A SYNOPSIS

of the thesis

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

To be Submitted
As a partial fulfilment for the award of the degree of

DOCTOR OF PHILOSOPHY
in
Environmental Science

By
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April 2021

Synopsis of the Thesis

To be submitted to The Maharaja Sayajirao University of Baroda for the award of the degree of DOCTOR OF PHILOSOPHY in Environmental Science.

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Title of the Thesis: "***SYNTHESIS AND CHARACTERIZATION OF NOVEL HYBRID MATERIALS FOR ADSORPTION AND SENSING OF ORGANIC/INORGANIC POLLUTANTS***"

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The Thesis will be presented in form of the following chapters:

Chapter I
Introduction

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

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

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

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

Chapter V (B)
***Citrus limetta* derived eco-friendly bioadsorbent for efficient elimination of organic dyes and heavy metal ions.**

Chapter: I

Introduction

The industrial development, increasing population and rapid destruction of resources leads to increasing pollution load in environment. The pollutants released from chemical industries such as textiles, paper, tanneries, electroplating, color photography, printing, dye, and food industries etc. produce 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 [1]. Precisely in developing countries environmental protection and remediation of water, air and soil pollution are of special concern around the world. Unfortunately, the elimination of pollutants from environment remains a challenge when considering four general points, efficiency, recyclability, environmental benign and cost. Several approaches have been considered for the removal of environmental pollutants such as adsorption, irradiation and membrane processes, oxidation, photodegradation, ozonation, ionic exchange, electrocoagulation, and coagulation– flocculation and other methods. Among other mentioned methods, adsorption is considered as most appropriate, convenient, easy to operate and cost-effective technique for effluent treatment methods [2].

Inorganic Pollutants: Inorganic pollutants comprise mainly of heavy metals like Cd, Hg, Pb, As, Cr etc. they are toxic even at low concentration. They are one of the major classes of pollutants released by various chemical and allied industries like fertilizers, pharmaceuticals and refineries. Heavy metals, trace elements, metals, mineral acids, metal compounds and inorganic salts etc. have higher concentration in water than permissible limit [3].

Organic Pollutants: Organic pollutants mainly includes phenols, chlorinated phenols, endocrine disrupting chemicals, azo dyes, polyaromatic hydrocarbons, polychlorinated biphenyls and pesticides, etc. released from domestic sewage (raw or treated), agricultural run-off, farm waste and industrial (trade) effluents. Among all, domestic waste is considered as greatest source of organic pollutants discharge to freshwaters [4,5].

Dyes: Dyes are one of the organic pollutants that bear color component or chromophores. They are generally soluble in water and depend on physical or chemical reactions to impart their colors. Textile, paper, leather, cosmetics, food and other industries are using dyes due to their ease and cost effectiveness. Estimations reveal that functioning of these industries releases around 10-15% dyes into processing water. The disposal of dye wastewater without proper treatment emerged as big challenge and caused harm to the aquatic environment, such as reducing light penetration and photosynthesis [6].

Adsorption: Adsorption is a surface phenomenon that leads to transfer of molecule from a fluid bulk to solid surface mainly due to physical forces or chemical bonding. Physical and chemical adsorption often occurs together. Generally this process is reversible and the phenomenon is called desorption. It binds the substance as well as release it describing equilibrium to quantify the substance attached on the surface in given concentration solution. In waste water technologies, the adsorption process depends on several parameters including kind of adsorbate, adsorbent etc. that plays leading role. Adsorption is one of the most important physicochemical processes proved to be effective for pollutants removal from dilute effluents [7,8].

Adsorbents: Adsorbent is probably the main parameter of adsorption process for removal of pollutants. Various kinds of adsorbents have been synthesized, modified and further applied in environmental remediation process. Good adsorbent possess some characteristics like larger surface area, more active sites for binding, high sorption capacity, regenerative and more sites for surface functionalization. Some commonly used adsorbents are magnetic adsorbents, aerogels, hydrogels, bioadsorbents, activated carbon, clay, zeolites, silica, chitosan based that has been successfully utilized for removal of organic and inorganic pollutants. On the basis of size they comprise category of nanomaterials, mesoporous materials and supra-molecular materials. Desirable surface functionalization helps in attaining better results of adsorption using the above mentioned adsorbents [9,10].

AIM:

To synthesize and characterize novel hybrid materials for adsorption and sensing of Organic/Inorganic Pollutants.

