Extended Abstract

"Prussian Blue Nanoparticles Mediated Sensing and Removal of Hazardous Materials"

Submitted by: Mr. Hari Prakash Yadav

Roll No.: 19051015

Degree for which Submitted: Doctor of Philosophy (Ph.D)

Name of the Department: Chemistry

Signature of the Supervisor

Prof. P. C. Pandey
Department of Chemistry
IIT (BHU), Varanasi 221005

Extended Abstract

Selective screening followed by the sensing of radionuclides, and heavy metals from contaminated water is a challenging technical issue. In this study, Prussian blue nanoparticles with controlled nano-geometry were synthesized from the single precursor (potassium hexacyanoferrate) in the presence of different reducing agents which enabled the controlled nucleation and stabilization of PBNPs of variable plasmonic activity for selective sensing and removal of cesium radionuclides. The results of this study show sensing as well as the removal of cesium based on the nano-geometry, magnetic behavior, and fluorescence quenching ability of Prussian blue nanoparticles. An efficient PB nanoparticle-modified screen-printed electrode (SPE) in the three-electrode configuration was developed for the electrochemical sensing of arsenic, cesium, and catalytic activity of hydrogen peroxide and removal of Cesium ion. A similar process was used to 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 in mesoporous silica was calculated to be $3.2x10^4$ ml/g^{-1}, displaying both Langmuir and Freundlich adsorption isotherms. 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. Using this electrochemical adsorption system (EAS) based on chronoamperometry, the maximum adsorption capacity (Q_{max}) of cesium ions in the PB nanoparticle-modified SPE reached up to 325 ± 1 mg·g^{-1} in a 50 ± 0.5 µM Cs^+ solution, with a distribution coefficient (K_d) of 580 ± 5 L·g^{-1} for Cs^+ removal. Prussian blue nanoparticles display superparamagnetic behavior; these magnetic properties were noted to be linearly dependent on the cesium ion concentration.

The entire thesis is framed into three chapters with brief remarks as given below:

Chapter 1 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.

Chapter 2 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 $K_3[Fe(CN)_6]$ in the presence of PEI, THF-H2O2, and EETMS at 60 ℃ get converted into stable nanocrystalline Prussian blue nanoparticles with crystalline size of 6.00 nm, 59.00 nm, and 28.00 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 described the application of as-synthesized PBNPs play an important role in fluorometric and electrochemical sensing of cesium, arsenic, and electrocatalytic activity of THF-H_2O_2 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, catalytic activity of 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. PBNPs in both homogeneous and heterogeneous phases display supermagnetic behavior, which was noted to be a function of the cesium ion concentration.

The thesis contents have been published in Chemosensors 2021, 9(9), 253; Frontiers in Enviornmental Science Volume 11 – 2023, doi: 10.3389/fenvs.2023.1230983.