-1
- PANI/MCC Composite-2
- PANI/MCC Composite-3

Individual Materials are also checked for their adsorbent ability such as,

- MCC
- PANI
- MCC + PANI (mixed by mechanical grinding)

Stock Cr (VI) solution was prepared having concentration (X) = 0.3399 mM
From the UV-Visible calibration curve for Cr(VI), the following equation is obtained-

$$y = 3.4982x + 0.0254 \text{ --------------- } (1)$$

Where, y-axis gives the absorbance and x-axis gives the concentration.

Using equation (1), the concentration of Cr (VI) and Cr (III) adsorbed by the above adsorbents can be measured.

For PANI/MCC Composite-1

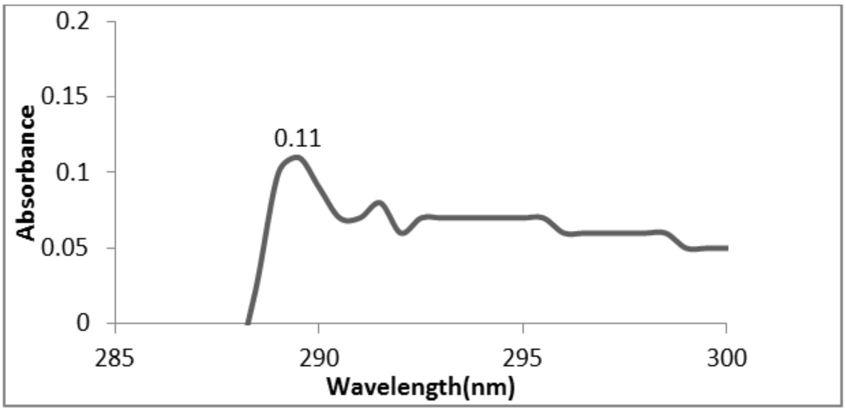

Fig-11: UV-Visible spectra of Composite-1(filtrate)

From the above spectra, absorbance for filtrate = 0.11
Using equation (1),

$$y = 3.4982x + 0.0254$$
$$\text{or} \quad 0.11 = 3.4982x + 0.0254$$
$$\text{or} \quad x = 0.0241$$

Therefore, concentration for filtrate (Y) = 0.0241 mM

Total concentration of Cr (VI) adsorbed= Concentration of Stock solution- Concentration of treated composite-1 filtrate (X-Y) = 0.3399- 0.0241 = 0.3158 mM

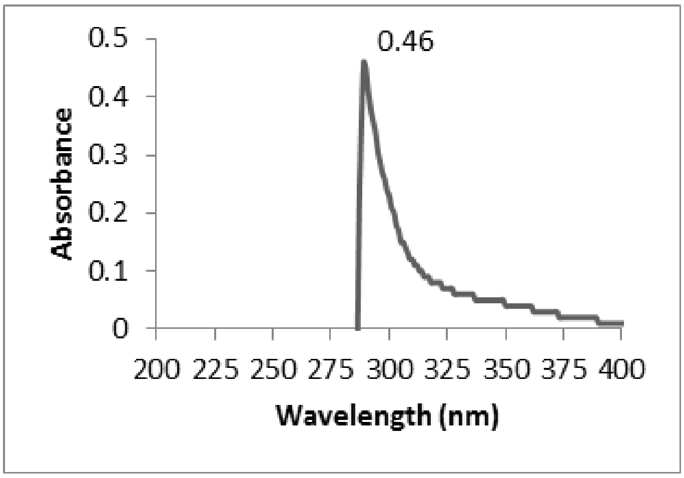

Fig-12: UV-Visible spectra of Composite-1 (oxidized filtrate)

From the above spectra, absorbance for oxidized filtrate = 0.46
Using equation (1),

$$y = 3.4982x + 0.0254$$

or $$x = 0.1242 \text{ mM}$$

Here x is the concentration of oxidized filtrate (Z)
Therefore, concentration of Cr (III) adsorbed = Z - Y = 0.1242 – 0.0241
= 0.1001 mM

For PANI/MCC Composite – 2

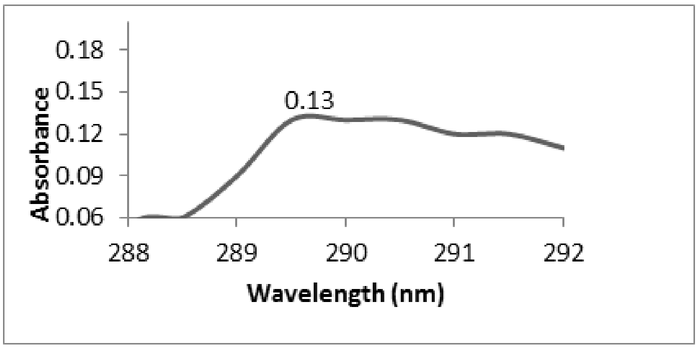

Fig.13. UV-Visible spectra of Composite-2 (filtrate)

Similarly,
Total concentration of Cr (VI) adsorbed = X-Y = 0.31 mM

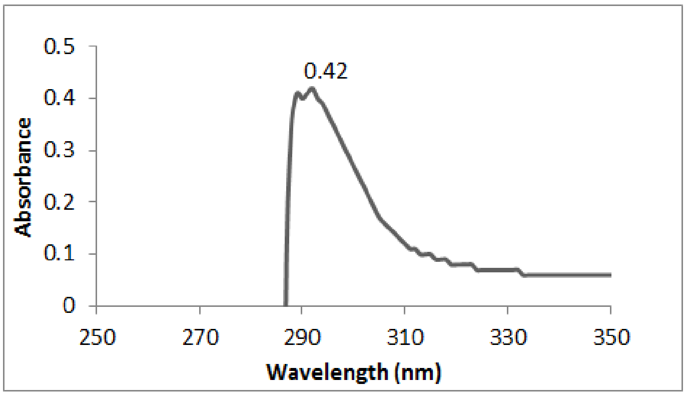

Fig-14: UV-Visible spectra of Composite-2 (oxidized filtrate)

