Executive Summary

of the thesis entitled

SYNTHESIS AND CHARACTERIZATION OF NOVEL HYBRID MATERIALS FOR ADSORPTION AND SENSING OF ORGANIC/INORGANIC POLLUTANTS

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Table of Contents of Thesis

Chapter III:

The application of dextran based hydrogel for elimination of organic dyes and reduction of nitrophenols

Table of Contents of Executive Summary

Chapter I:

Introduction

1. Introduction: The industrial development, increasing population and rapid destruction of resources leads to increasing pollution load in environment[1]. The pollutants released from chemical industries such as textiles, paper, tanneries, electroplating, color photography, printing, dye, and food industries etc. produces large amount of organic and inorganic contaminants. These contamination loads affect the environment adversely by posing severe threat to agriculture, water, soil, food chain and ultimately the human beings [2]. The aquatic flora and fauna are negatively affected by presence of pollutants in natural environment.

1.1. Organic Pollutants: Organic pollution term has been originated from urban run-off, domestic sewage, agricultural wastewater and industrial effluents containing large amount of organic compounds. Several organic pollutants present in environment primarily due to anthropogenic activities are phenols, hydrocarbons, fertilizers, biphenyls, pesticides, oil, detergents, grease, dyes, pharmaceuticals, PAHs and many more has been reported so far[3]. Organic pollutants containing wastewater have huge amount of suspended solids that reduces light penetration ultimately affecting the photosynthetic activity and altering the characteristic of water body[4]. Other than elevated green house gases like CO_2, NO_x, SO_2; load of organic pollutants are also contributed by anthropogenic activities such as discharging household sludge, rapid urbanization, utilization of chemical pesticides in agriculture and so on[5].

1.2. Inorganic Pollutants: Environmental Protection Agency (EPA), United States has listed various water quality parameters in order to quantify the quality of water. The list contains different inorganic materials like barium, arsenic, boron, chloride, calcium, cobalt, lead, chromium, fluoride, iron, nickel, mercury, potassium, magnesium, silica, silver, sulfide, tin, uranium, zinc, vanadium and many more. The elemental forms of these materials or in combination with different compounds are considered as inorganic pollutants after exceeding the permissible limits. Aquatic systems are being polluted by higher concentration of heavy metals as well as other inorganic pollutants like mineral acids, trace elements, inorganic salts, sulfates, metals, metal complexes, cyanides etc. in an alarming rate[6]. The pollutants are commonly chemicals of mineral origin and their existence are due to geogenic activities, while industrial activities, domestic and agricultural wastes elevated their level and mobility in environment[7]. Anthropogenic activities such as manufacturing, handling, storing and disposing of chemicals introduces inorganic pollutants in environment. Lead is one of the commonly existing ions in industrial wastewater, agricultural wastewater and acidic leachate of landfill sites. The advancement of lead batteries over lithium batteries might lead to higher production as well as consumption of toxic lead metals. Consequently, leading to enhanced lead contaminated discharge and polluting environment[8]. Lead intake could be harmful for livings things as well as humans. Their long term high level intake may cause severe disorders like convulsions, nausea, coma, cancer, renal failure as well as sharp effect on intelligence and metabolism. Adsorption of lead ions has been studied in detail in Chapter V (B).

1.3. Dyes: Discharges of large quantity of colored effluents are major concern of industries like textile, plastic, paper, leather and ink manufacturing. The direct discharge of dyes loaded effluent without prior treatment are hazardous for organisms and adversely affect the ecosystem[9]. These colored compounds blocks light penetration that decreases the photosynthetic activity of aquatic plants ultimately hindering their growth and development[10]. Some dyes become persistent in environment as they are difficult to degrade because of complex aromatic structure. They can adversely affect human beings due to their carcinogenic and mutagenic nature causing kidney problems, affecting central nervous system and reproductive system[11]. Methylene blue is a commonly used cationic dye among other dyes of its category, generally utilized for dyeing silk, cotton and wood. Although not utterly hazardous but it does cause some negative effects being in contact with humans[12]. Malachite green is a cationic dye that has been primarily utilized in dyeing wool, jute, silk, leather, paper, distilleries, acrylic industries, food coloring agents, food additives, aquaculture, fish industries and many more[13]. The toxicological symptoms of malachite green comprise pregnancy disorders, pleural infections, developmental abnormalities, carcinogenic nature as well as oral-nasal inflammation. Malachite green induced chromosomal disorders may result in multi-organ tissue damage and its residual products are also toxic in nature. Methyl orange, is a type of p-amino- azobenzene (p-AAB) dye that is anionic in nature. This dye is broadly utilized in textile and dyeing industries as well as in chemical experiments as acid-base indicator. Their aqueous solution is poisonous in nature and cause irritation of eyes, skin and respiratory tract [14]. Rhodamine 6G, is a monocationic xanthene dye that has been broadly used in textile industry as colorant. Rhodamine B is highly water soluble organic chloride salt of xanthenes class dye imparting basic red color. This is broadly used textile industries colorant and food stuffs. They are well known water tracer fluorescent to determine flow rate and flow direction[15]. They can cause carcinogenic effect and on ingestion might be responsible for irritation of nose, eyes, tongue, skin, gastrointestinal tract and reproductive damages. Dyes are helpful in different types of industries but they also possess various detrimental effects. It critically affects the photosynthetic activity by hindering the sunlight penetration in water body. Therefore, removal of these notorious dyes from their aqueous solution using different types of adsorbents has been studied in detail.

1.4. Adsorption: In order to eliminate inorganic and organic pollutants from wastewater, several effective techniques have gathered significant attention. Several methods have been reported for treatment of wastewater out of which adsorption process using solid adsorbents has been considered as most convenient and effective method. This method has various advantage over other convenient methods in terms of cost-effectiveness, simple and facile designing, ease of operation, reusability, less chemical consumption and waste generation[16]. In this process, the liquid adsorbate and solid adsorbent with highly porous surface structure comes in contact with each other and solid-liquid intermolecular force of attraction transfer adsorbate molecules on adsorbent surface. The accumulation of adsorbate on the surface of adsorbent is termed as adsorption that defines the basis of separation using adsorption technology[17].

1.5. Adsorbent: The adsorption process occurs at solid-liquid interface, where the contaminant being adsorbed is known as adsorbate whereas the adsorbing phase is termed as adsorbent[18]. Availability of broad range of adsorbents simplifies the process of adsorption and helps in better wastewater treatment. The different types of adsorbents are used for different types of pollutants. Initially, activated carbon was used as adsorbent system for removal of contaminants from wastewater that was replaced by various cost-effective adsorbents[19]. Since, the adsorption process is restricted on the basis of adsorption capacity therefore, several surface functionalization process could modify the native adsorbent with active sites for pollutant removal. The unique characteristic of nanomaterials like small size, specific surface area, high reactivity etc. helps in synthesis of new high-tech nanoadsorbents. These nanoadsorbents exhibit faster remediation as well as better removal efficiency in comparison to traditional materials. Carbon nanotubes (CNTs), metal oxides and graphene are some categories of nanoadsorbents[20]. Magnetic nanoadsorbents are economical and magnetic decantation helps in easy separation of adsorbent with adsorbate molecules[21]. The three-dimensional polymeric network possessing ability to absorb huge amount of water within their structure and swell accordingly gives rise to hydrogels. Several macromolecules have ability to form hydrogels such as starch, polysaccharides, alginates, cellulose etc. have been reported. These are also beneficial in terms of renewable nature, wide availability and low-cost[22]. These hydrogels successfully eliminates pollutants from aqueous solution. The biomaterials have attracted the attention of researchers as potential bioadsorbent for removal of pollutants from contaminated water body due to their wide-range natural availability, high adsorption efficiency, less expensive, regenerative and environmentally compatible nature. The adsorbents derived from biomass become an alternative to traditional adsorbent system due to their operational flexibility[23]. Several bioadsorbents have been reported so far utilized for elimination organic and inorganic pollutants from wastewater, some of them are egg shell, cabbage waste, olive stone, banana peel, ectodermis of opuntia, fruit peels, *Citrus limetta* peels and many more[24]. Dried seaweed and modified *Citrus limetta* based bioadsorbents have been synthesized for successful removal of organic and inorganic pollutants and detail discussion has been done in Chapter V.

1.6. Sensing: Detection and monitoring of different compounds and elements requires analytical tool such as High performance liquid chromatography, inductively coupled plasma-mass spectroscopy, chromatography, flame atomic absorption spectroscopy, electrophoresis etc. however, these methods are expensive and complicated in context of operation[25]. These techniques could not be utilized for in-situ analysis due to their multi-step and complicated sample preparation, high maintenance cost, time consumption and controlled experimental conditions. Chemosensors have several advantages over conventional sensing systems like sensitivity, non-destructive nature, inexpensive, selectivity, lower detection limit, fast response time and so on. They can be used for on-site detection of compounds without any sophisticated instrument based on optical method. The visual detection of color change can be seen through naked eyes. Therefore, different studies have been reported based on colorimetric sensing of various compounds such as proteins, amino acids, heavy metals, organic molecules etc. [26,27]. The cyclodextrin crosslinked polymer with pthalic anhydride was used with gold solution to develop stable gold nanoparticles based sensor. The nanosensor was utilized for rapid, colorimetric detection of amino acid (cysteine) and agrochemical (diethyldithiocarbamate), detailed discussion has been done in Chapter IV.

