Organically Functionalized Mesoporous SBA-15 Type Material Bearing Fluorescent Sites for Selective Detection of Hg\textsuperscript{II} from Aqueous Medium

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ABSTRACT: Hg(II) contamination in water resources is one of the major health issues in keeping the purity standard of the municipal water supply. Herein, we report a new mesoporous sensor probe material SBA-ABZ-PEA having a 2D-hexagonally ordered mesoporous framework bearing covalently bonded fluorescent sites, and this has been synthesized through a two-step post-synthesis grafting route. A pure silica mesoporous SBA-15 material has been functionalized with (3-chloropropyl)triethoxysilane (CPTES) to obtain chloro-functionalized SBA-15, which was further reacted with 4-aminobenzaldehyde followed by treatment with 2-(2-pyridyl)-ethylamine resulting in functionalized 2D-hexagonal mesoporous sensor probe SBA-ABZ-PEA. Small angle PXRD, N\textsubscript{2} adsorption/desorption, HRTEM, TGA, and FT-IR studies have been carried out to characterize these materials. Our experimental results suggested successful grafting of the organic moiety on the SBA-15 surface along with preservation of mesoporosity throughout the grafting process. Photoluminescence measurements were carried out in the aqueous suspension of SBA-ABZ-PEA in the presence of different metal cations, like Na\textsuperscript{+}, Mg\textsuperscript{2+}, Al\textsuperscript{3+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mn\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+}, and Hg\textsuperscript{II}. This result revealed that, among the various metal-ions, the emission intensity of the mesoporous sensing probe material SBA-ABZ-PEA has been dramatically quenched in the presence of the Hg\textsuperscript{II} ion. To check the sensitivity of the sensor probe, the fluorescence emission was also studied in the presence of different concentrations of Hg\textsuperscript{II} ions. A perfect linear plot between the concentrations of Hg\textsuperscript{II} ions in the aqueous medium with their corresponding fluorescence intensities with a detection limit of 1.2 × 10\textsuperscript{−6} M has been observed.

1. INTRODUCTION

Rapid industrial development in technologically advanced countries resulted in a serious environmental problem due to the large release of chemical wastes and subsequent contamination of heavy metal ions in water resources.\textsuperscript{1−3} Among the heavy metal ions, mercury (Hg) is one of the most hazardous metals in its different forms like metallic, ionic, and organometallic. They can cause severe life threatening diseases such as acrodynia or pink disease, Minamata disease, and Hunter-Russell syndrome.\textsuperscript{5} Large-scale contamination of Hg(II) can occur by a variety of natural and anthropogenic activities.\textsuperscript{6} Electrical appliances like lamps, arc rectifiers, and mercury cells necessary for industrial activities are very easy sources of Hg\textsuperscript{II} contamination when discharged into water bodies. It has been analyzed that even the presence of an ultratrace amount of Hg\textsuperscript{II} ions beyond its permissible limit (1 to 10 µg/L) damages our central nervous system tremendously. The aquatic living bodies\textsuperscript{8} also face severe damage by Hg\textsuperscript{II} contamination. Abnormal chromosome distribution is a fatal effect of Hg\textsuperscript{II} poisoning, and divisional malfunction of chromosomes leads to genetic defects with abnormal cell division. Therefore, rapid and selective detection as well as the removal of Hg\textsuperscript{II} ions is very challenging in the context of safe water supply and healthy living of plants and animals.\textsuperscript{9}

Nanomaterials act as biosensors for the removal of bioaccumulative mercury with great efficacy. It is applied for in vivo purpose also as Hg\textsuperscript{2+} can be anchored with a DNA base pair.\textsuperscript{10,11} Nanocrystals are used as adsorbents to remove the Hg(II) from wastewater.\textsuperscript{12} Magnetic nanosorbents as well as thiol-functionalized nanomaterials are widely employed for the fast removal of mercury because of their high adsorption capacity.\textsuperscript{13−15}

Different detection methods including atomic absorption spectroscopy,\textsuperscript{16,17} inductively coupled plasma-mass spectroscopic method (ICP-MS),\textsuperscript{18} and voltammetry\textsuperscript{19} are conventionally employed to measure and detect the metal ions present in solutions. However, most of these methods are either time-consuming, costly, and require sophisticated instruments. On the other hand, fluorescent chemosensors can detect heavy metal ions as well as various analytes with less effort and also in quite a cost-effective way.\textsuperscript{20} They also show advantages in easy and quick detection together with high selectivity. Since the side effect of the industrialization is so severe especially in the case of Hg\textsuperscript{II} contamination, a large-
scale research activity has been focused in developing fluorescent sensors to combat Hg\textsuperscript{II} contamination in pure water. So, it becomes an obvious challenge that sensor probes are designed in such a way so that they can be applied in water with good efficacy to detect toxic and poisonous metals in the presence of other nonharmful metal ions.\textsuperscript{21,22}