Therefore, concentration of Cr (III) adsorbed = Z –Y = 0.0829 mM

For PANI/MCC Composite -3

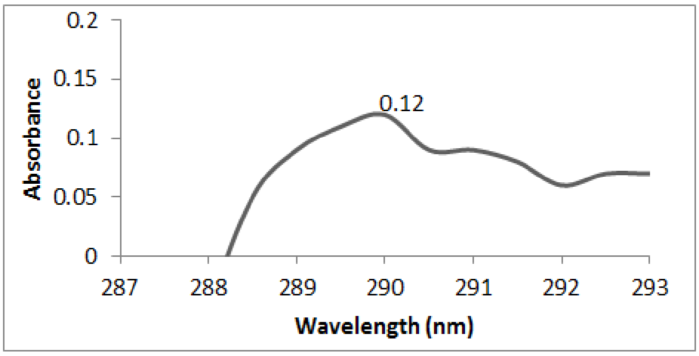

Fig-15: UV-Visible spectra of Composite-3 (filtrate)

Similarly,
Total concentration of Cr (VI) adsorbed = X-Y = 0.3129 mM

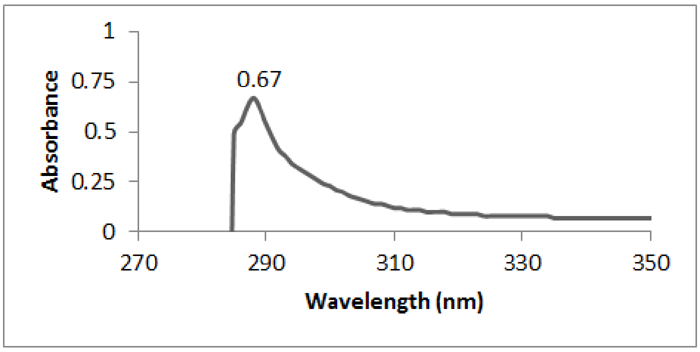

Fig.16. UV-Visible spectra of Composite-3 (oxidized filtrate)

Therefore, concentration of Cr (III) adsorbed = Z –Y = 0.1572 mM

For MCC

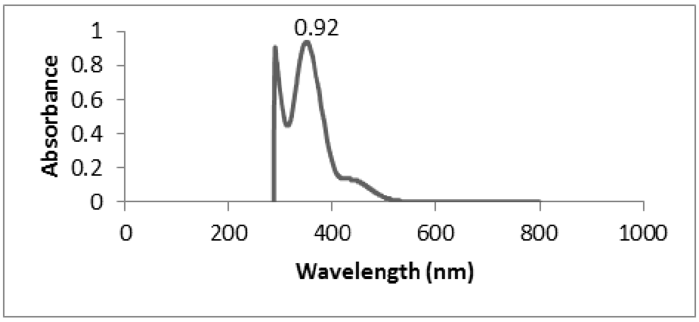

Fig-17: UV-Visible spectra of MCC (filtrate)

Total concentration of Cr (VI) adsorbed = X-Y = 0.0842 mM

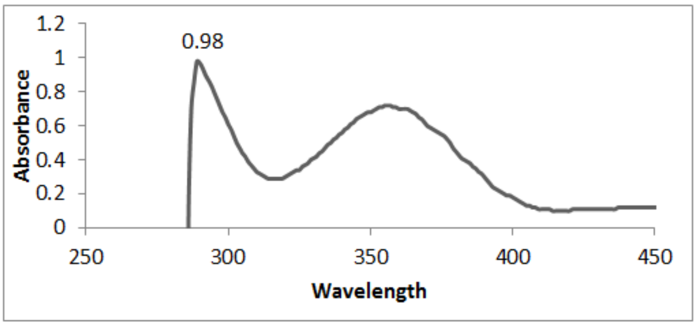

Fig-18: UV-Visible spectra of MCC (oxidized filtrate)

Therefore, concentration of Cr (III) adsorbed = Z –Y = 0.0171 mM

For PANI salt

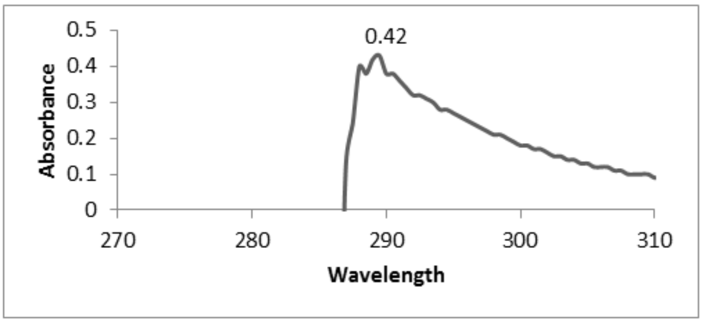

Fig-19: UV-Visible spectra of PANI (filtrate)

Total concentration of Cr (VI) adsorbed = X-Y = 0.2271

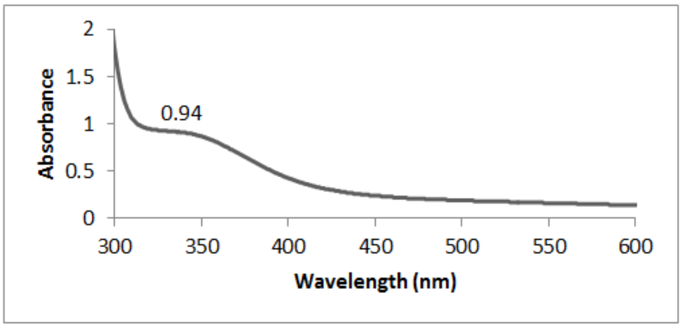

Fig-20: UV-Visible spectra of PANI (oxidized filtrate)

Therefore, concentration of Cr (III) adsorbed = Z –Y = 0.1486

For MCC + PANI

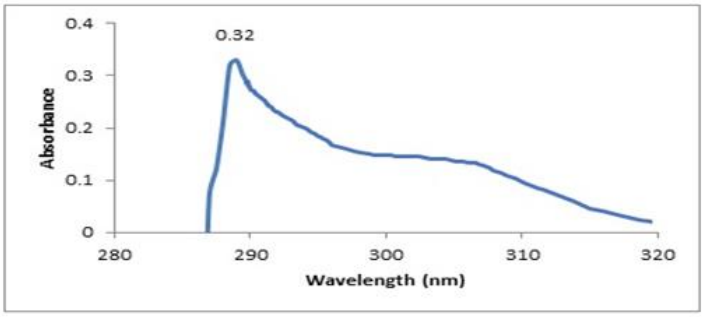

Fig-21: UV-Visible spectra of MCC + PANI (filtrate)