Chapter II:

Synthesis, characterization and application of β-cyclodextrin based magnetic nanoadsorbent for simultaneous adsorption of hydrophilic and hydrophobic dyes

2.1. Introduction: Chemical industries such as textiles, paper, color photography, printing, dye, and food industries discharges contains large amounts of contaminants such as dyes and paints that pose severe risk on environment. Synthetic dyes have complex aromatic molecular structures and are more resistant toward biodegradation and oxidizing agents therefore, their addition leads to many disadvantages and hazards such as hindrance of light penetration as well as mutagenic changes. Methylene blue (MB), malachite green (MG), and rhodamine are dyes with commercial significance and widely used for dyeing textile fibers like cotton, wool etc. They can cause adverse effect such as sweating, irritation, eye burn and carcinogenic upto some extent. Magnetic nanoparticles (MNPs) such as Fe_3O_4 are useful in environmental remediation applications due to rapid dissociation of target molecules from the samples easily by applying an external magnetic field[28,29]. Magnetic nanoparticles are anticipated to be an efficient heavy metal adsorbent because of its high surface area as well as magnetic recoverability that overcomes the instinctive difficulties of nanoadsorbents to separate from wastewater after use. β-CD is a natural cyclic oligosaccharide with hydrophilic outer and hydrophobic inner cavity, giving rise to a phenomenal capacity to form inclusion complexes in solution with several organic molecules through host-guest interaction.

2.2. Materials and Methods: A superparamagnetic nanoadsorbent was synthesized by covalent conjugation of MNPs with a crosslinked CD-maleic anhydride copolymer (**Figure 1**). The crosslinking of CD with maleic anhydride leads to decrease in its solubility, making it more suitable as an adsorbent. The synthesized adsorbent has been characterized by using several analytical techniques such as NMR, FTIR, XRD, HR-TEM, DLS, VSM, TGA and BET. The efficiency of SPNA as an adsorbent for hydrophobic as well as hydrophilic dyes was assessed under varying concentrations, time and pH. The sorption kinetics and probable mechanism of the adsorption were determined and the data were fitted into various isotherm models. Simultaneous adsorption of dyes as well as regeneration and reusability of super paramagnetic nanoadsorbent (SPNA) was also investigated.

The adsorption capacity, removal percentage and adsorption at particular time 't' were calculated using the following equations[30]:

$$\boldsymbol{q_e = \frac{(C_0 - C_e)}{m} * V \ldots\ldots\ldots\ldots\ldots (1)}$$

$$\boldsymbol{\%R_e = \frac{C_0 - C_e}{C_e} * 100 \ldots\ldots\ldots\ldots. (2)}$$

$$\boldsymbol{q_t = \frac{C_0 - C_t}{m} * V \ldots\ldots\ldots\ldots... (3)}$$

where,

q_e denote adsorption capacity (mg/g), q_t is adsorption capacity at particular time '*t*' (mg/g) and *%Re* is the removal percentage of dyes; C_0 represents initial concentration (mg/L), C_e is equilibrium concentration (mg/L) and C_t denote the concentration at time '*t*' (mg/L) of dyes in aqueous solution; '*V*' denotes the volume of solution (L) and '*m*' denotes the weight of the adsorbent (g).

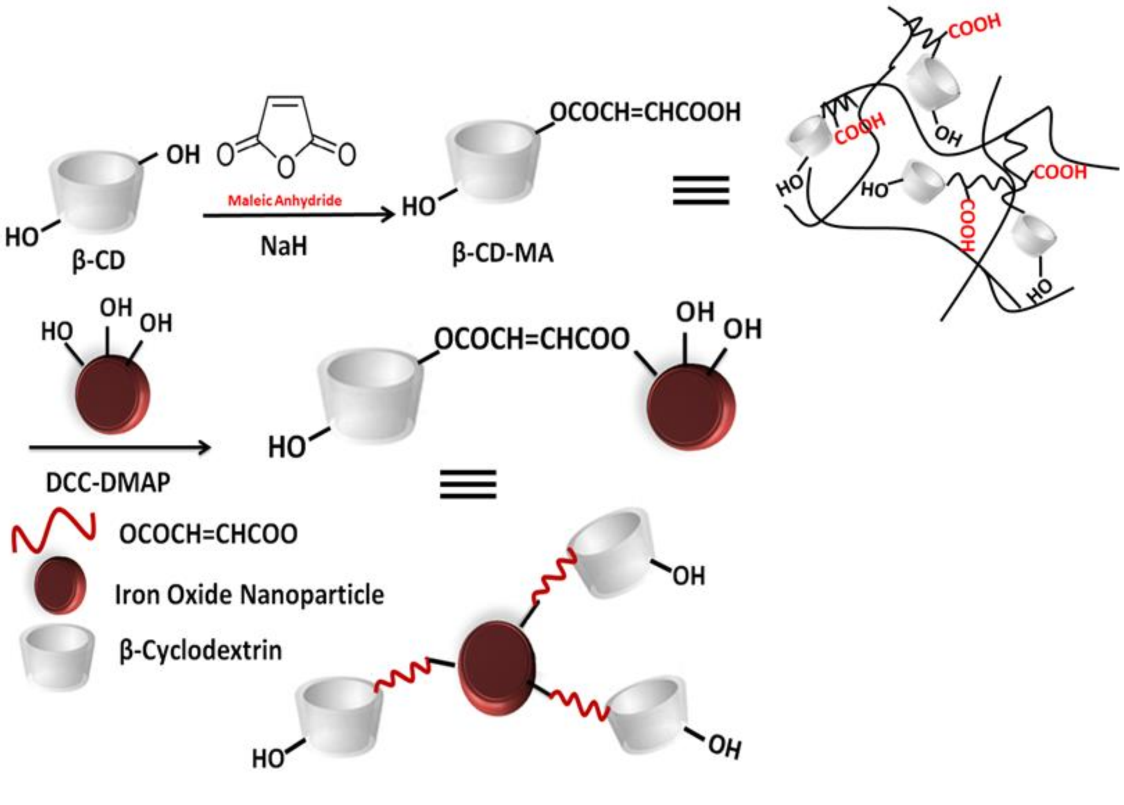

Figure 1: Schematic for synthesis of SPNA

2.3. Results and Discussion: The efficiency of SPNA as an adsorbent for hydrophobic as well as hydrophilic dyes was estimated under various adsorption parameters such as concentrations, adsorbent quantity, times, temperature and pH. The adsorption kinetics and probable mechanism of the adsorption were determined and the experimental data were fitted into various isotherm models. Adsorption process follows pseudo-second-order kinetic model and the equilibrium data fitted well into Langmuir adsorption isotherm model. The study reveals that SPNA is an excellent nanoadsorbent and eliminates dyes with maximum removal efficiency of 97.2, 85.1, and 37.3% for MB, MG, and R6G, respectively [31]. The reutilization of the adsorbent is an important index for defining the efficiency of the adsorbent; therefore, desorption process was also investigated using dye loaded SPNA.

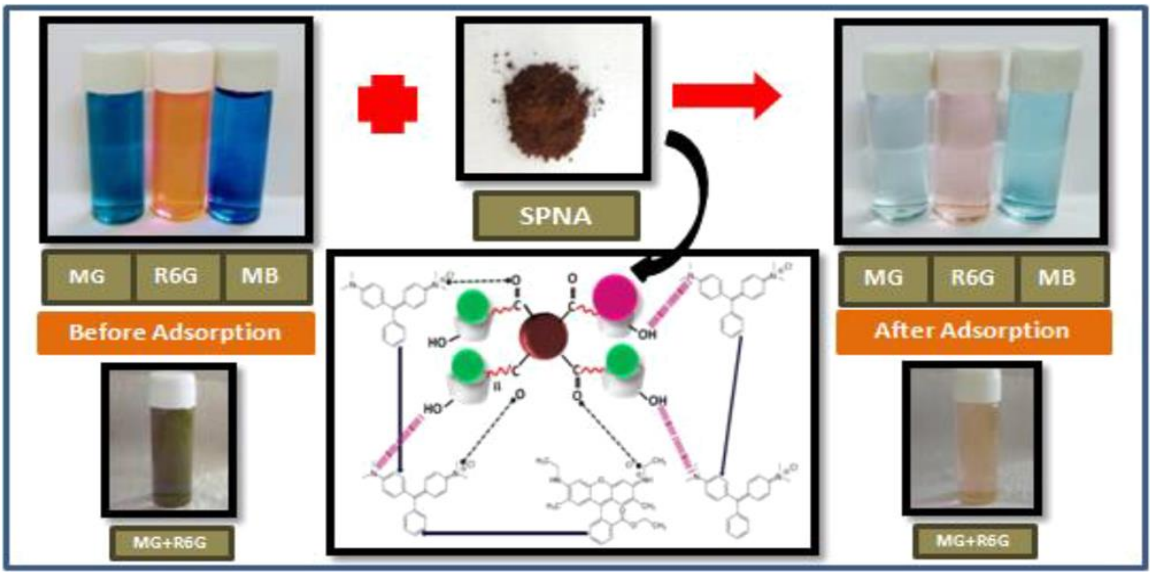

Figure 2: Image of magnetic adsorbent and vials containing dye solutions (Methylene Blue, Malachite Green and Rhodamine-6-G) before and after adsorption with superparamagnetic nanoadsorbent; Photographs and mechanism of adsorption for Malachite Green + Rhodamine-6-G mixture using superparamagnetic nanoadsorbent

Results show that the adsorption capacity decreases after five cycles for all the three dyes and more than 90% of the dye was effectively removed during the desorption cycles. The adsorbate in this case is dye molecule which is planar and can be readily adsorbed on the adsorbent via van der Waals force and hydrogen bonding interactions in addition to CD cavity (**Figure 2**). Further, in case of cationic dyes the electrostatic forces of interaction play a role in the sorption process. The cavity of cyclodextrin can encapsulate all the three types of organic dyes[30]. But lower adsorption of R6G suggests that its larger size and hydrophobic nature prevent any other interaction with the SPNA. On the other hand MB and MG are able to bind to the CD-MA polymer via electrostatic forces of interaction, van der Waals forces and hydrogen bonding in addition to the host guest interaction with the cavity of cyclodextrin.