Porous nanomaterials with pore dimensions varying from sub-nanometer (microporous) to several nanometer (mesoporous) length scales are intensively studied over the years due to their potential in several frontline application areas and their reusability.\textsuperscript{23—26} These solids are quite stable in water, which could make them ideal candidates for ground water purification. Among them, the mesoporous SBA-15\textsuperscript{27—30} material is often employed as a support to enhance the material properties due to its structural features such as high surface area with a thick pore wall, uniformly ordered pore channels, high thermal stability, optical transparency in the visible region, and high biocompatibility.\textsuperscript{31} Due to such beneficial factors, it is widely explored in adsorption,\textsuperscript{32} catalysis,\textsuperscript{33,34} optoelectronics,\textsuperscript{35} and optical sensors.\textsuperscript{36} The mesoporous silicas can be surface-functionalized through different organic functional groups by grafting or co-condensation approaches,\textsuperscript{37} so that the resulting material can bind different metal ions via strong coordination. So, organic fluorophore moieties bound at the surface of the mesoporous silicas have become an important research area for selective adsorption and sensing applications.\textsuperscript{38—41} Thus, considerable research efforts have been devoted in developing novel sensor probes based on mesoporous SBA-15 to detect Hg and other heavy metals from water resources.\textsuperscript{42—45}

In this context, it is pertinent to mention that chelating functional groups bearing a simultaneous presence of polarizable imine-N and pyridinic-N can offer selective binding of Hg\textsuperscript{II} present in the aqueous media, and this has not been explored before. Here, we have functionalized the surface of SBA-15 with a fluorescent probe bearing simultaneous imine-N and pyridinic-N species, which can detect Hg\textsuperscript{II} ions from contaminated water with great efficacy. The synthesis is based on the stepwise surface functionalization of mesoporous silica material SBA-15 with organic functional groups (after functionalization of SBA-15, the material is abbreviated as SBA for simplicity), and this is outlined for the synthesis of SBA-ABZ-PEA in Scheme 1. This probe exhibits excellent efficacy in Hg\textsuperscript{II} detection in a water medium with a detection limit of 1.2 × 10\textsuperscript{-6} M.

### 2. RESULTS AND DISCUSSION

#### 2.1. Characterization of Materials

**2.1.1. Ordered Mesophase.** Small angle powder X-ray diffraction (PXRD) plots of chloro-functionalized SBA-15, that is, SBA-Pr-Cl, and organic ligand grafted sensing probe SBA-ABZ-PEA are presented in Figure 1. Both of them exhibited three well-resolved broad Bragg reflections at (100), (110), and (200) at the small 2\(\theta\) angle range between 0.6 and 2.5°. These are the characteristic peaks of the 2D-hexagonal mesophase, which confirmed their ordered mesoporous framework.\textsuperscript{46} The incorporation of organic components into the pore channels caused the decrease of the mesoscopic order of the pores, and it was confirmed by the significant decrease of intensities of the (110) and (200) peaks in SBA-ABZ-PEA. However, in both cases, the strongest peak for \(d_{100}\) appears in the position 2\(\theta\) = 0.98°, which confirmed the retention of 2D-hexagonal periodicity of the mesophase after the stepwise functionalization.

**2.1.2. Nanostructure.** The HRTEM image of the present sensor probe SBA-ABZ-PEA (Figure 2) showed the uniform distribution of ordered mesopores with a hexagonal arrangement and honeycomb-like fashion. It was found that the pore width lies in the range of approximately 7—7.5 nm throughout the specimen, whereas for the nonfunctionalized SBA-15 material it generally lies between 8 and 9 nm. So, the lowering of the pore diameter in SBA-ABZ-PEA revealed the successful grafting of organic ligands into the porous framework.

**2.1.3. Porosity and Surface Area.** The texture of pores of the sensor probe SBA-ABZ-PEA was measured by N\textsubscript{2}...
adsorption/desorption analysis at 77 K, and this is shown in Figure 3. An isotherm of type IV along with a typically large hysteresis loop was obtained in the pressure range \(P/P_0\) of 0.5−0.7, which revealed the mesoporous nature of the complex. The surface area and pore volume of SBA-ABZ-PEA obtained by this study were 272 m\(^2\) g\(^{-1}\) and 0.357 cm\(^3\) g\(^{-1}\), respectively. Periodic hexagonal arrangements of 4.1 nm size pores were found throughout the mesostructure of SBA-ABZ-PEA estimated by the nonlocal density functional theory (NLDFT, shown in the inset of Figure 3) method.