Total concentration of Cr (VI) adsorbed = X-Y = 0.2529 mM

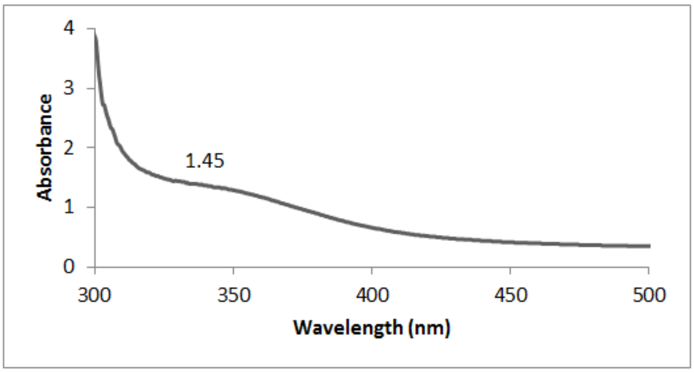

Fig-22: UV-Visible spectra of MCC + PANI (oxidized filtrate)

Therefore, concentration of Cr (III) adsorbed = Z –Y = 0.4072 mM

TABLE FOR RESULTS OBTAINED

Table below shows the molar amount of Cr (VI) and Cr (III) adsorbed by the above discussed adsorbents:

Sl. No.	Adsorbent	Conc. of stock solution (X) mM	Conc. of Cr(VI) Absorbed (X-Y) mM	Conc. of Cr(III) Absorbed (Z-Y) mM
01	PANI/MCC COMP-1	0.3399	0.3158	0.1001
02	PANI/MCC COMP-2	0.3399	0.310	0.0829
03	PANI/MCC COMP-3	0.3399	0.3129	0.1572
04	MCC	0.3399	0.0842	0.0171
05	PANI salt	0.3399	0.2271	0.1486
06	MCC + PANI	0.3399	0.2529	0.4072

From the above table, it is evident that PANI/MCC COMPOSITE-2 is a better adsorbent among the enlisted adsorbents since the concentration of Cr (III) adsorbed (Z-Y) is lowest i.e. 0.0829 mM

FTIR Analysis
FTIR spectra of α-cellulose

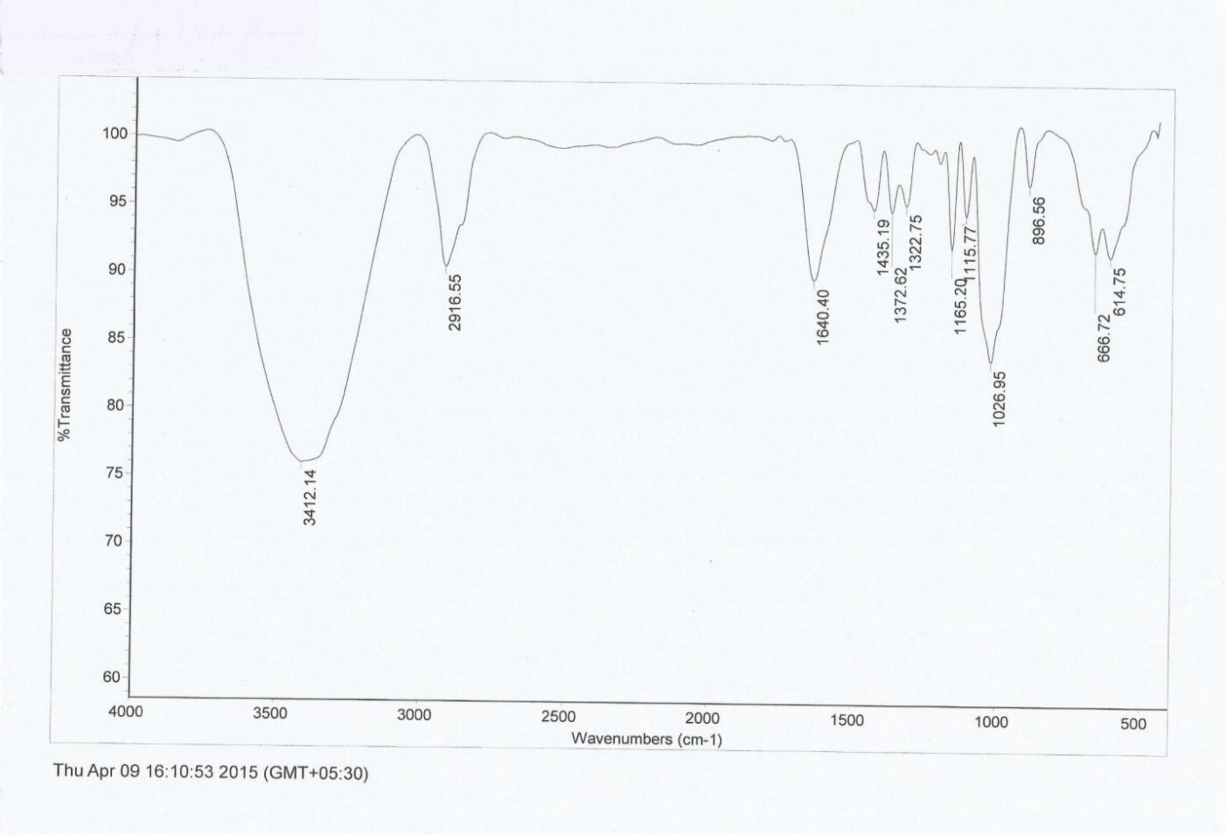

Fig-

Fig-23: FTIR spectra of α-cellulose

BAND (cm^{-1})	ASSIGNMENT
3100- 3600	OH- stretching vibration signifying hydrogen bonds
2916	C-H stretching
447-1500	Reduced in intensity