OBJECTIVES:

1. SYNTHESIS OF NOVEL HYBRID MATERIALS FOR ADSORPTION AND SENSING OF ORGANIC/INORGANIC POLLUTANTS
2. CHARACTERIZATION OF THE HYBRID ADSORBENTS AND SENSORS BY SOPHISTICATED TECHNIQUES
3. ADSORPTION STUDIES OF ORGANIC DYES, AROMATIC POLLUTANTS AND METAL IONS

4. OPTIMIZATION OF SENSING AND QUANTIFICATION OF ORGANIC COMPOUNDS USING NANOSENSORS

Chapter: II

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

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 beneficial for environmental applications because of the rapid magnetic decantation of molecules from the samples. 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.

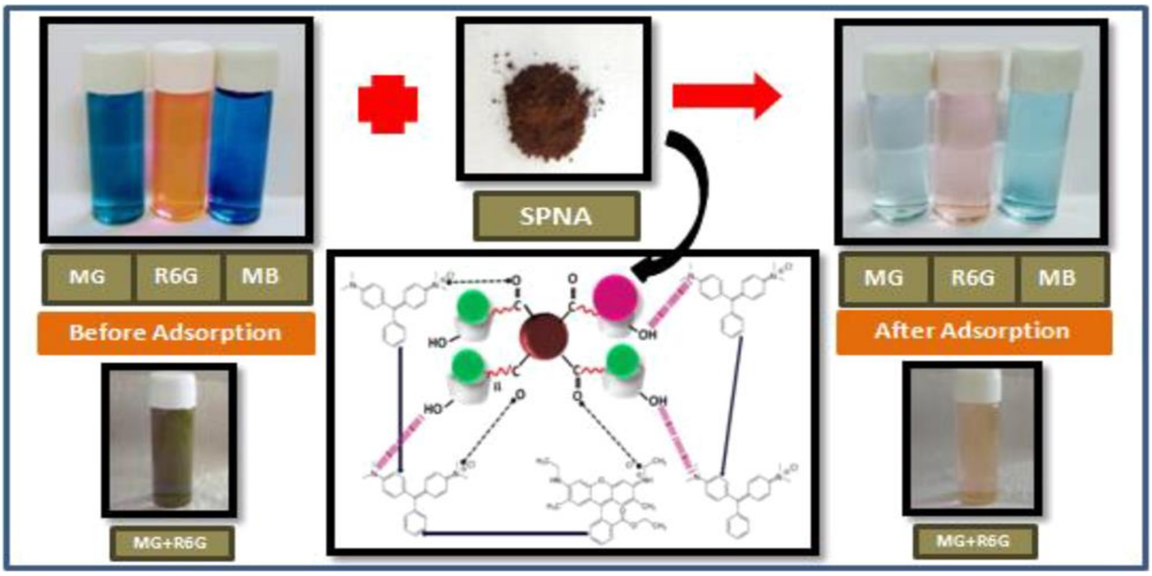

Figure 1: Image of magnetic adsorbent and vials containing dye solutions (Methylene Blue, Malachite Green and Rhodamine 6 G) before and after adsorption with superparamagnetic nanoadsorbent. Photographs and mechanism of adsorption for Malachite Green + Rhodamine 6 G mixture using superparamagnetic nanoadsorbent.

Materials and Methodology:

A superparamagnetic nanoadsorbent was synthesized by covalent conjugation of MNPs with a crosslinked CD–maleic anhydride copolymer. 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, HE-TEM, DLS, VSM, TGA and BET.

Result and Discussion:

The efficiency of SPNA as an adsorbent for hydrophobic as well as hydrophilic dyes was assessed under varying concentrations, adsorbent quantity, times, temperature and pHs. The sorption kinetics and probable mechanism of the adsorption were determined and the 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 for removal of dyes with maximum removal efficiency of 97.2, 85.1, and 37.3% for MB, MG, and R6G, respectively [11]. The reuse of the adsorbent is an important index for defining the efficiency of the adsorbent. 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.

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 detailed investigation of adsorption behavior of the SPNA exhibited that the adsorption process occur due to electrostatic forces of interaction, van der Waals forces, and hydrogen bonding in addition to the host−guest interaction with the cavity of CD. 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

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 composed of a three dimensional network of hydrophilic polymers have shown high adsorption capacities due to a controllable swelling property and the ability to hold a large amount of water while maintaining their structure. 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.

Materials and Methodology:

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 [12]. 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.