2.4. Conclusions: A proficient and simple approach was applied to synthesize a novel magnetic nanoadsorbent (SPNA), which can efficiently remove organic dyes particularly MB, MG, and R6G individually as well as simultaneously from mixture. The results indicate that SPNA is an excellent nano-adsorbent for removal of dyes with maximum removal efficiency of 97.2%, 85.1% and 37.3% for MB, MG and R6G, respectively. The detailed investigation of adsorption behavior of the SPNA exhibited that the adsorption process occur due to host-guest interaction with cyclodextrin cavity, electrostatic forces of interaction, van der Waals forces and hydrogen bonding. Thus, convenient, highly efficient and technically feasible properties make this novel nanoadsorbent a promising low-cost adsorbent for dye removal that can be used for environmental remediation effectively.

Chapter III:

The application of dextran based hydrogel for elimination of organic dyes and reduction of nitrophenols

3.1. Introduction: The release of hazardous pollutants due to anthropogenic activities and the subsequent deterioration of water quality is a serious concern being faced globally. Amongst several other classes of pollutants the elimination of harmful organic contaminants like dyes and phenolic compounds from water requires attention. Their release from printing, dyeing, textile, oil refineries and pharmaceutical industries cause risk to human health as well as on environment. Hydrogels are composed of a three dimensional network of hydrophilic polymers representing high adsorption capacities due to a controllable swelling property and the ability to hold a large amount of water while maintaining their structure. These hydrogels are utilized as adsorbent for removal of pollutants. The hydrogels synthesized from synthetic polymers has various benefits due to their precised chemical structure that could be effectively designed at molecular level. Various environmentally responsive hydrogels could be created by modification[32]. Further disposal or recycling problem of the already recycled adsorbents were solved by transforming such materials to value added products. The metallopolymers generated after entrapment of metal nanomaterials in hydrogel matrix are potential catalytic systems for organic transformations of industrially important molecules[33,34].

3.2. Materials and Methods: A single step and facile novel strategy was utilized for surface modification of dextran using hexamethylene diisocyanate synthesizing adsorbent for removal of both cationic [methylene blue (MB)] and anionic [methyl orange (MO)] dyes [35]. The photocatalytic degradation of 4-nitrophenol using an Ag loaded metallopolymer as a catalyst has been used for reduction of hazardous and toxic nitroaromatics present in water. The synthesized hydrogel and metallopolymer was characterized by using NMR, FTIR, EDS, XRD and TGA. Desorption study was also studied to investigate the recyclability of DEX-HMDI hydrogel.

3.3. Results and Discussion: The swelling behaviour of dextran based hydrogel was investigated in deionized water, different pH value and salt concentration. Water retention profile of hydrogel has also been observed (**Figure 4**).

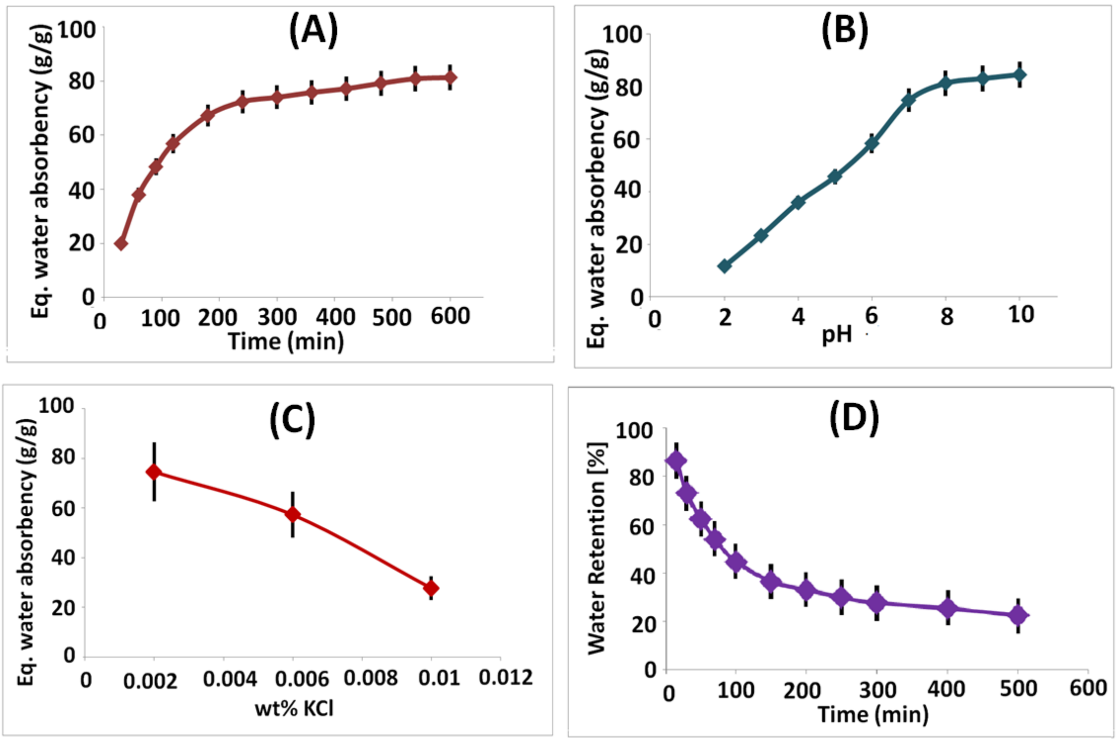

Figure 4: Swelling characteristics of hydrogel in (A) distilled water (B) buffer solutions of pH (2-10) (C) KCl solutions (D) water retention profile

Adsorption of Methylene Blue and Methyl Orange has been investigated via various adsorption parameters like initial concentration, adsorbent quantity, pH and temperature (**Figure 5**).

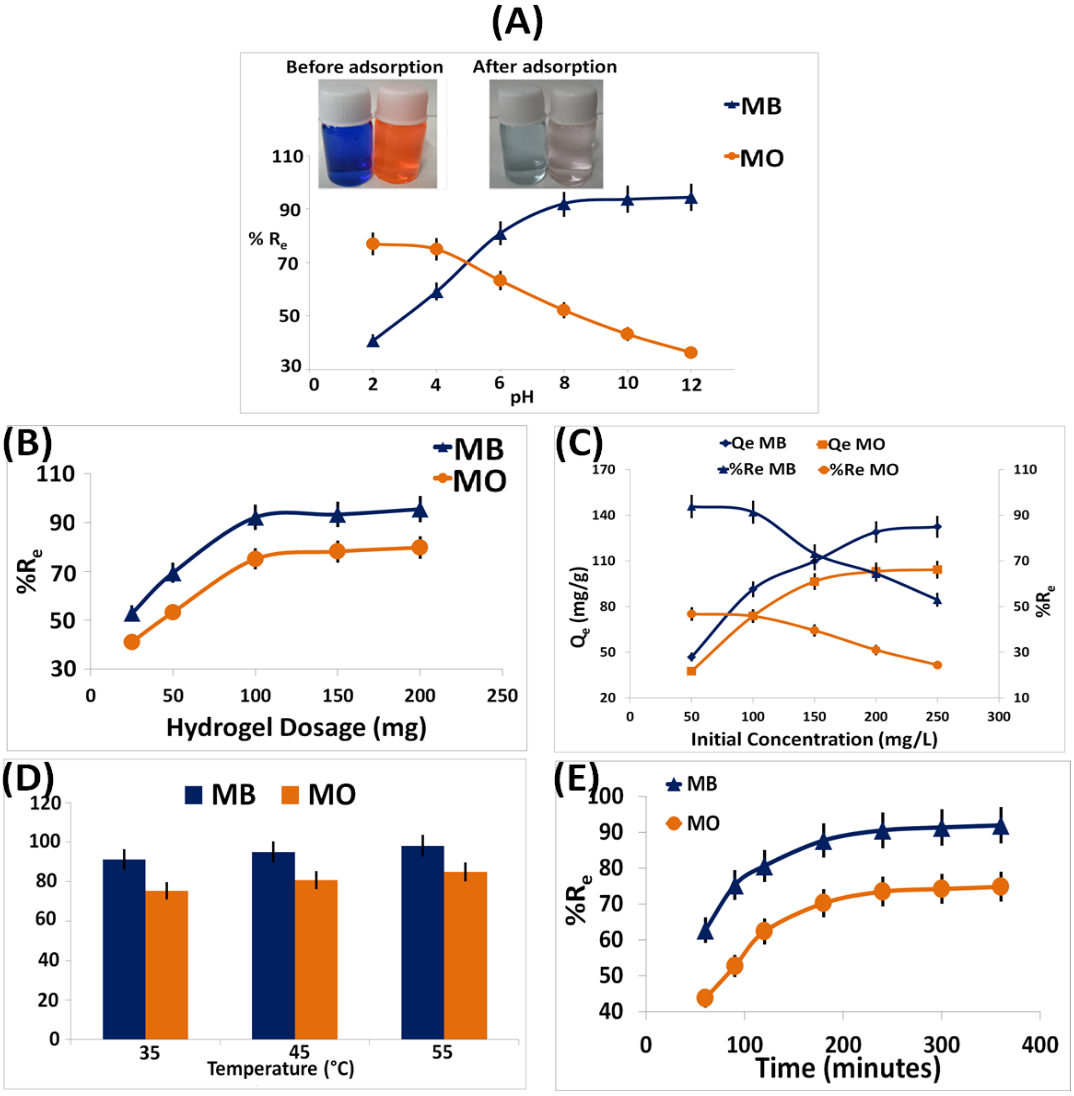

Figure 5: Effect on removal efficiency of MB and MO by varying parameters (A) pH; Inset: Photographs of vial before and after adsorption, pH 12 for MB and pH 2 for MO (B) adsorbent dosage (C)initial concentration (D) at 35°C, 45°C and 55°C temperature (E) contact time (For all the experiments 100 mgL^{-1}dye solution was and 0.1 g of hydrogel was used)