FTIR spectra of MCC

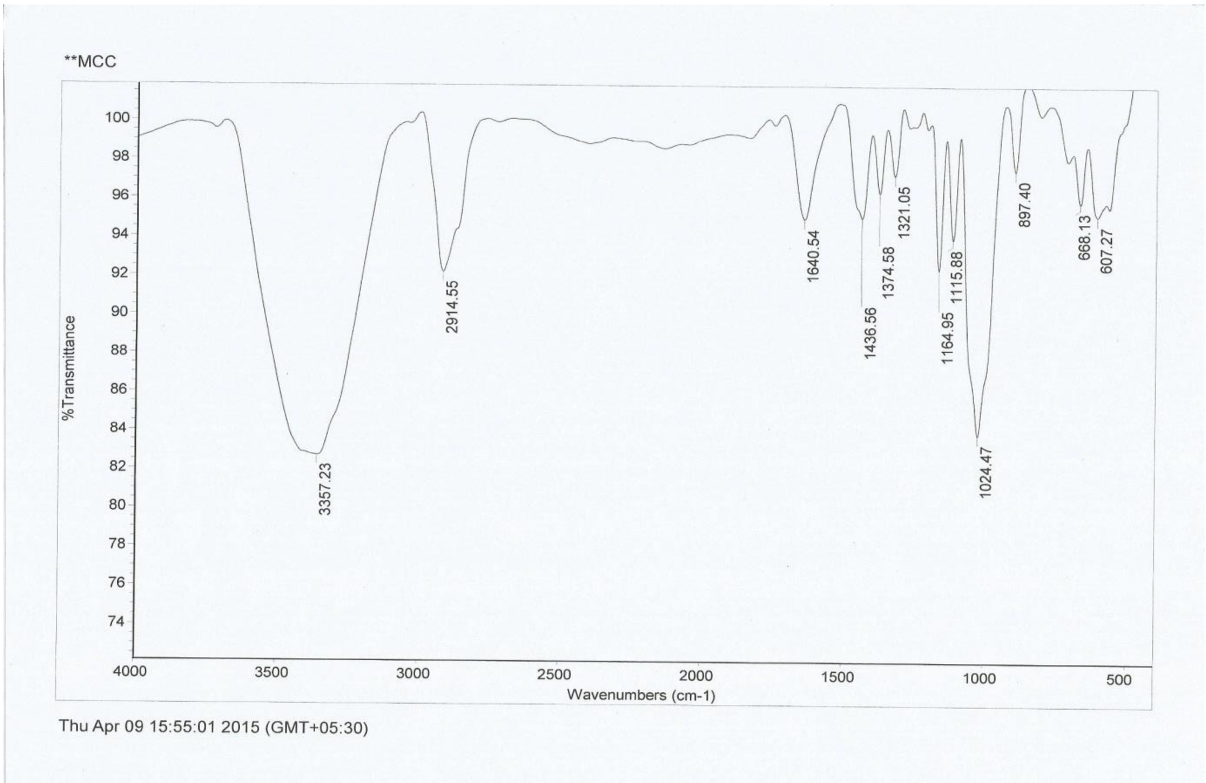

Fig-24: FTIR spectra of MCC

BAND (cm^{-1})	ASSIGNMENT
3100-3600	OH-stretching vibration signifying hydrogen bonds
2914	C-H stretching vibration
1645	Bending of absorbed water
1436	CH_2 bending vibration called “crystallinity band”
1374	OH in bending vibration
1024	C-O-C pyrannose ring skeletal vibration

FTIR spectra of PANI salt

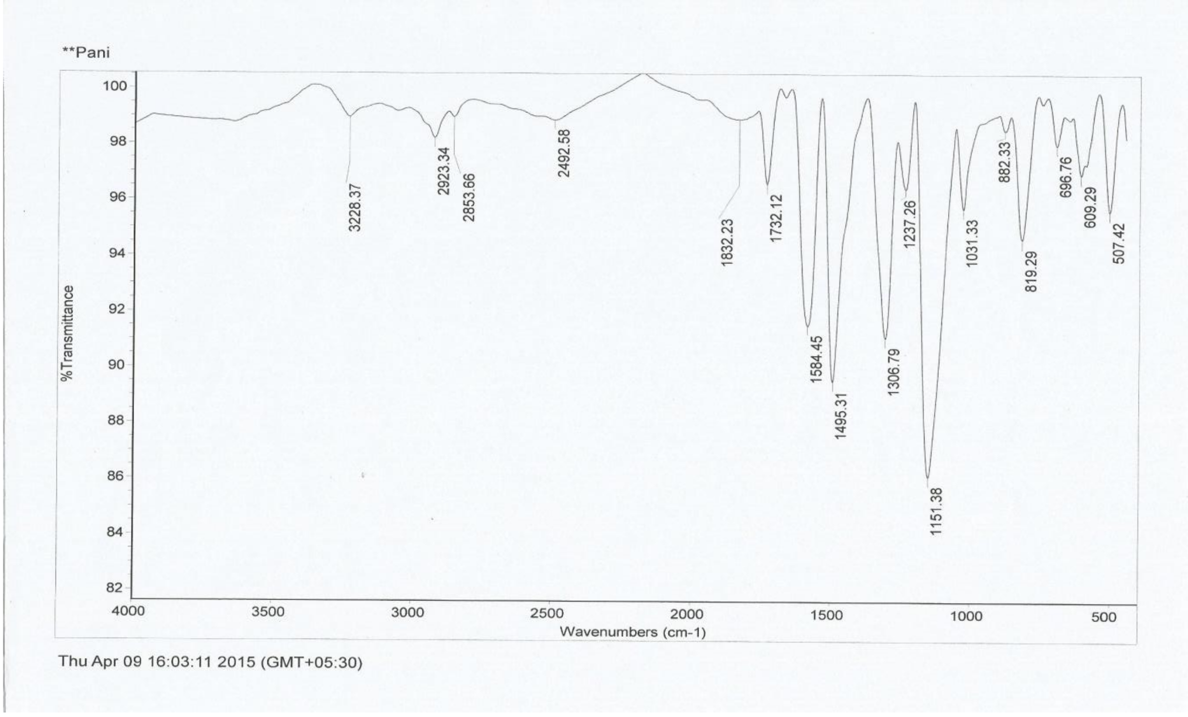

Fig-25: FTIR spectra of PANI salt

BAND(cm^{-1})	ASSIGNMENT
3228	N-H stretching vibration
2923	Benzenoid C-H stretching vibration
1584	C=C ring stretching vibration of the benzenoid ring
1495	C-N stretching of the quinoid ring
1306	N-H bending vibration
1237	Symmetric component of the C=C
1031	In plane C-H bending mode
819	Out of plane C-H bending mode