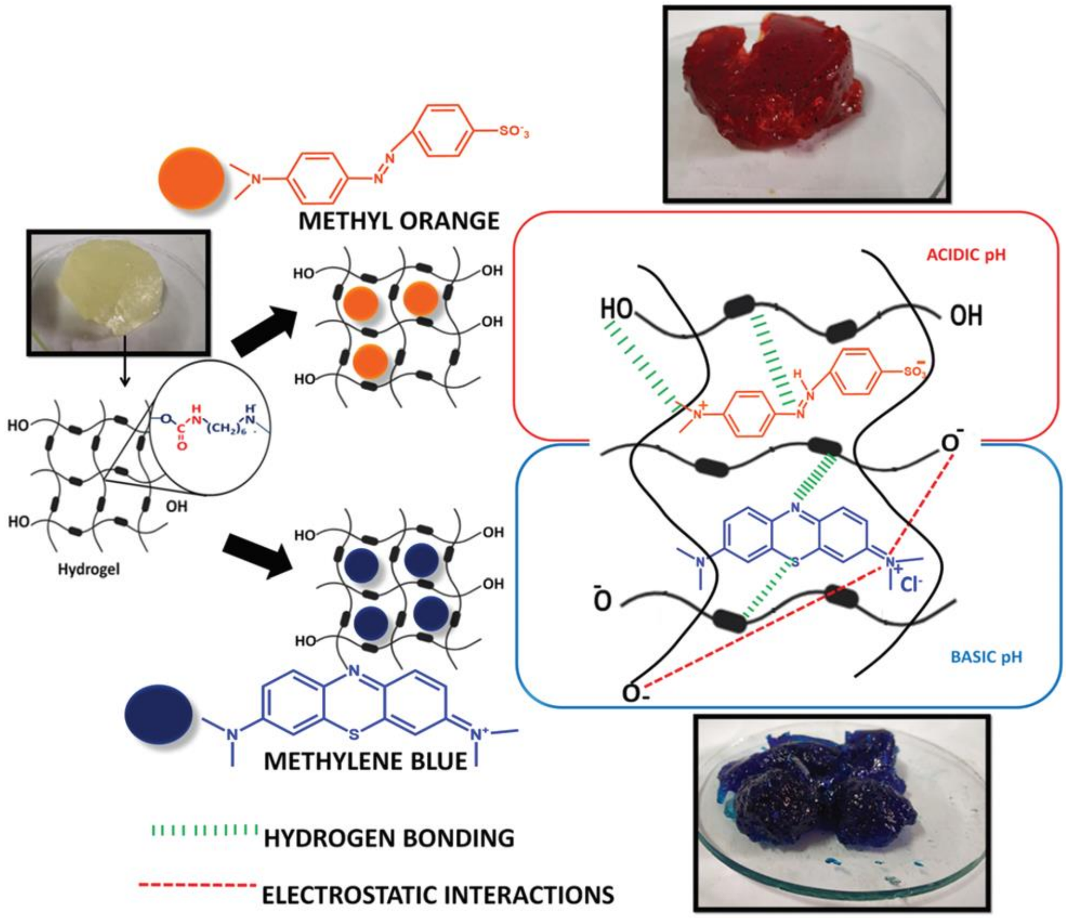

Figure 2: Adsorption of Methylene Blue and Methyl Orange dyes using Dextran based hydrogel. Photographs of hydrogel before and after adsorption and mechanism of adsorption.

Result 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 been observed. Adsorption of Methylene Blue and Methyl Orange has been investigated via various adsorption parameters like initial concentration, adsorbent quantity, pH and temperature. Adsorption kinetics follows pseudo-second order model. Adsorption thermodynamics and isotherm was also determined. Adsorption 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. The mechanism of adsorption was governed by electrostatic force of attraction and hydrogen bonding. 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.

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 removal efficiency of 98% and 84% respectively. The single layer adsorption and chemisorptions is rate determining step and the process is spontaneous according to thermodynamic study. 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

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 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.