Several adsorption kinetic models were applied on experimental data such as zero order, first order, second order, third order, pseudo-first and pseudo-second order. The data based adsorption kinetics follows pseudo-second order model. Adsorption thermodynamics based on temperature variation and adsorption isotherm was also investigated. Adsorption of dyes in a binary mixture of MO and MB shows greater removal of MB (99%) in comparison to

MO (76%). Successive adsorption/desorption cycles were performed to investigate the reusability and stability of the hydrogel. For the assessment of the catalytic performance of silver loaded dextran based hydrogel, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (p-AP) was selected as a model nitroaromatic reduction reaction. The progress of the reaction was monitored using UV-vis spectrophotometric determinations.

The adsorption mechanism, in general, can be governed by various interactions like electrostatic forces of interactions, ion-exchange, hydrogen bonding, hydrophobic interactions and van der Waals forces. Of all these interactions, the forces actually being involved in adsorption will depend upon structural properties and functional groups of substrates and dye molecules [36,37]. The planarity of dye molecules leads to formation of van der Waals forces between the dye molecules and hydrogel (**Figure 6)**. The presence of surface functionalities leads to hydrogen bond formation [31]. The probable interaction of cationic and anionic dye with hydrogel occurs *via* these interactions [38,39].

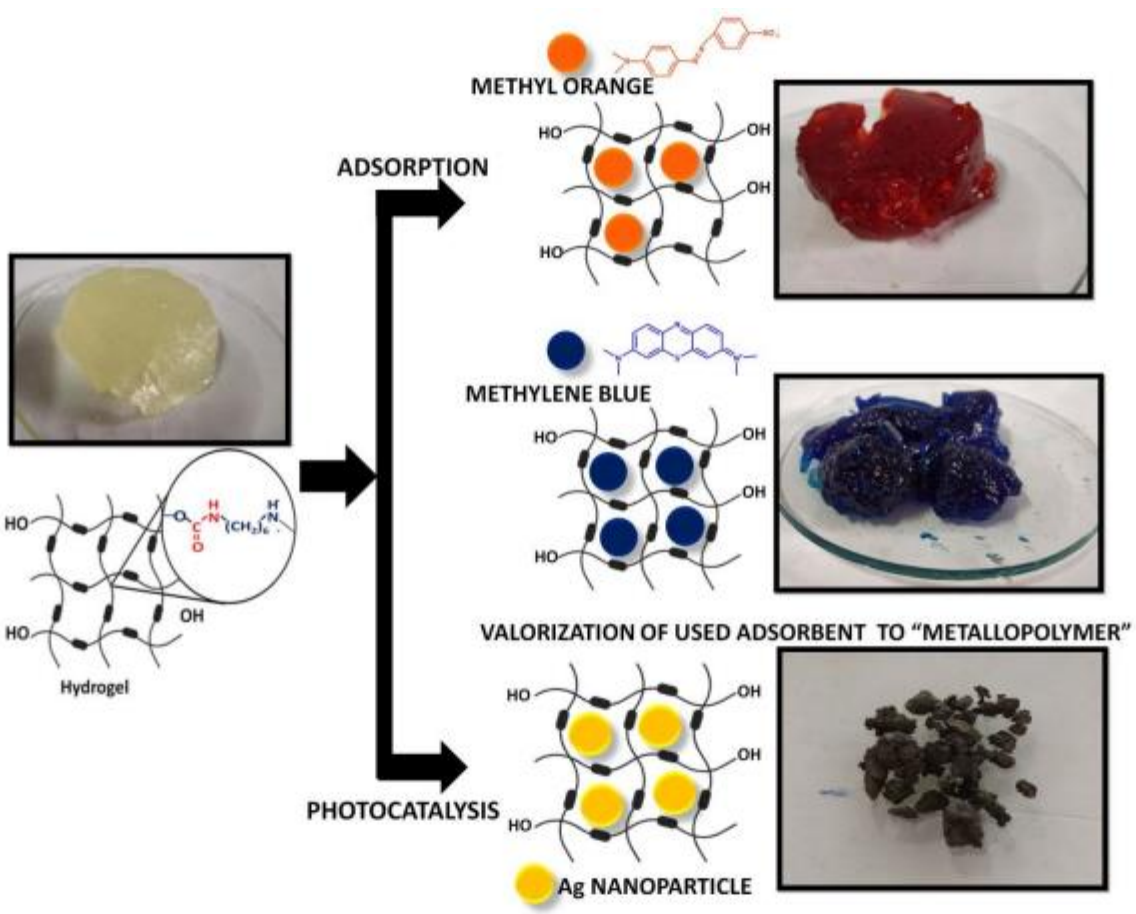

Figure 6: Probable mechanism for adsorption of cationic and anionic Dyes as well as Silver onto hydrogel depicting some possible interactions

3.4. Conclusions: Sustainable approach for using agro-waste for effluent treatment has been investigating to eliminate various co-existing pollutants as well as value addition of used adsorbent. In this system MB and MO has been taken as model of cationic and anionic dyes showing excellent removal efficiency of 98% and 84% respectively. The single layer adsorption and chemisorptions is rate determining step investigated by adsorption isotherms study. The positive values of $\Delta S°$ and $\Delta H°$ express that the process of adsorption is spontaneous and endothermic in nature according to thermodynamic study. The increase in temperature increases removal efficiency. The hydrogel could also efficiently entrap Ag metal ions and the resulting metallopolymer exhibited excellent sunlight mediated photocatalysis, reducing 4-NP to 4-AP in less than 30 seconds.

Chapter IV:

Development of crosslinked β -cyclodextrin polymer functionalized gold nanosensor for detection of sulphur based amino acid and agrochemicals

4.1. Introduction: Recognition of chemical and biological agents present in environment plays crucial role in forensic, biomedical, and environmental sciences application. Advance technology along with basic knowledge in chemistry, material science and biology is required for the development of cost-effective and highly sensitive sensor system. Sensors have two functional components i.e. a recognition element and transducer. The sensor efficacy relies on the above-mentioned components for remarkable sensing on the basis of the limit of detection, response time, selectivity etc. Therefore, the efficient sensor synthesis depends on generation of new materials with better recognition and transduction processes. The nanomaterials imparts various unique physicochemical properties in case of chemical and biological sensors, helping in generation of novel transduction and recognition processes[40]. The utilization of nanomaterials as an active component for sensing exhibits better result due to their unique properties. Gold nanoparticles tuned up with the variation in shape, size and chemical environment around them. The physicochemical properties of transducer gold nanoparticles could be altered during binding event in between sensor and analyte [41]. The gold nanoparticles possess LSPR band that could be utilized for colourimetric assessment of metal ions, amino acids, DNA, pharmaceutical compounds, proteins etc. as well as the formation of microscale optical devices [42–46].

4.2. Materials and Methods: A facile and rapid colorimetric method has been developed using stable gold nanoparticle based nanosensor synthesized using crosslinked cyclodextrin phthalic anhydride (CDPA) polymer[47]. The unique ability of beta-cyclodextrin (β-CD) binds with both hydrophilic and hydrophobic compounds [31,48] along with Au-thiol interactions. The nanosensor has been used for sensing of amino acid (i.e. Cysteine) as well as agrochemical (i.e. diethyldithiocarbamate). For selective detection of sulfur based compound, silver based nanosensors have also been synthesized to compare with gold nanosensor (**Figure 7)**. The colourimetric assessment of nanosensor shows red shift (from 524 nm to 670 nm) within 5 seconds for sulfur-based compounds. A detailed qualitative and quantitative study of Cysteine and Sodium diethyldithiocarbamate sensing was carried out. The synthesized nanosensor has been characterized by using NMR, FTIR, DLS, Zeta Potential, HR-TEM, FESEM-EDX etc.