FTIR of PANI/MCC Composite-1

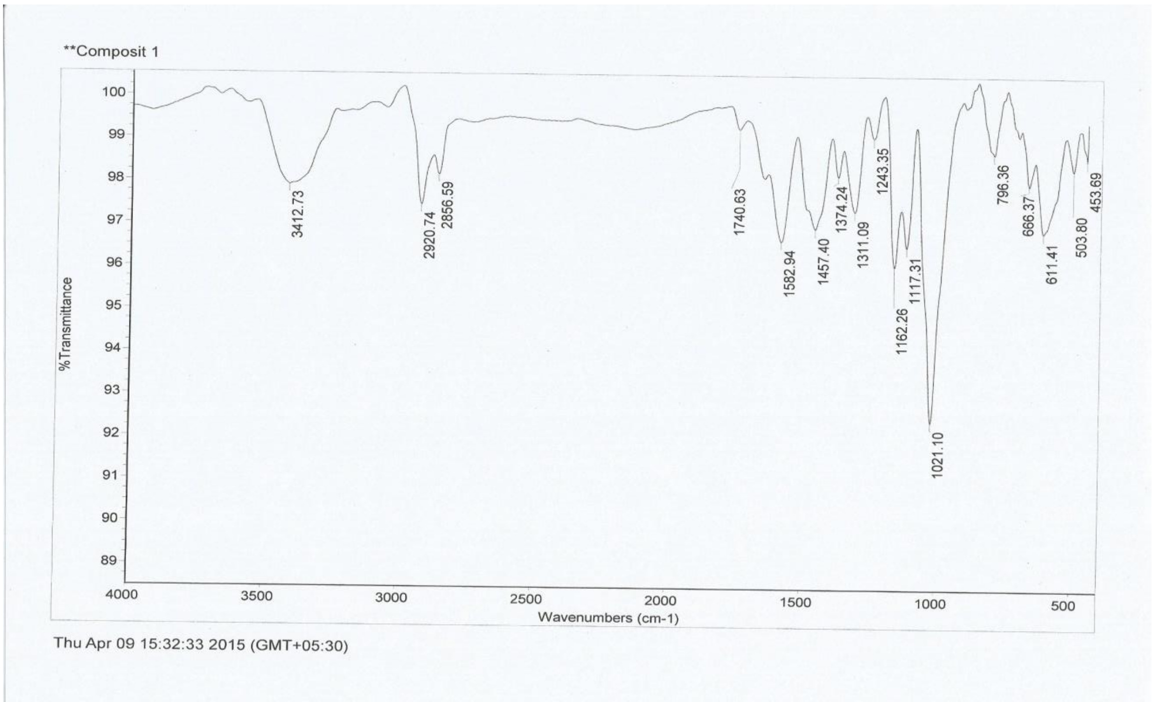

Fig-26: FTIR of PANI/MCC Composite-1

BAND(cm^{-1})	ASSIGNMENT
3412	O-H stretching vibration signifying hydrogen bonds
2920	C-H stretching vibration
1582	C=C ring stretching vibration of the benzenoid ring
1457	CH_2 bending vibration
1311	N-H bending vibration
1374	OH in bending vibration
1243	Symmetric component of the C=C
1021	C-O-C pyrannose ring skeletal vibration
796	Out of plane C-H bending mode