2.1.4. Framework and Bonding. The infrared spectral study showed two characteristic peaks at 792 and 1063 cm\(^{-1}\), which were due to the Si−O−Si stretching vibration present in all the materials, that is, in SBA-15, SBA-Pr-Cl, SBA-Pr-ABZ, and SBA-ABZ-PEA. So, the silica framework was present in all the complexes. All of them contained a common band around 1635 cm\(^{-1}\) due to the water molecules adsorbed in the frameworks. In spectra (b), the incorporation of the CH\(_2\)−Cl group in pristine SBA-15 was confirmed by the observed bands at 2935 and 2988 cm\(^{-1}\) due to the symmetric and asymmetric stretching of −CH\(_2\)− groups. Thus, it can be said that the chloropropyl chain was present in SBA-Pr-Cl. In the third step of the complex synthesis, 4-aminobenzaldehyde was anchored onto the framework, which was named SBA-Pr-ABZ. The spectrum recorded for this complex (Figure 4c) showed the stretching vibration at 2961 cm\(^{-1}\), characteristic of a secondary N−H group. In the SBA-ABZ-PEA (spectra (d)) due to imine bond formation, a peak was observed near 1706 cm\(^{-1}\), whereas a peak at 1532 cm\(^{-1}\) confirmed the C=N stretching frequency of the pyridinyl moiety.

2.1.5. Thermogravimetric Analysis. Thermal analysis of the SBA-ABZ-PEA material (Figure 5) showed that it is stable up to 210 °C. The initial weight loss (≈4%) near the 200 °C temperature could be attributed to the removal of the physically adsorbed solvent and water molecules from the mesoporous surface and inner channels. However, a further increase in temperature causes gradual loss of the covalently anchored organic moieties, and we observed the maximum weight loss of ≈11.0% in the temperature range of 200−600 °C.

2.2. Photoluminescence Property. After the successful synthesis of the mesoporous SBA-ABZ-PEA, the next step was to investigate its solution-phase luminescence property. In a typical experiment, the aqueous dispersion of SBA-ABZ-PEA was excited at 270 nm and the emission spectrum was recorded instantaneously. It showed an intense emission peak at 486 nm with a shoulder situated at 408 nm. The same results were obtained in the case of several other commonly used organic solvents like CH\(_3\)CN, CH\(_3\)OH, C\(_2\)H\(_5\)OH, and DMSO.

2.3. Sensing of Metal Ions. The interaction at the molecule-material interface plays a crucial role in the overall selectivity for the particular ion/molecule. We have measured the sensory aptitude of this mesoporous Hg-sensor toward different metal ions via interaction of the aqueous suspension of SBA-ABZ-PEA with 2 mM solution of several metal ions like Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), and Hg\(^{2+}\). All the spectral changes were recorded immediately after addition of the metal ion solution. Interestingly, the characteristic peak of SBA-ABZ-PEA appeared at 486 nm diminishes rapidly upon addition of Hg\(^{2+}\) solution, whereas in other cases no significant changes of emission intensity were observed under the same experimental condition (Figure 6). Fluorimetric titration with incremental addition of Hg\(^{2+}\) solution leads to turn-off fluorescence quenching, which clearly indicates that our mesoporous...
material shows high affinity toward Hg\textsuperscript{II} ions over all other cations (Figure 7).

In order to investigate the mechanism of quenching, the entire sensing phenomena were reanalyzed with the Stern−Volmer equation $I_o/I = K_{sv}[Q] + 1$, where $I_o$ is the emission intensity of the fluorophore probe, $I$ is the intensity after addition of the required amount of Hg\textsuperscript{II} solution in the reaction medium, $K_{sv}$ denotes the quenching constant, and $Q$ is the concentration of the added analyte. After fitting in the aforementioned equation, a linear increase of $(I_o/I - 1)$ with the incremental addition of Hg\textsuperscript{II} solution was observed with a slope value of 1.5 $\times$ 10\textsuperscript{4} M\textsuperscript{-1} (Figure 8a). Hence, it can be presumed that the quenching pattern showed a static nature (obtained from the linearity of the curve) leading to a direct binding between the Hg\textsuperscript{II} ion with some specific part of the SBA-ABZ-PEA. The high quenching constant value (1.5 $\times$ 10\textsuperscript{4} M\textsuperscript{-1}) also satisfies the fact of the strong binding interaction between the Hg\textsuperscript{II} and SBA-ABZ-PEA.