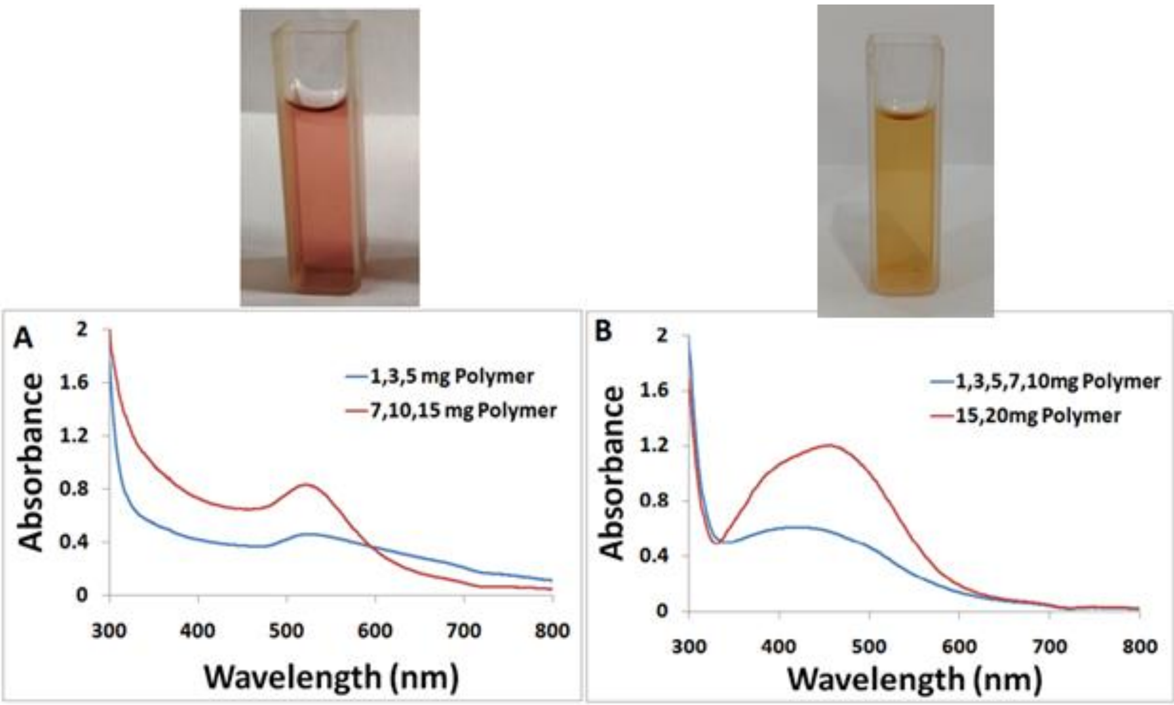

Figure 7: UV-visible determinations demonstrating spectral properties of synthesized nanoparticles (A) AuNS@CDPA and (B) AgNS@CDPA (inset images of cuvettes containing sensor solutions)

4.3. Results and Discussion: The nanostructures of gold and silver nanoparticles have major benefit of surface functionalization using organic and biological molecules. Several colorimetric probes have been reported till date for detection of metal ions as well as other analytes. To investigate the selectivity of AuNS@CDPA towards sulfur-based amino acid i.e. cysteine, competitive sensing experiments were carried out with other non-sulfur based amino acids. The simple and rapid detection of analytes has been significantly measured using nanosensors due to their affinity towards sulfur group.

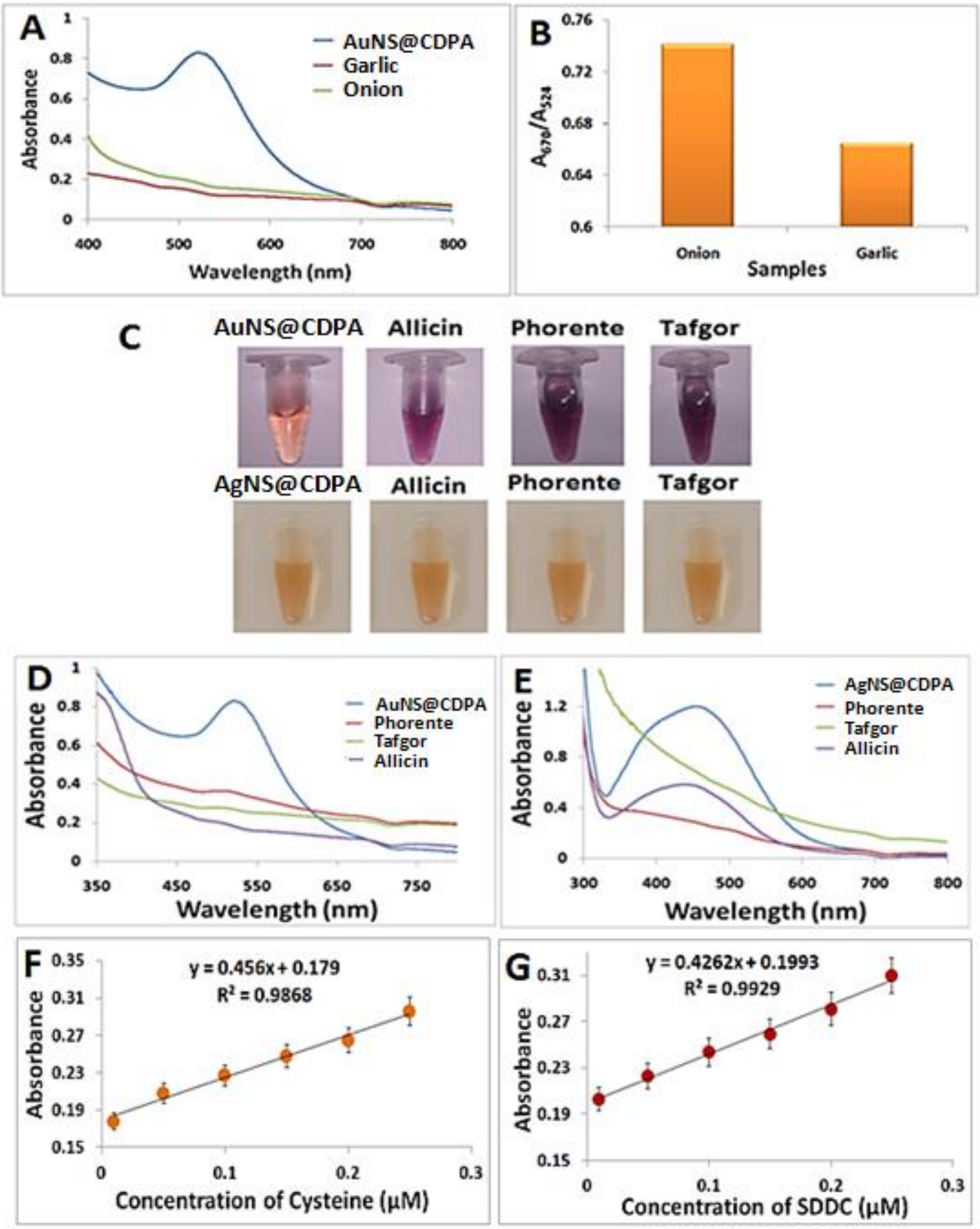

Figure 8: (A) UV-vis spectra and (B) Absorption ratio (A_{670}/A_{524}) of AuNS@CDPA in presence of allicin containing onion and garlic extract. (C)Photographs of AuNS@CDPA and AgNS@CDPA in presence of sulfur based pesticide samples and their (D&E) Absorption spectra. Linear relationship of (F) Cysteine and (G) SDDC with absorbance at 670 nm for quantification and determination of LOD (Sensing samples were prepared by adding 700 µL of AuNS@CDPA solution with 300 µL of different

concentration of Cysteine and SDDC, the error bars represent standard deviation obtained from three independent measurements)

The colorimetric assessment of sulphur based amino acid and agrochemicals have been demonstrated along with quantification of selected model. The presence of sulphur based allicin has been sensed from onion and garlic extract. As the sensor was able to detect sulfur compounds in a complex extract matrix, the scope was further extended to the detection of hardcore sulfur pesticides utilized daily. For this study, Phorente and Tafgor were selected pesticides. They were spiked in known quantities in water samples and the sensitivity of AuNS@CDPA in their detection was investigated. A similar colour change from wine red to blue was observed in the case of both these pesticides agrochemicals (**Figure 8)**. In case of gold nanoparticles, aggregation changes red color to blue whereas with silver nanoparticles yellow color changes into red due to coupling of surface-plasmon resonance among particles. The UV-vis spectrum also represented a significant increase in absorption ratio. The selectivity of cysteine detection is due to the presence of the –SH group in its structure which has an affinity for gold. A rapid colour change in the SDDC solution is probably due to the reaction of a stable sodium diethyldithiocarbamate complex with AuNS@CDPA. A decrease in SPR absorbance was observed accompanied by a bathochromic shift arising from the influence that sulfur atom has on gold nanoparticles. Similarly, the dithiocarbamate compound containing the disulfide group also shows sensitivity towards the gold nanosensor. The possible mechanism for the detection of Cysteine and SDDC in this work is based on dispersion-aggregation mechanism. The detailed semi-quantitative and quantitative studies suggest that the presence of S containing model compounds like cysteine (amino acid) or SDDC (agrochemical) is capable of inducing aggregation of AuNS@CDPA. This is quantitatively proved from experiments that demonstrated an increasing absorption ratio i.e. $A_{670}/A_{524}$for cysteine and SDDC.