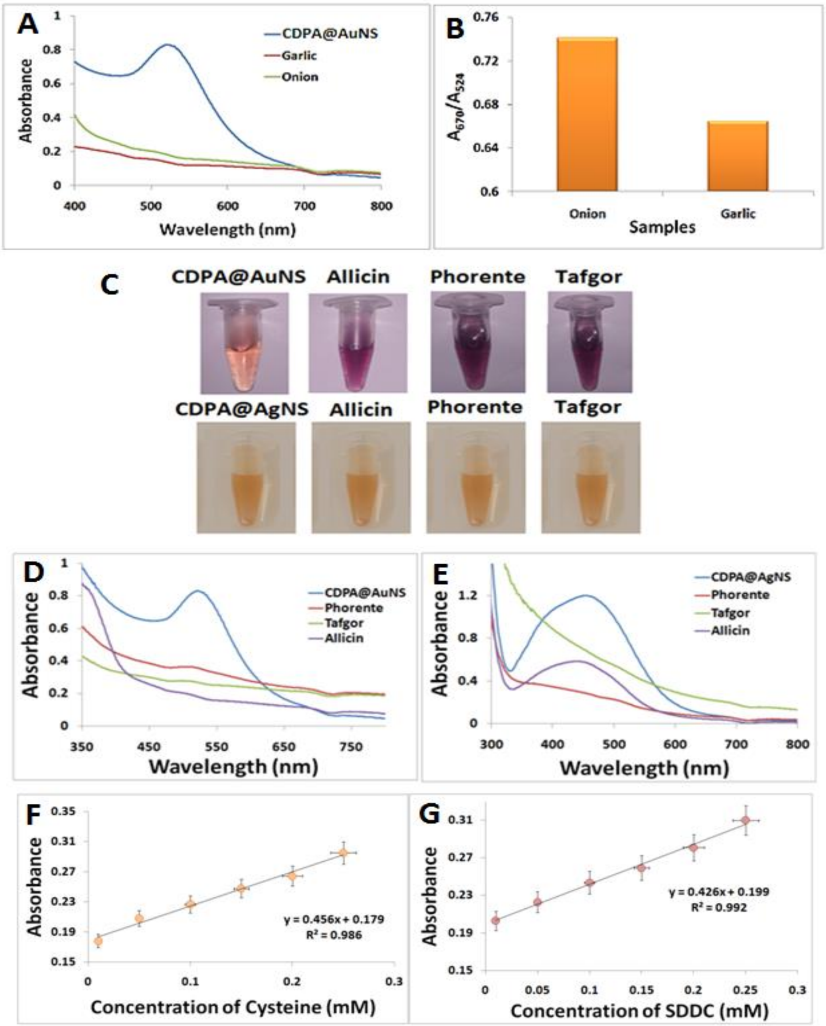

Figure 3: (A) UV-vis spectra and (B) Absorption ratio (A_{670}/A_{524}) of CD-AuNP sensor in presence of allicin present in onion and garlic extract. (C)Photographs and Absorption spectra (D&E) of Au and Ag nanosensor in presence of sulfur based pesticide samples. Linear relationship of increasing concentration of (F) Cysteine and (G) SDDC with absorbance for quantification and determination of Limit of Detection

Materials and Methodology:

A facile and rapid colorimetric method has been developed using stable gold nanoparticle based nanosensor synthesized using crosslinked cyclodextrin phthalic anhydride (CDPA) polymer. The nanosensor has been used for sensing of amino acids as well as agrochemicals. The detail qualitative and quantitative study of Cysteine (Cys) and Sodium diethyldithiocarbamate (SDDC) sensing has been discussed. For selective detection of sulfur based compound, silver based nanosensors have also been synthesized to compare with gold nanosensor. The synthesized nanosensor has been characterized by using NMR, FTIR, DLS, Zeta Potential, HR-TEM, FESEM-EDX etc.

Result 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. The simple and rapid detection of analytes has been significantly measured using nanosensors due to their affinity towards sulfur group. 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. 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 possible mechanism for the detection of Cys and SDDC in this work is based on dispersion-aggregation mechanism.

Conclusions:

The synthesis of CDPA functionalized gold nanosenor was carried out by facile two step reaction that exhibit better sensitivity towards colorimetric recognition of Cys and SDDC. 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.

Chapter: V(A)

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

***Introduction*:**

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. This has been referred as biosorption, the passive attachment of ions to a biomass. 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.

Materials and Methodology:

The brown seaweed (*Fucus vesiculosus*) has been collected, washed thoroughly, dried and crushed. The powdered seaweed was used for adsorption of Methylene Blue and Rhodamine B. Analytical tools like FTIR, TGA, BET etc. will be used for characterization.

Result 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* was around 85-90%. The adsorption parameters have been investigated in detail. The recycling and regeneration experiments were also performed. The adsorption isotherm and kinetics models will be generated using experimental data.