For better understanding of the promptness of detection, the limit of detection (LOD) was calculated using the equation $3\sigma/slope$, where $\sigma$ is the standard deviation calculated during the measurement of five consecutive scans and the slope obtained via plotting the fluorescence intensity against the concentration of Hg\textsuperscript{II}. The obtained LOD was found to be 1.2 $\times$ 10\textsuperscript{-6} M (Figure 8b). This value clearly indicates that a very low concentration of Hg\textsuperscript{II} is enough for the instant fluorescence quenching of the synthesized material.

Previous experiments for exploring the sensing ability for metal cations over functionalized mesoporous materials\textsuperscript{49} have limited success due to the stability of the material. Interestingly, in comparison with those literature values, the synthesized SBA-ABZ-PEA displayed excellent chemosensing of Hg\textsuperscript{II} together with several aspects like extensive water phase stability, very low detection limit toward Hg\textsuperscript{II}, and instant fluorescence quenching (Figure 9). In fact, a very small amount of prepared SBA-ABZ-PEA was enough to carry out the entire sensing experiment.

2.4. Selectivity and Specificity. Apart from the aforementioned utilities, selectivity and specificity are the major requirements for an efficient chemosensor. Hence, the specificity of the fluorophore probe toward Hg\textsuperscript{II} in the concomitant presence of other metal ions was analyzed. In a prolonged experiment, some other metal ions were added simultaneously to the uniformly dispersed solution of the SBA-ABZ-PEA containing Hg\textsuperscript{II} ions in it. Strikingly, no obvious change of the fluorescence intensity was observed. This phenomenon lucidly indicates the high selectivity and specificity of the mesoporous probe toward the Hg\textsuperscript{II} ion over a variety of cations.

2.5. Mechanistic Insights. The high selectivity of mesoporous sensor probe SBA-ABZ-PEA toward the Hg\textsuperscript{II} ion could be ascribed due to strong Hg--N bond formation.
by coordination, which leads to a six-membered chelate structure. The structure of the sensor probe SBA-ABZ-PEA is quite selective due to some underlying reasons. Hg$^{II}$ is a soft metal center and larger in size, so preferentially it avoids covalent bond formation with hard donor centers.50 Moreover, the soft acidic nature of the Hg$^{II}$ ion can make good coordination with the soft basic/borderline ligand system having nitrogen centers.51 The preferential and selective quenching by the Hg$^{II}$ ion can be ascertained by the heavy atom effect as well as the spin–orbit coupling effect in fluorescence emission$^{32,35}$ and the high electrophilic nature of Hg$^{II}$, which causes an appreciable amount of chelation between fluorophoric organic moiety bearing imine-N and pyridinic-N and Hg$^{II}$ centers$^{54}$ over other cations. Strong coordination of the lone pairs from nitrogen centers of the ligand system to metal is the reason for high quenching efficiency.57 The suggested mechanistic pathway for Hg(II) adsorption is illustrated in Scheme 2.

3. CONCLUSIONS

We can conclude that an organically functionalized mesoporous SBA-15-based Hg$^{II}$ sensor SBA-ABZ-PEA can be developed by a simple surface functionalization strategy. It was found that SBA-ABZ-PEA performed as a solid fluorescent sensor probe for the detection of the Hg$^{II}$ ion in an aqueous medium. When a large number of other metal cations were present, then this mesoporous sensor could detect Hg$^{II}$ ions with great selectivity. Upon addition of the Hg$^{II}$ ion in the aqueous suspension of the probe, its emission intensity decreases drastically and quenching of fluorescence occurred. Selective fluorescence sensing behavior of SBA-ABZ-PEA bearing imine and pyridinic N-sites grafted at the mesopore surface provides a successful chemosensor for the detection of Hg$^{II}$ from contaminated water, and this has huge future potential for the detection of Hg$^{II}$ from contaminated ground water resources.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Triblock copolymer Pluronic P123, (3-chloropropyl)triethoxysilane (ClPTES), triethylorthosilicate (TEOS), 4-aminobenzaldehyde, and 2-(2-pyridyl) ethylamine were purchased from Sigma Aldrich. Ethanol, toluene, and all other solvents were obtained from Merck. These materials were not further purified before use. The chloride salts of all the metals (Sigma Aldrich) were used to prepare the stock solutions.