4.4. Conclusions: The synthesis of CDPA functionalized gold nanosenor (AuNS@CDPA) was carried out by facile two step reaction that exhibit better sensitivity towards colorimetric recognition of Cysteine and SDDC. The polymer and sensors were thoroughly characterized by various analytical techniques. The microscopic imaging via FE-SEM and HRTEM suggest spherical morphology and formation of <15 nm-sized sensors. Other sulfur based agrochemicals such as phorente, tafgor and allicin have also been sensed from real samples using gold nanosensor. The colorimetric assessment is based on red shift (from 524nm to 670nm) in presence of sulphur based compounds. The silver nanosensor was also synthesized for comparative study but gold nanosensor has better sensitivity than silver nanosensor. The effect of ionic strength and pH of solution on spectral characteristics of sensing has also been discussed. The quantitative studies suggested straight line linearity in the range of 0.01-0.25 µM for SDDC and Cysteine with LOD values of 0.05 and 0.07 µM respectively for these compounds

Chapter V (A):

Assessment of seaweed bioadsorbent (*Fucus vesiculosus*) for removal of methylene blue and rhodamine B dyes

5.1.1. Introduction: The dyes impart several adverse effects on the environment such as enhancement of chemical oxygen demand of water body, obstruction to the usual photosynthetic activity of aquatic flora and irregular aquatic organism metabolism[49]. Other than imparting colors, dyes could cause severe teratogenic carcinogenic and mutagenic effect[50]. The use of dead biomass has advantages over the use of living biomass since it is not necessary to add nutrients, the adsorbent is immune to the toxicity or adverse operating conditions and processes does not governed by biological constraints. Recently interest has been turned towards non-living biomass having advantage of increased tolerance of environmental condition without nutrient requirement[51–53]. This has been referred as biosorption, the passive attachment of ions to a biomass. The bioadsorbents exhibit the advantages of high sorption capacity, ease of availability, regeneration, less financial input, less sludge generation, ecofriendly and harmless nature due to which it gathers the attention of researchers now-a-days for elimination of contaminants from polluted water [54]. An ideal bioadsorbent should be freely available at low cost, efficient and rapid uptake of pollutant as well as reusable. *Fucus vesiculosus*, brown seaweed has been used for removal of Methylene Blue and Rhodamine B. Marine algal biosorbent is a potential material for removal of dyes due to its algal surface chemistry and hetero atom containing functional groups.

5.1.2. Materials and Methods: The brown seaweed (*Fucus vesiculosus*) has been collected, washed thoroughly, dried and crushed. The uniformed sized powdered seaweed was used for adsorption of Methylene Blue and Rhodamine B. Analytical tools like FTIR, TGA, BET etc. will be used for characterization. Adsorption parameters such as dosage, pH, concentration and temperature variation have been explored. Simultaneous adsorption of MB and RB were assessed by considering the practical relevance.

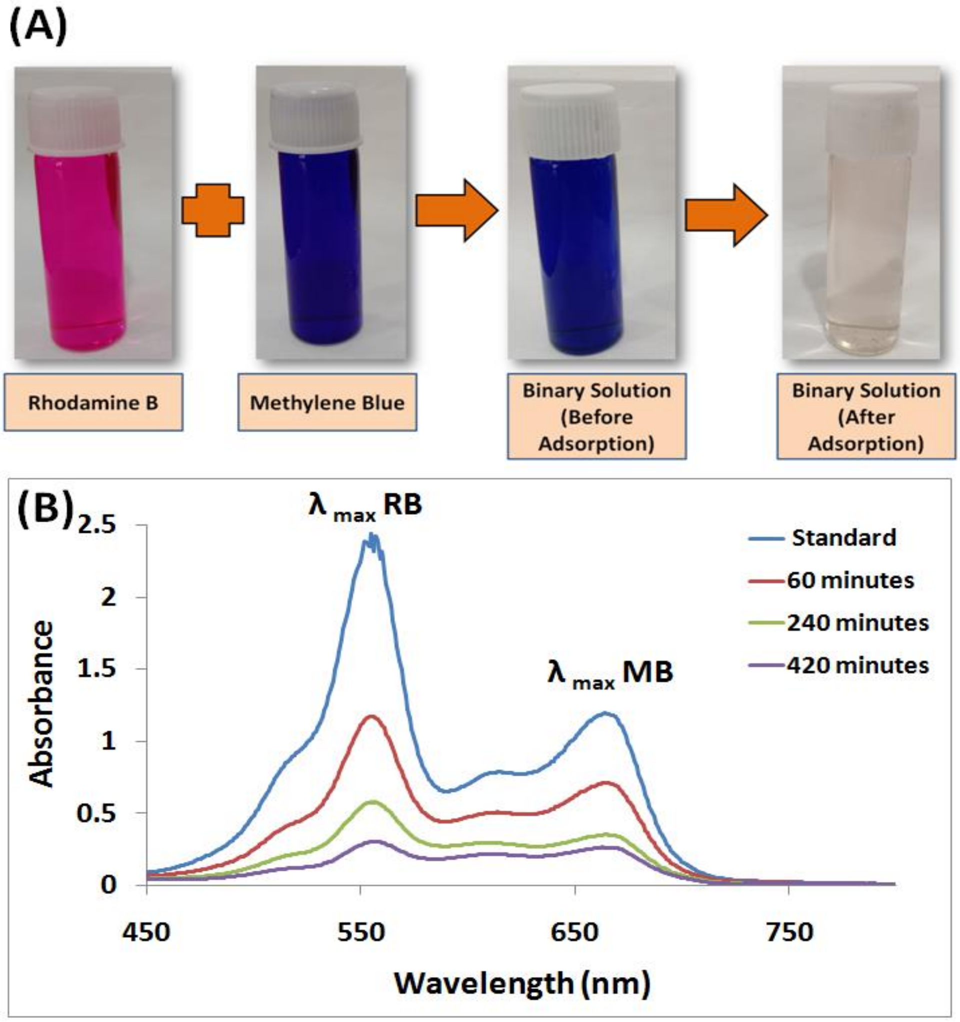

Figure 9: (A) Photographic images of binary solution before and after adsorption (B) UV-visible spectra of MB and RB in binary solution with time

5.1.3. Results and Discussion: Seaweed possesses several functional groups that enhance the removal of dyes from aqueous solutions. The removal efficiency of Methylene Blue and Rhodamine B using *Fucus vesiculosus* seaweed bioadsorbent (FVSB) was around 85-90%. The adsorption parameters have been investigated in detail. The recycling and regeneration experiments were also performed. Simultaneous adsorption of MB and RB has been studied to investigate the removal efficiency in binary system (**Figure 9)**. Recycling and reuse of dye loaded FVSB was carried out via desorption process. The maximum removal efficiency obtained after the first desorption cycle was 96.3% and 92.2% for MB and RB, respectively. The removal efficiency decreases slowly after every cycle reuse of FVSB. The experimental data follows the pseudo-second order kinetic model and monolayer adsorption with high co-relation coefficient value of Langmuir adsorption isotherm model. The surface of FVSB, contains several active functional groups like hydroxyl, carboxylic and amine groups that govern the process of adsorption. The MB and RB dye uptake was basically facilitated by the electrostatic interaction and hydrogen bonding between adsorbate and bioadsorbent surface (**Figure 10)**. The FVSB could be considered as effective, sustainable and eco-friendly adsorbent system for efficiently removing the dyes from single and binary component system. The removal of color from real environmental sample has been investigated using textile effluent. The result shows decrease in color intensity visibly as well as supported by UV visible spectra of solutions before and after adsorption demonstrating successful environmental remediation process.

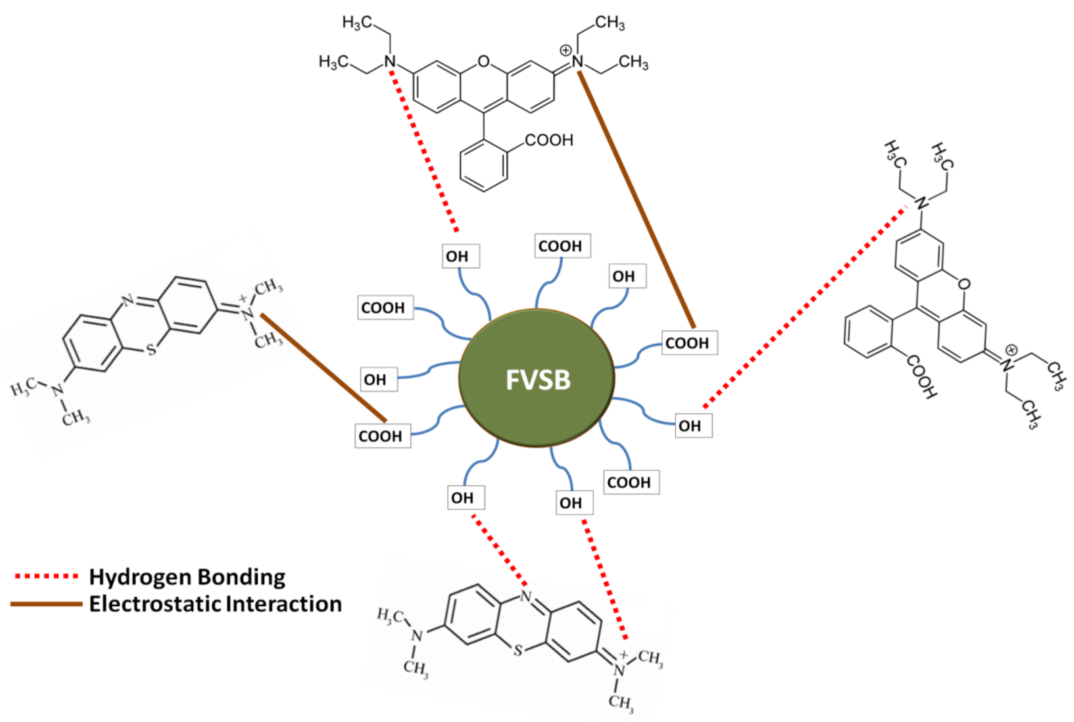

Figure 10: Probable mechanism of adsorption of MB and RB on FVSB

5.1.4. Conclusions: The present work investigated the adsorption of organic dyes i.e. MB and RB using *Fucus vesiculosus* seaweed bioadsorbent (FVSB). The FVSB is economically viable, efficient, sustainable, eco-friendly and easily available approach of pollutant removal. The removal efficiency of MB and RB was found to be 98.71% and 96.68%, respectively. The investigation of various adsorption parameters includes adsorbent dose, concentration, pH as well as temperature variation. The Langmuir adsorption isotherm model fitted well with experimental data representing monolayer adsorption and follows the pseudo-second-order kinetic model exhibiting chemisorption mechanism for adsorption. The thermodynamics study exhibits spontaneous process of adsorption of dyes. The detailed observation revealed that adsorption of MB and RB on FVSB is governed by electrostatic interaction and hydrogen bonding. At last, the FVSB was regenerated and reutilized by using 0.1M HCl in desorption process.