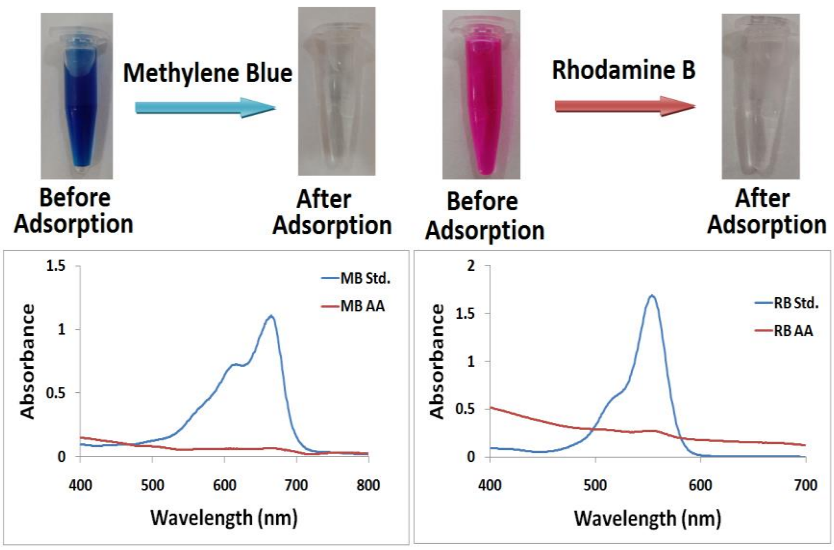

Figure 3: Adsorption of Methylene Blue and Rhodamine B dyes using *Fucus vesiculosus seaweed bioadsorbent.* **Photographs of before and after adsorption of dyes and UV-visible spectra.**

Chapter: V(B)

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

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. 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.

Materials and Methodology:

The adsorbent was synthesized by modifying *Citrus limetta* fruit peel in a simple and facile method using crosslinker hexamethylene diisocyanate. The utilization of bioadsorbent in removal of Methylene Blue dye and Lead ion has been investigated. Synthesized bioadsorbent has been characterized via several analytical techniques like XRD, FTIR, BET, TGA etc. for structural confirmation and establishing successful adsorption process.

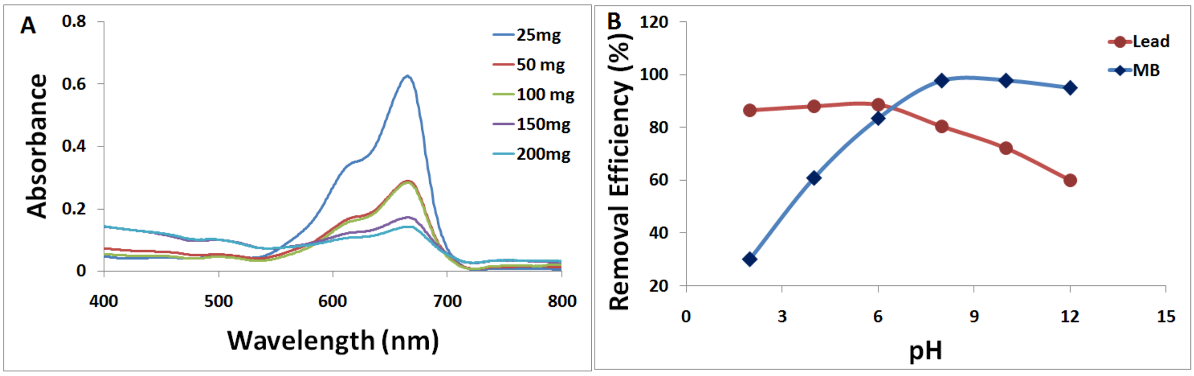

Figure 5: (A) UV-visible spectra of adsorption of Methylene Blue dye with increasing *Citrus limetta* bioadsorbent loading. (B) Removal efficiency of methylene blue and lead ions with increasing pH using bioadsorbent.

Result and Discussion:

The modified *citrus limetta* bioadsorbent successfully eliminate 90-98% of Methylene Blue and Lead ions from aqueous solution. The adsorption parameters such as initial concentration variation, quantity, pH, contact time, temperature have been investigated in detail. The equilibrium data fitted well into adsorption isotherm and kinetics model. The regeneration and recycling of adsorbent has also been studied using different batches of MB and lead solutions.