FTIR of PANI/MCC Composite-2

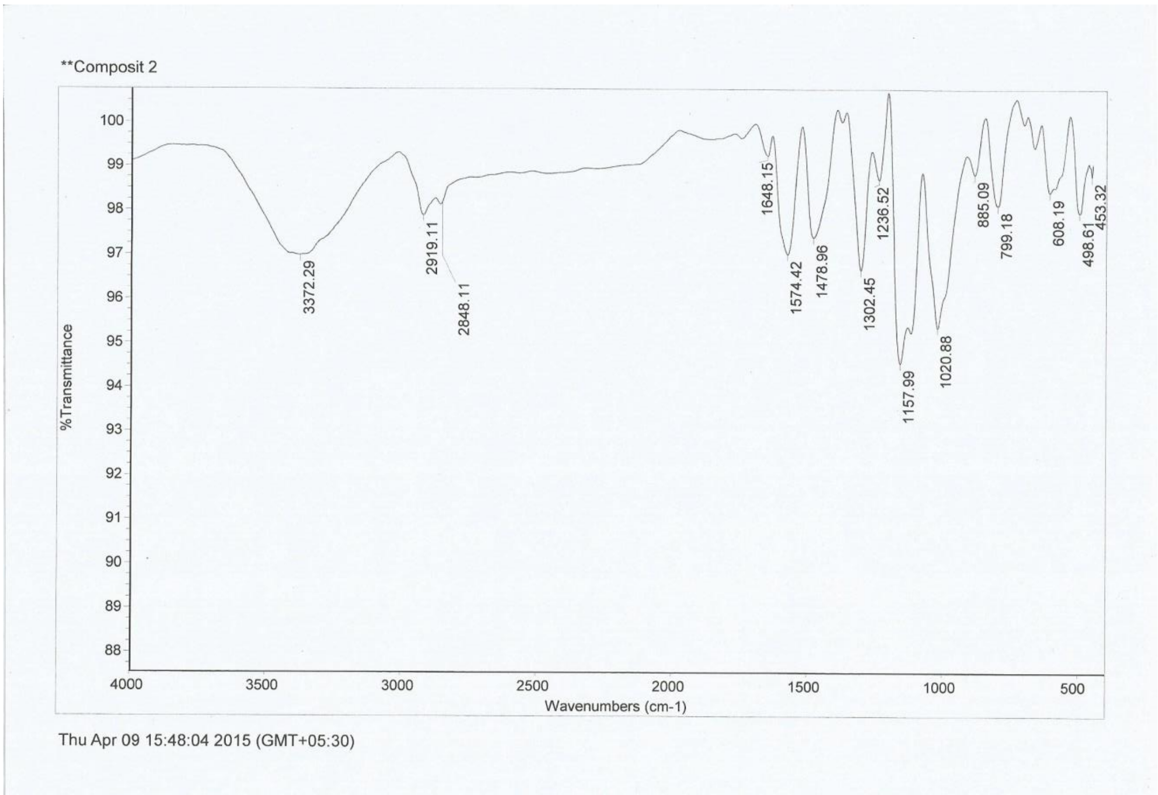

Fig-27: FTIR of PANI/MCC Composite-2

BAND(cm^{-1})	ASSIGNMENT
3372	O-H stretching vibration signifying hydrogen bonds
2919	C-H stretching vibration
1574	C=C ring stretching vibration of the benzenoid ring
1478	CH_2 bending vibration
1302	N-H bending vibration
1236	Symmetric component of the C=C
1020	C-O-C pyrannose ring skeletal vibration
799	Out of plane C-H bending mode

FTIR of PANI/MCC composite- 3

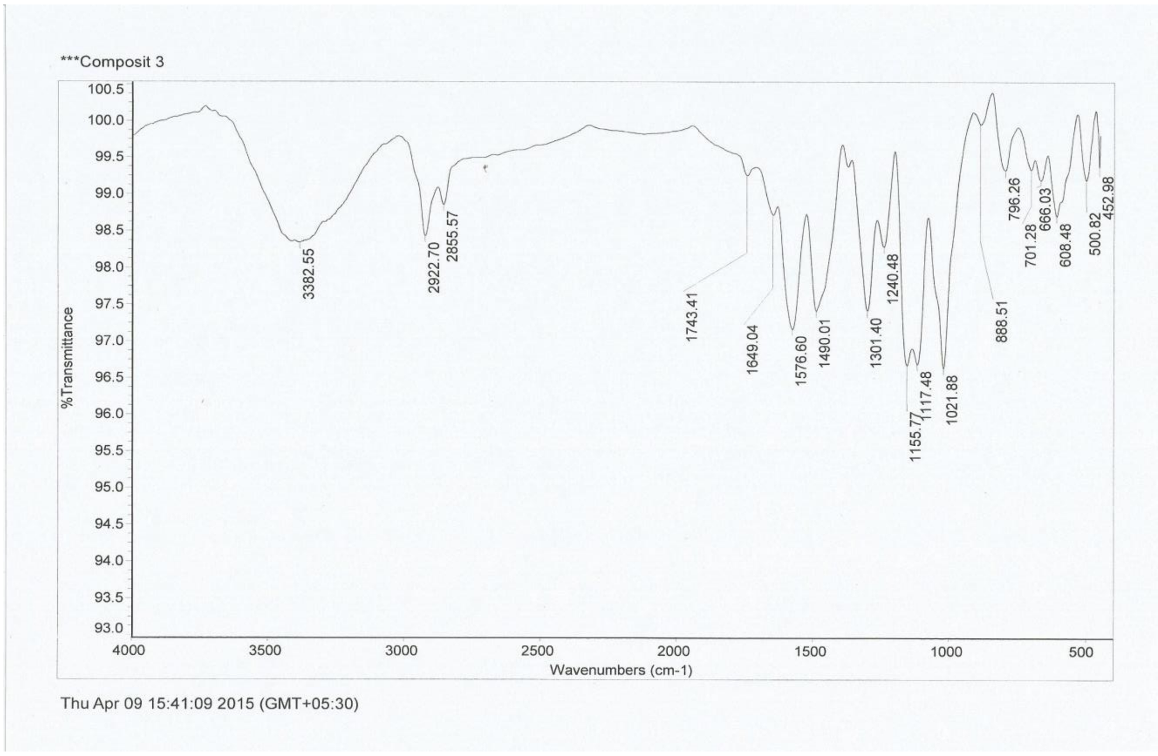

Fig-28: FTIR of PANI/MCC composite- 3

BAND(cm^{-1})	ASSIGNMENT
3382	O-H stretching vibration signifying hydrogen bonds
2922	C-H stretching vibration
1576	C=C ring stretching vibration of the benzenoid ring
1490	CH_2 bending vibration
1301	N-H bending vibration
1240	Symmetric component of the C=C
1021	C-O-C pyrannose ring skeletal vibration
796	Out of plane C-H bending mode

Thermal Analysis

The figure below presents thermal curves of α-cellulose, MCC, PANI, PANI/MCC Composite-1, PANI/MCC Composite-2 and PANI/MCC Composite-3

