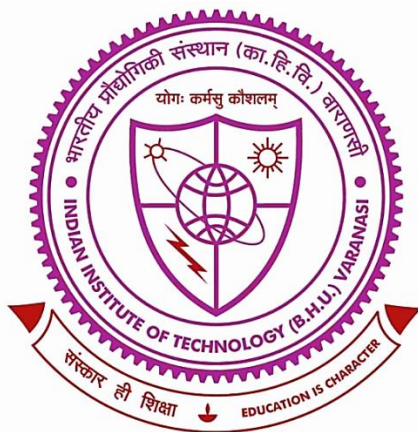


Prussian Blue Nanoparticles Mediated Sensing and Removal of Hazardous Materials



THESIS SUBMITTED FOR THE AWARD OF DEGREE OF

DOCTOR OF PHILOSOPHY

By

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Conclusion

Prussian blue nanoparticles of controlled nano-geometry were synthesized using a single precursor and different organic reducing agents and reported in homogeneous and heterogeneous mesoporous silica support for efficient sensing of arsenic, hydrogen peroxide, and cesium and removal of Cs ion from water. PB nanoparticles were found to display analyte-dependent redox electrochemistry for selective sensing of hydrogen peroxide, arsenic (III), and cesium ions. The analyte-dependent intervalence transition between Fe^{3+} and Fe^{2+} in PB nanoparticles was for electrochemical sensing of As (III) and hydrogen peroxide based on differential pulse voltammetry. The opposite electrochemical interaction between As (III) and H_2O_2 with PB nanoparticles was recorded, indicating an analyte-dependent intervalence transition between the two iron centers. Cesium ion sensing based on differential pulse voltammetry and impedance spectroscopy was demonstrated. The results were described based on the fluorescence quenching ability of Prussian blue nanoparticles made from single precursors. The quenching ability of PBNPs was noted to be a function of the nano-geometry of the PBNPs. Further, when cationic polymers are used to stabilize Prussian blue nanoparticles, the quenching ability of Prussian blue nanoparticles depends on the concentration of cesium ions, justifying the fluorescence sensing of the same. PB nanoparticle-mediated fluorescence sensing of the analyte, involving the intervalence transition between Fe^{3+} and Fe^{2+} , was assessed. PBNPs in both homogeneous and heterogeneous phases display paramagnetic behavior, which was noted to be a function of the cesium ion concentration. The PB nanoparticle-modified SPE induced a cesium adsorption-dependent chronoamperometric signal based on ion exchange as a function of cesium concentration. This ion exchange, which is reversible and rapid, is associated with electron transfer in the PB

nanoparticle-modified SPE. The PB nanoparticle-SPE may serve as a cost-effective material for the removal of Cs^+ from contaminated water, with (Q_{max}) of Cs^+ ions on the order of $325 \text{ mg}\cdot\text{g}^{-1}$ in a $50 \text{ }\mu\text{M}$ Cs^+ solution, a distribution coefficient K_d on the order of $580 \text{ L}\cdot\text{g}^{-1}$, and excellent reversibility for Cs^+ removal. A synthetically incorporate Prussian blue nanoparticles in mesoporous silica with potential use for the selective adsorption of ^{137}Cs , followed by the detection of radioactivity. The distribution coefficient (K_d) for adsorption of the cesium nuclide ^{137}Cs was calculated to be $3.2 \times 10^4 \text{ ml/g}^{-1}$, displaying both Langmuir and Freundlich adsorption isotherms.

Summary

The thesis entitled “Prussian blue nanoparticles (PBNPs) mediated sensing and removal of hazardous material” has been divided into following three chapters:

1. General Introduction.
2. Polyethylenimine (PEI), Tetrahydrofuran-Hydrogenperoxide (THF-H₂O₂), and 2-(3,4-Epoxy-cyclohexyl)-Ethyltrimethoxysilane (EETMS) mediated synthesis of nanocrystalline Prussian Blue Nanoparticles and their Characterization.
3. Sensing of arsenic, hydrogen peroxide, and cesium ion and removal of Cesium through synthesized Prussian blue nanoparticles.