❖ ***Conclusions:***

A number of novel hybrid materials have been synthesized and characterized using various analytical techniques such as FTIR, NMR, XRD, SEM, HRTEM, FESEM-EDX, DLS, Zeta Potential, UV-visible spectroscopy, TGA etc. The utilization of synthesized materials in removal of organic and inorganic pollutants has been investigated via adsorption process. The successful elimination of pollutants with high removal efficiency demonstrates the performance of adsorbents. The regeneration of adsorbents and subsequent adsorption using the same batch makes the adsorbent cost effective and easy to operate. The adsorption mechanism follows Pseudo-second order kinetics and data fitted very well into Langmuir isotherm model representing chemisorption as rate determining step of adsorption. Cyclodextrin polymer stabilised gold nanoparticles demonstrated selective and rapid sensing as well as quantification of sulphur based amino acid and agrochemicals from aqueous solution.

References:

[1] P.Z. Ray, H.J. Shipley, Inorganic nano-adsorbents for the removal of heavy metals and arsenic: A review, RSC Adv. 5 (2015) 29885–29907. doi:10.1039/c5ra02714d.

[2] G. Wu, J. Ma, S. Li, J. Guan, B. Jiang, L. Wang, J. Li, X. Wang, L. Chen, Magnetic copper-based metal organic framework as an effective and recyclable adsorbent for removal of two fluoroquinolone antibiotics from aqueous solutions, J. Colloid Interface Sci. 528 (2018) 360–371. doi:10.1016/j.jcis.2018.05.105.

[3] K.L. Wasewar, S. Singh, S.K. Kansal, Process intensification of treatment of inorganic water pollutants, INC, 2020. doi:10.1016/b978-0-12-818965-8.00013-5.

[4] R.D. Ambashta, M. Sillanpää, Water purification using magnetic assistance: A review, J. Hazard. Mater. 180 (2010) 38–49. doi:10.1016/j.jhazmat.2010.04.105.

[5] M. Namdeo, Magnetite Nanoparticles as Effective Adsorbent for Water Purification-A Review, Adv. Recycl. Waste Manag. 02 (2018). doi:10.4172/2475-7675.1000135.

[6] D. Yang, L. Qiu, Y. Yang, Efficient Adsorption of Methyl Orange Using a Modified Chitosan Magnetic Composite Adsorbent, J. Chem. Eng. Data. 61 (2016) 3933–3940. doi:10.1021/acs.jced.6b00706.

[7] Y. Artioli, Adsorption, Encycl. Ecol. Five-Volume Set. (2008) 60–65. doi:10.1016/B978-008045405-4.00252-4.

[8] S. Nasirimoghaddam, S. Zeinali, S. Sabbaghi, Chitosan coated magnetic nanoparticles as nano-adsorbent for efficient removal of mercury contents from industrial aqueous and oily samples, J. Ind. Eng. Chem. 27 (2015) 79–87. doi:10.1016/j.jiec.2014.12.020.

[9] M.M. Lakouraj, R.S. Norouzian, S. Balo, Preparation and Cationic Dye Adsorption of Novel Fe3O4 Supermagnetic/Thiacalix[4]arene Tetrasulfonate Self-Doped/Polyaniline Nanocomposite: Kinetics, Isotherms, and Thermodynamic Study, J. Chem. Eng. Data. 60 (2015) 2262–2272. doi:10.1021/acs.jced.5b00080.

[10] S. Singh, K.C. Barick, D. Bahadur, Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens, J. Hazard. Mater. 192 (2011) 1539–1547. doi:10.1016/j.jhazmat.2011.06.074.

[11] M. Yadav, M. Das, C. Savani, S. Thakore, R. Jadeja, Maleic Anhydride Cross-Linked β -Cyclodextrin-Conjugated Magnetic Nanoadsorbent : An Ecofriendly Approach for Simultaneous Adsorption of Hydrophilic and Hydrophobic Dyes, ACS Omega. 4 (2019) 11993–12003. doi:10.1021/acsomega.9b00881.

[12] M. Das, M. Yadav, F. Shukla, S. Ansari, R.N. Jadeja, S. Thakore, Facile design of a dextran derived polyurethane hydrogel and metallopolymer: A sustainable approach for elimination of organic dyes and reduction of nitrophenols, New J. Chem. 44 (2020) 19122–19134. doi:10.1039/d0nj01871f

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