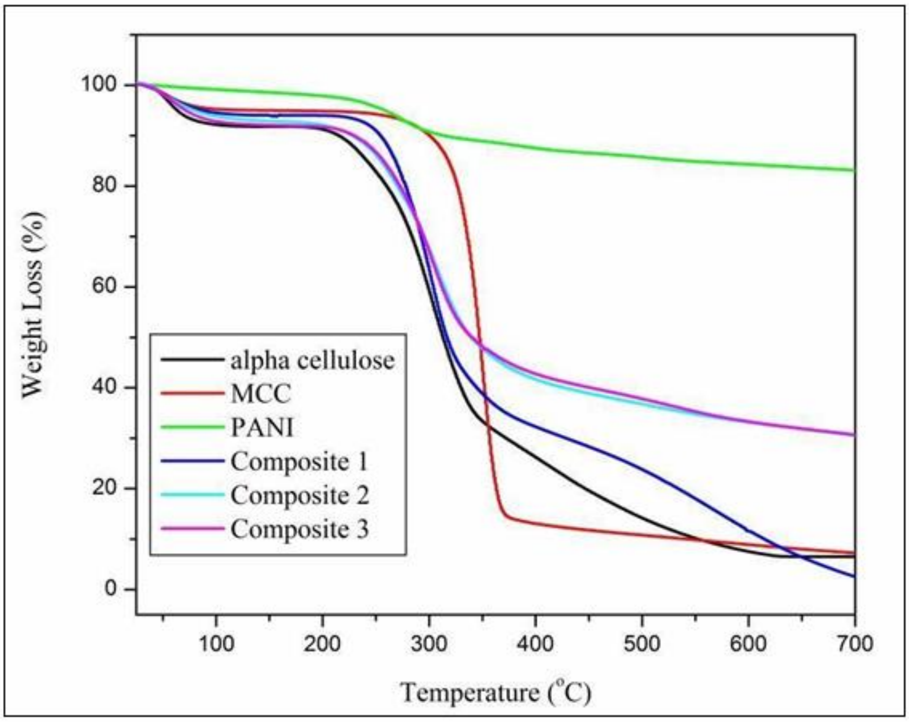

Fig-29: TGA thermogram

Both α-cellulose and MCC showed two step degradation pattern. The initial loss in weight is due to removal of moisture. First weight loss in α-cellulose began at 210˚C whereas for MCC at 270˚C which may be due to the decomposition of cellulose content. The weight loss in the second step began at 340˚C for α-cellulose and at 370˚C for MCC. Since material with higher crystallinity requires higher degradation temperature. The degradation temperature for MCC indicated higher crystallinity in comparison to α-cellulose. Since during industrial processing the temperature rises abruptly, thermal stability of the material is highly desirable. In the present study, the MCC obtained was found to be highly stable till 270 ˚C and therefore it can be expected that MCC prepared from *Imperata cylindrica* would remain stable during industrial processing for varied applications.

PANI showed good thermal stability until 240˚C. On preparing composites, the thermal stability of MCC decreased. All the composites showed two step degradation patterns indicating the initial weight loss due to the degradation of the cellulose content and finally the polymer backbone.

Powder- XRD Analysis

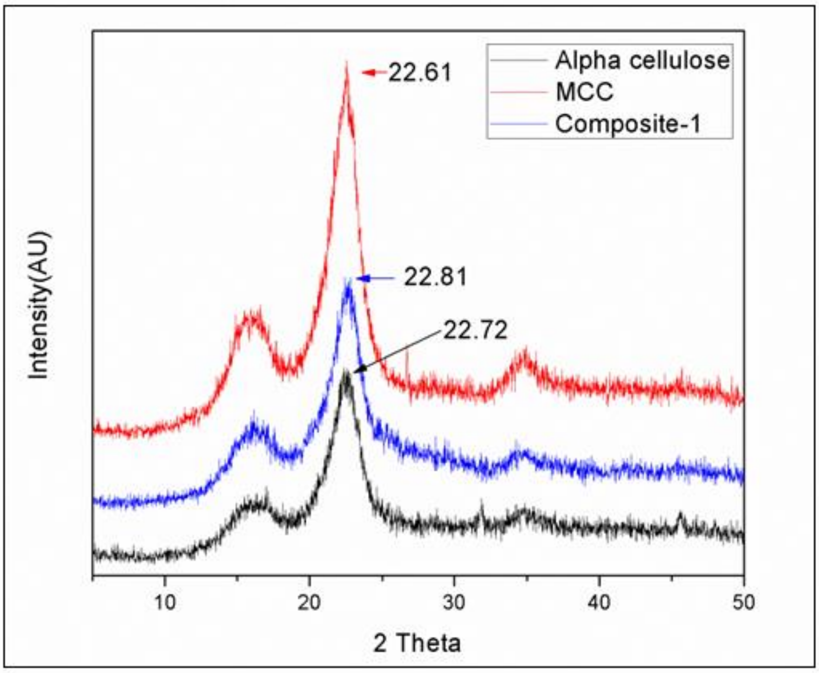

Fig-30: X-Ray Diffractogram of α-cellulose, MCC and Composite-1

The XRD diffractogram studies of the samples were carried to investigate the crystallinity. The diffractogram for MCC in Fig-30 showed peak at 2θ = 22.61˚ while for α-cellulose a peak was observed at 2θ = 22.72˚ which represents a cellulose I structure. The strong reduction of peaks indicates an amorphous structure for the α-cellulose. An increase of the crystallinity degree was found in MCC which may be attributed to an increase in the intra and inter-molecular hydrogen bonding which occurs during the continuous transformation of α-cellulose to MCC. It has been reported that the higher crystallinity in case of MCC was due to its tensile strength and also due to the removal of the hemicellulose and the lignin otherwise present in cellulose. It may be noted that MCC with high crystallinity can be useful as a better reinforcement agent for preparation of composite materials. On preparation of composite with MCC and PANI, the crystallinity decreased in comparison to MCC but increased in comparison to α-cellulose.

CONCLUSION

Microcrystalline cellulose prepared from a common fast growing grass species *Imperata cylindrica* was found to be with higher crystallinity and thermally stable at high temperature. An integrated process concept for detoxification of Cr (VI)-contaminated water with Polyaniline/MCC composite was proposed. The composite was prepared by in-situ oxidative polymerization of aniline in the presence of MCC; the industrially favourable ammonium persulphate was used as the oxidant. The preliminary results showed that the proposed concept was quite effective in the detoxification of the model solution. It is worth expecting that the use of PANI-engineered cellulose fibers prepared using low cost oxidant may serve as an interesting alternative for industrial water treatment.

ACKNOWLEDGEMENT

The author gratefully acknowledge Prof. (Dr) D.K.Kakati , Department of Chemistry, Gauhati University for his inspirational guidance, overall support and providing access to all the instrumental facilities throughout the course of this work.

REFERENCES

1. Prasad, P. D., & Prasa, P. D. (1982). Effect of cadmium, lead and nickel on three freshwater green algae. *Water, Air, and Soil Pollution*, *17*(3), 263-268.
2. Avudainayagam, S., Megharaj, M., Owens, G., Kookana, R. S., Chittleborough, D., & Naidu, R. (2003). Chemistry of chromium in soils with emphasis on tannery waste sites. In *Reviews of Environmental Contamination and Toxicology* (pp. 53-91). Springer, New York, NY.

