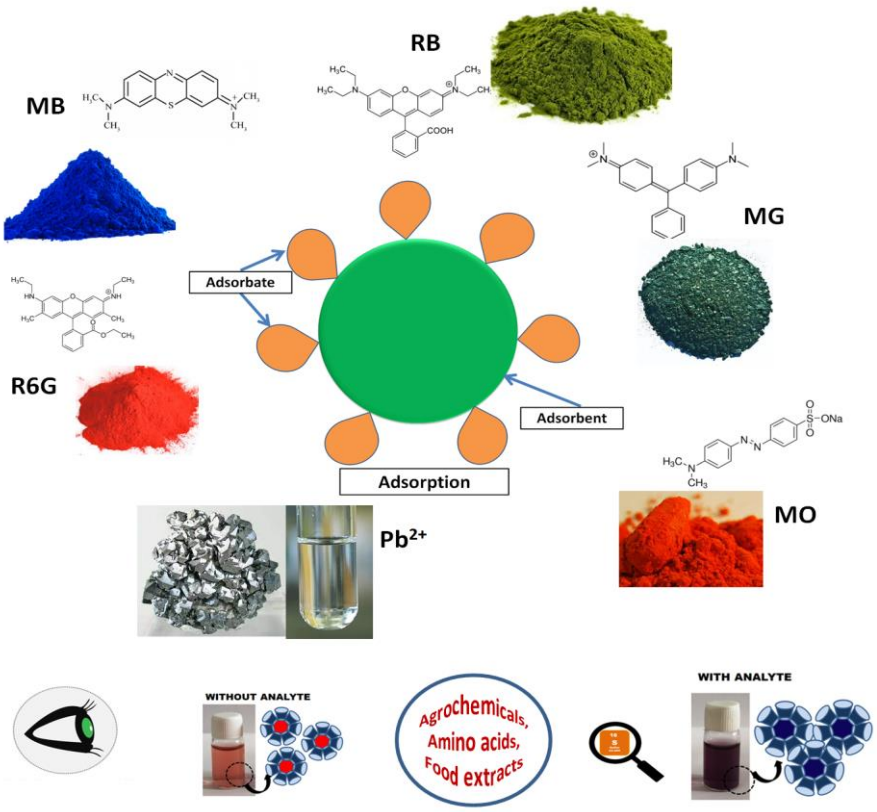
SYNTHESIS AND CHARACTERIZATION OF NOVEL HYBRID MATERIALS FOR ADSORPTION AND SENSING OF ORGANIC/INORGANIC POLLUTANTS

Chapter 1: 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. 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. 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. Several water quality parameters have been listed by Environmental Protection Agency (EPA) of United States in order to quantify the quality of water. The list contains some 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. 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. These colored compounds blocks light penetration that decreases the photosynthetic activity of aquatic plants ultimately hindering their growth and development. This work covers the synthesis of various novel hybrid adsorbents such as magnetic nanoadsorbents, hydrogels and bioadsorbent for removal of organic and inorganic pollutants via the process of adsorption. The colorimetic detection of sulfur based compounds were also explored with the help of newly synthesized gold nanosensor.

Chapter II: The study of this chapter includes synthesis of a super paramagnetic nanoadsorbent (SPNA) via covalent conjugation of magnetic nanoparticles with crosslinked cyclodextrin-maleic anhydride copolymer. Cyclodextrin has host-guest interaction, hydrophobic interaction, or hydrogen-binding interaction and is widely used in drug administration, molecular recognition, supramolecular self-assembly, or catalysis. It interacts with certain environmental contaminants, such as aromatic molecules or heavy metals. As a result, β-cyclodextrin can be utilized in the cleanup of environmental pollutants. 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.

Chapter III: In this chapter, we report a single step facile novel approach for surface modification of dextran with crosslinker hexamethylene diisocyanate resulting in excellent adsorbent system for elimination of anionic and cationic dyes Methyl Orange (MO) and Methylene Blue (MB), respectively. The synthesized hydrogel DEX-HMDI has been characterized by several analytical techniques and their adsorption properties were investigated by various experimental parameters such as dosage variation, concentration variation, temperature and pH variation, regeneration cycle etc. Detail study of adsorption isotherm and kinetics of adsorption process utilizing hydrogel was also carried out. Since, hydrogel is polymeric in nature, with several hydroxyl groups, therefore; they can also act as effective capping agents for the elimination of heavy metals from contaminated water. The sunlight-induces photocatalysis in aqueous phase provide motivation for exploring photocatalytic degradation of 4-Nitrophenol using catalyst (Ag entrapped metallopolymer i.e. Ag@Hydrogel) to reduce the toxic and hazardous nitroaromatics from water. This approach has significant potential of adsorbent waste management after remediation as well as its further valorization.

Chapter IV: In this chapter, the facile, robust and rapid colourimetric method has been developed utilizing a stable gold nanoparticle-based sensor synthesized by cyclodextrin crosslinked polymer with phthalic anhydride (CDPA). Herein, we have implemented the unique ability of beta-cyclodextrin (β-CD) that binds with both hydrophilic and hydrophobic compounds along with Au-thiol interactions. The sensing of amino acid (i.e. Cysteine) as well as agrochemical (i.e. diethyldithiocarbamate) has been accomplished by using nanosensor. The colourimetric assessment of nanosensor shows red shift (from 524nm to 670nm) within 5 seconds for sulfur-based compounds. A detailed qualitative and quantitative study of Cysteine and Sodium diethyldithiocarbamate sensing was carried out. Various analytical characterizations proved the mechanism of sensing unveiling the role of functionalized cyclodextrin. The simple, rapid and selective detection of the sulfur compound was demonstrated utilizing pesticide samples as well as allicin, a reported agrochemical present in extracts of onion and garlic. Silver based nanosensor was also synthesized for comparison study. The efficacy of gold nanosensor was found to be much superior in comparison to silver-based nanosensor.

Chapter V (A): In this chapter, *Fucus vesiculosus*, a brown seaweed has been used as bioadsorbent for elimination of cationic dyes like Methylene Blue and Rhodamine B from their aqueous solution. The presence of various functional groups on *Fucus vesiculosus* seaweed bioadsorbent (FVSB) surface helps in elimination of dyes from single and binary system with high removal efficiency and adsorption capacity. Several techniques such as Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy dispersive X-ray (EDX) has been utilized for characterization of FVSB. Adsorption parameters such as dosage, pH, concentration and temperature variation have been explored. The experimental data were fitted into adsorption isotherm, kinetics and thermodynamic models. FVSB, successfully remove dyes from their aqueous solution and environmental sample with high removal efficiency and could be used as promising approach for environmental remediation.

Chapter V (B): In this chapter, we report a simple, facile 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 Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Scanning Electron Microscope (SEM), Brunauer-Emmett-Teller (BET), X-ray Diffraction (XRD), Energy dispersive X-ray (EDX) etc. have been used for characterization of synthesized bioadsorbent. All adsorption parameters like dosage, concentration, temperature, pH variations have been studied in detail. Experimental data fitted well on thermodynamic, kinetics and isotherm models. MCL bioadsorbent was successfully used to eliminate dye and heavy metal from aqueous solution as well as color from environmental sample. This adsorbent system could be utilized as a promising approach in contaminated water treatment.