Chapter V (B):

Citrus limetta derived eco-friendly bioadsorbent for efficient elimination of organic dyes and heavy metal ions

5.2.1. Introduction: Organic dyes and heavy metals are commonly discharged by textile, printing, and tanning industries and are major concerns in natural water and wastewater systems. It is well known that some ionic dyes and heavy metals are toxic to aquatic organism and are potential threats to human health. Trace amounts of heavy metals and dyes in the water are undesirable and harmful because they are carcinogenic, mutagenic and toxic. Methylene Blue (MB), an organic dye have tendency to cause sore throat, skin irritation, asthma, eye irritation etc. whereas, Lead (Pb), is a hypertoxic heavy metal causes damage of liver, kidney as well as disorders of central nervous system[55]. The application of raw agricultural by-products and food waste suffers from some drawbacks such as low sorption capacity or poor physical stability. Therefore, chemical modification using base solutions (e.g., sodium hydroxide), acid solutions (nitric acid, sulfuric acid, citric acid, etc.), oxidizing agent (hydrogen peroxide) or crosslinking (diisocyanate, dimethylurea) etc. increases dyes and metal ions adsorption. The existence of several functional groups like -NH_2 , -COOH, and -OH on bioadsorbent surface helps in pollutants adsorption [56]. Several bioadsorbent based pollutant removal studies have been reported[23,24,57]. Simultaneous adsorption of organic and inorganic pollutants is of great importance for treatment of wastewater.

5.2.2. Materials and Methods: A simple and superficial method to synthesize *Citrus limetta* based bioadsorbent modified with cross-linker hexamethylene diisocyanate

(HMDI). The synthesized modified *Citrus limetta* (MCL) bioadsorbent has been successfully used for organic and inorganic pollutants removal from aqueous solution within few hours of application. The formation of urethane linkage due to HMDI with native *Citrus limetta* surface results stable bioadsorbent system with various active sites. The synthesized bioadsorbent was characterized using different methods like FTIR, TGA, SEM, BET, XRD, EDX etc. have been used for characterization of synthesized bioadsorbent. All adsorption parameters like dosage, concentration, temperature, pH variations have been studied in detail.

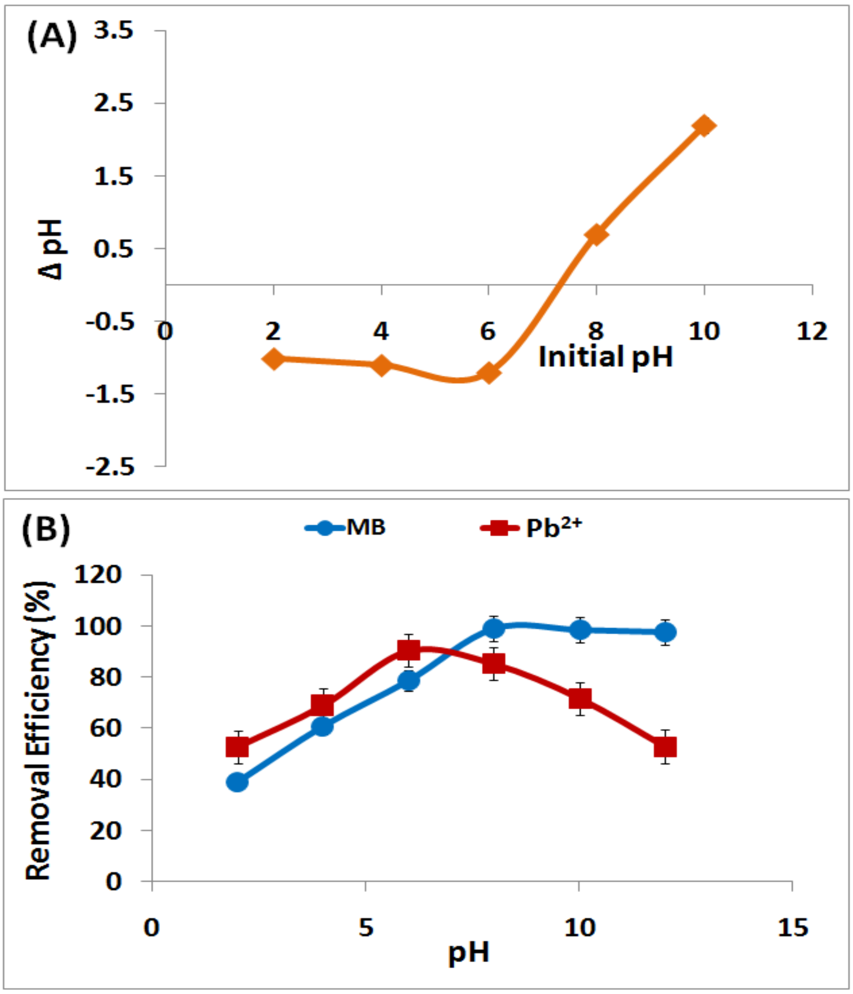

Figure 11: (A) point zero charge (pH_{PZC}) estimation, (B) Effect of pH on removal efficiency of MB and Pb^{2+} on MCL at 35°C

5.2.3. Results and Discussion: The elemental composition and surface morphology of MCL and pollutant loaded MCL were explored with the help of Scanning Electron Microscope coupled with Energy Dispersive Spectrometer. According to EDS analysis of MCL the carbon and oxygen dominate the composition and presence of nitrogen confirms the urethane linkage with *Citrus limetta* surface. The thermal decomposition of MCL bioadsorbent was explored in the range of 30-550°C that represents three stages of mass loss. The adsorption parameters such as adsorbent dosage variation, initial concentration variation, contact time variation and pH variation studies were investigated in detail. The variation in solution pH may result in change of ionization degree of adsorbate, surface charges associated with adsorbent and level of functional group dissociation on bioadsorbent active sites[58].

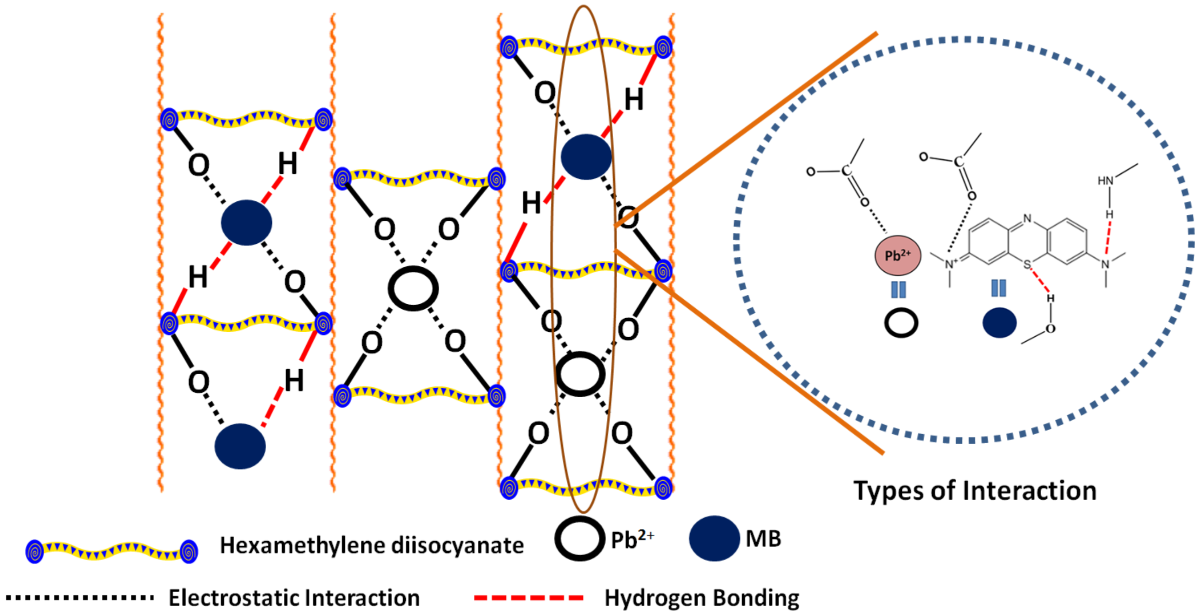

Figure 12: Probable mechanism of adsorption of MB and Pb^{2+}

Point of zero charge (pH_{PZC}) has been investigated to determine the charge associated with bioadsorbent. The pH_{PZC} is a facile index to investigate whether the surface charges of bioadsorbent are positive or negative. The pH_{PZC} of the bioadsorbent (MCL) was found to be 7.2, indicating that bioadsorbent will acquire positive charge on their surface on pH < 7.2, net zero charge at pH = 7.2 and negative charge at pH > 7.2 (**Figure 11**). Effect of temperature variation plays effective role in removal of dyes. The adsorption isotherm and thermodynamics studies were carried out to investigate the mechanism of adsorption process. The results of simultaneous adsorption of MB and Pb^{2+} represents that Pb^{2+} has higher adsorption capacity in comparison to MB in binary solution. The removal efficiency of MB and Pb^{2+} was investigated as 73.93% and 97.86% respectively. The bioadsorbent surface has been affirmed by presence of several functional groups such as -COOH, -OH, -NH etc. which in turn govern the process of adsorption. The uptake of Pb^{2+} molecule was regulated by electrostatic interaction and in case of MB, the hydrogen bonding and electrostatic interaction plays major role in adsorption (**Figure 12**).