3. Babula, P., Adam, V., Opatrilova, R., Zehnalek, J., Havel, L., & Kizek, R. (2009). Uncommon heavy metals, metalloids and their plant toxicity: a review. In *Organic Farming, Pest Control and Remediation of Soil Pollutants* (pp. 275-317). Springer, Dordrecht.
4. Zayed, A. M., & Terry, N. (2003). Chromium in the environment: factors affecting biological remediation. *Plant and soil*, *249*(1), 139-156.
5. Becquer, T., Quantin, C., Sicot, M., & Boudot, J. P. (2003). Chromium availability in ultramafic soils from New Caledonia. *Science of the Total Environment*, *301*(1-3), 251-261.
6. Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G., & Gardea-Torresdey, J. (2009). The biochemistry of environmental heavy metal uptake by plants: implications for the food chain. *The international journal of biochemistry & cell biology*, *41*(8-9), 1665-1677.
7. Cohen, M. D., Kargacin, B., Klein, C. B., & Costa, M. (1993). Mechanisms of chromium carcinogenicity and toxicity. *Critical reviews in toxicology*, *23*(3), 255-281.
8. Dayan, A. D., & Paine, A. J. (2001). Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. *Human & experimental toxicology*, *20*(9), 439-451.
9. Newman, D. (1890). A case of adenocarcinoma o the left inferior turbinated body and perforation of the nasal septum in the person of a worker in chrome pigments. *Glasgow Med J*, *33*, 469-470.
10. Sudha, J. D., Sivakala, S., Prasanth, R., Reena, V. L., & Nair, P. R. (2009). Development of electromagnetic shielding materials from the conductive blends of polyaniline and polyaniline-clay nanocomposite-EVA: Preparation and properties. *Composites Science and Technology*, *69*(3-4), 358-364.
11. Bansal, P., Hall, M., Realff, M. J., Lee, J. H., & Bommarius, A. S. (2010). Multivariate statistical analysis of X-ray data from cellulose: a new method to determine degree of crystallinity and predict hydrolysis rates. *Bioresource technology*, *101*(12), 4461-4471.
12. Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in polymer science*, *26*(9), 1689-1762.
13. Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, *44*(22), 3358-3393.
14. Feng, H., Zhang, L., & Zhu, C. (2013). Genipin crosslinked ethyl cellulose–chitosan complex microspheres for anti-tuberculosis delivery. *Colloids and Surfaces B: Biointerfaces*, *103*, 530-537.
15. Carlin, B. A. (2008). Direct compression and the role of filler-binders. In *Pharmaceutical Dosage Forms-Tablets* (pp. 189-232). CRC Press.
16. Shlieout, G., Arnold, K., & Müller, G. (2002). Powder and mechanical properties of microcrystalline cellulose with different degrees of polymerization. *AAPS PharmSciTech*, *3*(2), 45-54.
17. Suzuki, T., & Nakagami, H. (1999). Effect of crystallinity of microcrystalline cellulose on the compactability and dissolution of tablets. *European journal of pharmaceutics and biopharmaceutics*, *47*(3), 225-230.
18. Landin, M., Martinez-Pacheco, R., Gomez-Amoza, J. L., Souto, C., Concheiro, A., & Rowe, R. C. (1993). Effect of batch variation and source of pulp on the properties of microcrystalline cellulose. *International journal of pharmaceutics*, *91*(2-3), 133-141.
19. Doelker, E. (1993). Comparative compaction properties of various microcrystalline cellulose types and generic products. *Drug development and industrial pharmacy*, *19*(17-18), 2399-2471.
20. Sun, C. C. (2008). Mechanism of moisture induced variations in true density and compaction properties of microcrystalline cellulose. *International journal of pharmaceutics*, *346*(1-2), 93-101.
21. Bolhuis, G. K., & Anthony Armstrong, N. (2006). Excipients for direct compaction—an update. *Pharmaceutical development and technology*, *11*(1), 111-124.
22. Rowe, R. C. (1977). The adhesion of film coatings to tablet surfaces-the effect of some direct compression excipients and lubricants. *Journal of Pharmacy and Pharmacology*, *29*(1), 723-726.
23. Phan, C. M., Walther, H., Gao, H., Rossy, J., Subbaraman, L. N., & Jones, L. W. (2013). Insights to using contact lenses for drug delivery.
24. El-Sakhawy, M., & Hassan, M. L. (2007). Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues. *Carbohydrate polymers*, *67*(1), 1-10.
25. UV, I. (2007). Related aniline derivatives.
26. Letheby, H. (1862). XXIX.—On the production of a blue substance by the electrolysis of sulphate of aniline. *Journal of the Chemical Society*, *15*, 161-163.
27. Green, A. G., & Woodhead, A. E. (1910). CCXLIII.—Aniline-black and allied compounds. Part I. *Journal of the Chemical Society, Transactions*, *97*, 2388-2403.
28. Green, A. G., & Woodhead, A. E. (1912). CXVII.—Aniline-black and allied compounds. Part II. *Journal of the Chemical Society, Transactions*, *101*, 1117-1123.
29. Masters, J. G., Sun, Y., MacDiarmid, A. G., & Epstein, A. J. (1991). Polyaniline: allowed oxidation states. *Synthetic Metals*, *41*(1-2), 715-718.

30. MacDiarmid, A. G., Chiang, J., Ritcher, A. F., & Somasiri, N. (1987). *LD; Epstein, AJ In Conducting Polymers; Alcacer, L*(Doctoral dissertation, Ed).
31. Liu, X., Zhou, W., Qian, X., Shen, J., & An, X. (2013). Polyaniline/cellulose fiber composite prepared using persulfate as oxidant for Cr (VI)-detoxification. *Carbohydrate polymers*, *92*(1), 659-661.
32. Liu, X., Qian, X., Shen, J., Zhou, W., & An, X. (2012). An integrated approach for Cr (VI)-detoxification with polyaniline/cellulose fiber composite prepared using hydrogen peroxide as oxidant. *Bioresource technology*, *124*, 516-519.
33. Lei, Y., Qian, X., Shen, J., & An, X. (2013). A process of applying polypyrrole-engineered pulp fibers prepared using hydrogen peroxide as oxidant to detoxification of Cr (VI)-contaminated water. *Bioresource technology*, *131*, 134-138.
34. Camacho, D. H., Gerongay, S. P. C., & Macalinao, J. P. C. (2013). *Cellulose Chemistry and Technology* , 47, 1-2, 125-132.