Chapter 1

This section provides a brief summary of PBNP synthesis, characteristics, and applications. In this section, many methods for the synthesis of PBNP have been detailed, along with their well-known advantages. The significant properties (electrochemical, electrochromic, electro-catalysis, photo-physical, magnetic, ion exchange, etc.) and prospective uses of PBNP (electrochemical sensors, biosensors, transducers, photo-Fenton catalyst, etc.) have been briefly discussed. The control synthesis and the importance of nano-geometry in nanomaterials catalytic activity have also received attention. Thus, the origin, objective, and work plan of the current research have been described precisely.

Chapter 2

This chapter describes the synthesis of nanocrystalline Prussian blue nanoparticles (PBNPs) by using various reducing agents like- Polyethylenimine (PEI), Tetrahydrofuran-Hydrogenperoxide (THF-H₂O₂), and 2-(3,4- Epoxycyclohexyl)-Ethyltrimethoxysilane (EETMS) -cyclohexanone and their characterization through various techniques like- UV-vis., HRSEM, TEM, XRD, TGA, XPS, BET, and DLS. We found that potassium ferricyanide K₃[Fe (CN)₆] in the presence of PEI, THF-H₂O₂, and EETMS at 60 °C get converted into stable nanocrystalline Prussian blue nanoparticles with crystalline size of 6 nm, 59 nm, and 28 nm respectively which shows good sensing of hazardous material in application term. We have also synthesized PBNP-incorporated mesoporous silica nanoparticles that play an important role in the removal process.

Chapter 3

This section described the application of as-synthesized PBNPs by using PEI, THF-H₂O₂, and EETMS as a reducing agent in fluorometric and electrochemical sensing of cesium, arsenic, and electrocatalytic reduction and oxidation of THF-H₂O₂ through screen-printed electrode and graphite paste electrode. The as-synthesized PBNP-incorporated mesoporous silica nanoparticles have an important role in the adsorption of cesium and in magnetic movement-based sensing. Arsenic, hydrogen peroxide and cesium ion sensing based on cyclic voltammetry, differential pulse voltammetry and impedance spectroscopy was demonstrated. The results were described based on the fluorescence quenching ability of Prussian blue nanoparticles made from single precursors. The quenching ability of PBNPs was noted to be a function of the nano-geometry of the PBNPs. Further, when cationic polymers are used to stabilize Prussian blue nanoparticles, the quenching

ability of Prussian blue nanoparticles depends on the concentration of cesium ions, justifying the fluorescence sensing of the same. PBNPs in both homogeneous and heterogeneous phases display paramagnetic behavior, which was noted to be a function of the cesium ion concentration. PB nanoparticle-mediated fluorescence sensing of the analyte, involving the intervalence transition between Fe^{3+} and Fe^{2+} , was assessed. The PB nanoparticle-modified SPE may serve as a cost-effective material for the removal of Cs^+ from contaminated water, with (Q_{max}) of Cs^+ ions on the order of $325 \text{ mg}\cdot\text{g}^{-1}$ in a $50 \text{ }\mu\text{M}$ Cs^+ solution, a distribution coefficient K_d on the order of $580 \text{ L}\cdot\text{g}^{-1}$, and excellent reversibility for Cs^+ removal.

Future Projection

This Ph.D. work covers the challenges associated with synthesizing nanocrystalline Prussian blue nanoparticles (PBNPs) and their potential application in the sensing and removal process. The application of the present work involves single precursor-based synthesis of PBNPs which have been utilized for the electrochemical sensing of arsenic, hydrogen peroxide, and cesium ion; fluorometric sensing of cesium ion; magnetic movement-based sensing of cesium ion along with PBNPs in both homogenous and heterogenous conditions; and removal of cesium ion. The use of these materials in paramagnetism, sensing, and the removal of such nanoparticles would aid in the development of useful devices. Furthermore, nanocomposite materials containing as-synthesized PBNPs improve sensitivity and selectivity and have applications in the construction of electrochemical sensors/biosensors for a wide range of analytes. The fast kinetics and high uptake capacity of the PBNP-incorporated mesoporous silica make this material a suitable matrix for removing ^{137}Cs from contaminated water, so our main focus for future study is to suggest subsequent efforts to prepare granular beads at low cost with high sensitivity that can be used in column mode for removal of cesium from contaminated water.