4.2. Synthesis of Hg$^{II}$ Sensor. The sensing probe was prepared by post-synthesis functionalization of the SBA-15 material. At first, surface modification of porous SBA-15 has been carried out by treatment of (3-chloropropyl)-triethoxysilane followed by anchoring of 4-aminobenzaldehyde with it. Finally, 2-(2-pyridyl)ethylamine was condensed with the anchored material by the Schiff base condensation method to get the sensing probe SBA-ABZ-PEA. The outline of the synthesis is given in Scheme 1.

4.2.1. Synthesis of SBA-15. Mesoporous SBA-15 was synthesized by using the triblock copolymer Pluronic P123 poly(ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (EO$_20$PO$_{40}$EO$_20$). In a typical procedure, 4.0 g of Pluronic P123 was stirred with 30 g of water followed by 120 g of 2 M HCl at 40 °C. 8.50 g (40.8 mmol) of triethylorthosilicate (TEOS; Aldrich) was added to the whole mixture and kept at constant stirring conditions for 20 h maintaining the same above temperature. The aging process was done at 80 °C for 24 h to obtain the solid product. Finally, it was filtered, washed thoroughly with distilled water to make it acid-free, and dried at room temperature overnight. The calcination of the solid was performed at 550 °C for 6 h in air to remove all the residual organic templates to obtain the pure SBA-15.

4.2.2. Synthesis of Chloro-Functionalized SBA-15 (SBA-Pr-Cl). The mesoporous and calcined SBA-15 was synthesized as per the reported method.26 Chloro-functionalized SBA-15 was prepared in stirring and refluxing conditions for 24 h where 0.20 g of as-synthesized SBA-15 was taken in 10 mL of dry toluene and 0.6 mmol (0.144 g) of ClPTES was added to it dropwise under a N$_2$ atmosphere. A white solid was obtained after cooling the suspension at room temperature. Finally, it was filtered, washed several times with a measured amount of toluene, dichloromethane, and diethyl ether, and allowed to dry at room temperature.

4.2.3. Covalent Grafting of 4-Aminobenzaldehyde on SBA-Pr-Cl (SBA-Pr-ABZ). 0.30 g of methanolic suspension of SBA-Pr-Cl was stirred in a 50 mL round bottom flask. Then 10 mL of methanolic solution of 0.1175 g of 4-aminobenzaldehyde (1.03 mmol) was gradually added to it. Then 0.104 g of triethylamine (TEA) (1.029 mmol) was added under refluxing conditions to the whole mixture and kept for 24 h without further interruption. Finally, it was cooled,
washed thoroughly with methanol, and filtered through suction.

4.2.4. Synthesis of Sensor Probe SBA-ABZ-PEA. The powdered SBA-Pr-ABZ was taken in 30 mL of ethanolic solution of 0.135 g of 2-(2-pyridyl)ethyamine (1.12 mmol) and refluxed with stirring for 24 h. Finally, the solid was filtered, washed abundantly with ethanol, Soxhlet-extracted with CH2Cl2, and dried in vacuum. The yellowish material obtained was denoted as SBA-ABZ-PEA (Scheme 1).

4.2.5. Fabrication of SBA-ABZ-PEA for Fluorescence Analysis. To investigate the fluorescence activity of the synthesized mesoporous SBA-ABZ-PEA in an aqueous medium, 5.0 mg of the SBA-ABZ-PEA was dispersed in 100 mL of double distilled water by the ultrasonic method. During the fluorescence activity measurement process, 2.5 mL of the above dispersion was taken in a quartz cell and excited with a radiation of 270 nm wavelength light source. Sensor aptitude of the mesoporous probe toward different metal ions was checked using 2 mM aqueous solution of the chloride salts of Na(I), K(I), Mg(II), Al(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pb(II), Zn(II), Cd(II), and Hg(II) prepared in double distilled water. Considerable quenching of the emission intensity was observed only upon addition of varying amounts of Hg(II) solution (stock solution) in the aqueous dispersion of SBA-ABZ-PEA. The experiments were carried out under room temperature and similar conditions for each cationic solution.

4.3. Characterization of Materials. FT-IR spectra of the synthesized materials were recorded by a Nicolet MAGMA-FTIR 750 Spectrometer Series II. A Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu Kα radiation of wavelength 0.15406 nm was used to obtain PXRD patterns. The morphology of the material was detected by HR-TEM images with a JEOL 2010 TEM operated at potential of 200 kV. Thermogravimetric analysis (TGA) was performed in a TGA by using a PerkinElmer LS 55 fluorescence spectrometer instrument where the path length of quartz cell was 1 cm.

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**Notes**

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