5.2.4. Conclusions: This work establishes a facile and simple approach to prepare a novel modified *Citrus limetta* (MCL) bioadsorbent that effectively eliminate organic (MB) and inorganic (Pb^{2+}) pollutants from aqueous solution as well as removal of color from environmental sample. The results revealed that MCL is an excellent eco-friendly bioadsorbent system for removal of MB and Pb^{2+} with maximum removal efficiency of 99.02% and 91.9% for MB and Pb^{2+}, respectively. The main advantage of bioadsorbent with urethane linkage was evaluated to enhance its stability and facilitate the adsorption process. The detailed investigation of adsorption parameters included concentration, adsorbent dose, pH and temperature variation. The adsorption kinetic studies revealed that adsorption process follows pseudo second order model and equilibrium experimental data were best fitted with Langmuir isotherm model suggesting monolayer adsorption. Spontaneous and endothermic nature of adsorption was shown by thermodynamic study. MCL can be regenerated and reused upto five cycles with slight decrement in removal efficiency.

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Publications

Published Papers

1. **Maleic Anhydride Cross-Linked β- Cyclodextrin- Conjugated Magnetic Nanoadsorbent: An Ecofriendly Approach for Simultaneous Adsorption of Hydrophilic and Hydrophobic Dyes.**
   Monika Yadav, Manita Das, Chirag Savani, Sonal Thakore, Rajendrasinh Jadeja; ACS Omega 4 (2019) 11993-12003.

2. **Facile design of a dextran derived polyurethane hydrogel and metallopolymer: a sustainable approach for elimination of organic dyes and reduction of nitrophenols†.**
   Manita Das, **Monika Yadav**, Falguni Shukla, Sagufa Ansari, R. N. Jadeja, Sonal Thakore; ACS Omega 44 (2020) 19122.

3. **Rapid selective optical detection of sulfur containing agrochemicals and amino acid by functionalized cyclodextrin polymer derived gold nanoprobes.**
   Monika Yadav, Manita Das, Shivangi Bhatt, Pranav Shah, Rajendrasinh Jadeja, Sonal Thakore; Microchemical Journal 169 (2021) 106630.

4. **Removal of organic dyes using *Fucus vesiculosus* seaweed bioadsorbent an ecofriendly approach: Equilibrium, kinetics and thermodynamic studies.**
   Monika Yadav, Sonal Thakore, Rajendrasinh Jadeja; Journal of Environmental Chemical Engineering, Manuscript No. JECE-D- 21-06814 (**Communicated**)

5. **An ecofriendly approach for Methylene Blue and Lead (II) adsorption onto functionalized *Citrus limetta* bioadsorbent.**
   Monika Yadav, Rajendrasinh Jadeja, Sonal Thakore; Microchemical Journal. MICROC-D-21-02594. (**Communicated**)

Published Review Paper

1. **A review on remediation technologies using functionalized Cyclodextrin**

   Monika Yadav, Sonal Thakore, R. Jadeja, Environmental science and pollution research international, (2021). Environmental science and pollution research international. 10.1007/s11356-021-15887-y. PMID: 34420160

Published Book Chapters

1. **Phytoremediation for Heavy Metal Removal: Technological Advancements.**
   Monika Yadav, Gurudatta Singh, R. N. Jadeja; Pollutants and Water Management: Resources, Strategies and Scarcity. **John Wiley & Sons Ltd.** 2021, 128-150. https://doi.org/10.1002/9781119693635.ch6

2. **Physical and Chemical Methods for Heavy Metal Removal.**
   Monika Yadav, Gurudatta Singh, R. N. Jadeja; Pollutants and Water Management: Resources, Strategies and Scarcity. **John Wiley & Sons Ltd.** 2021, 377-397. https://doi.org/10.1002/9781119693635.ch15

3. **Fluoride Contamination in Groundwater, Impacts, and Their Potential Remediation Techniques.**
   Monika Yadav, Gurudatta Singh, R. N. Jadeja; Groundwater Geochemistry: Pollution and Remediation Methods. **John Wiley & Sons Ltd.** 2021, 22-41. https://doi.org/10.1002/9781119709732.ch2

4. **Surface Modified Magnetic Nanoparticles: A New Generation of Nanoadsorbents for Facile Remediation Protocols.**
   Monika Yadav, Manita Das, Sonal Thakore, R. Jadeja; Environment at Crossroads Challenges and Green Solutions. **Scientific Publishers**. 2020 291.

5. **Bioremediation of organic pollutants: a sustainable green approach.**
   Monika Yadav, Gurudatta Singh, R. N. Jadeja; Sustainable Environmental Clean-up Green Remediation. **Elsevier.** 2021, 131-147. https://doi.org/10.1016/B978-0-12-823828-8.00006-2.

Communicated Book Chapters

1. **Role of Biopolymer in Development of Sustainable Technologies.**

   Monika Yadav, Manita Das, Sonal Thakore, R. N. Jadeja; Innovative Bio-Based Technologies for Environmental Remediation.

2. **Waste to Bioenergy: A Sustainable Approach.**

   Monika Yadav, Gurudatta Singh, R. N. Jadeja; Bioenergy Crops: A Sustainable Means of Phytoremediation.

Conferences and Seminars

Paper/Poster/Oral Presentation in Conferences

1. National Conference on Pollution Management (NCPM-2018), Department of Environmental Studies, organized by The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat. 3rd February 2018. (**Poster Presentation**)

2. National Conference on Recent Trends in Materials Science (RTMS-2018), organized by Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat. 24-25th March 2018. (**Poster Presentation**)

3. National Conference on Recent Advances in Material Sciences (NCRAMS-18), organized by Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat. 23-24th November 2018. (**Poster Presentation**)

4. Climate Change and Sustainable Development: Facts, Impacts & Perspectives, organized by Faculty of Social Work, The Maharaja Sayajirao University of Baroda & Indian Society of Geomatics Vadodara Chapter, Gujarat. 14-15th March 2019. (**Paper Presentation**)

5. 56th Annual Convention of Chemists 2019 & International Conference on Recent Trends in Chemical Sciences, organized by Indian Chemical Society, School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, Chhatisgarh. 14-16th November 2019. (**Oral Presentation**)

6. National Conference on Advances in Chemical Sciences and Technology for Environment and Sustainability [ACSTES-2020], organized by Applied Chemistry Department, Sardar Vallabhbhai National Institute of Technology, Surat , Gujarat. 27th February 2020. (**Note: Won 2nd prize in Poster Presentation**)

7. Indian Council of Chemists, 39th Annual National Conference (**Online**), organized by Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat. 11th April 2021. (**Oral Presentation**)

Participation Certificates of Conferences/Seminars/Webinars

1. Seminar on Nuclear Magnetic Resonance (NMR) Spectroscopy: Concepts and Applications, organized by Department of Chemistry, Gujarat University and Oxygen Healthcare Research Pvt. Ltd., Sharmista Research Centre, Ahmedabad, Gujarat. 24-25th August 2018.

2. Environmental Impact Assessment, organized by Department of Environmental Studies, Faculty of Science, The Maharaja Sayajirao University of Baroda, Gujarat. 22nd March 2019.
3. One Day Seminar on Analytical Instrumental Techniques, organized by Department of Environmental Studies, Faculty of Science, The Maharaja Sayajirao University of Baroda, Gujarat. 9th April 2019.
4. A Green Conference on Save Mother Earth, organized by Vijnana Bharti, Vigyan Gurjari & Faculty of Science, The Maharaja Sayajirao University of Baroda, Gujarat. 10th October 2019.
5. National Seminar on Human Health: Need Of The Hour, organized by Indian Science Congress Association (ISCA-BC) and Faculty of Science, The Maharaja Sayajirao University of Baroda, Gujarat. 24th December 2019.
6. ACS Science Talk Virtual Lecture Series based on Exploring the Great Unknown: Characterization of Complex Environmental Mixtures (**Online**), organized by American Chemical Society. 12th August 2020.
7. India International Science Festival 2020 (IISF-2020) (**Online**), organized by Ministry of Science and Technology, Ministry of Earth Science, Ministry of Health and Family Welfare, Government of India in collaboration with Vijnana Bharti and Council of Scientific and Industrial Research. 22-12-2020 to 25-12-2020. (**Water Segment**)
8. Biodiversity and Public Health (**Online**), organized by Eco Club Shivaji College, University of Delhi and Society for Ecological Research and Natural Resources Management (SERNRM). 19th May 2020.
9. DBT Webinar: Showcasing Demonstrated Waste-To-Value Technologies (**Online**), organized by India Alliance. 1st October 2020.