Sensors

# Functionalized Cubic Mesoporous Silica as a Non-Chemodosimetric Fluorescence Probe and Adsorbent for Selective Detection and Removal of Bisulfite Anions along with Toxic Metal Ions

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Dual signaling and remediation systems for detection and adsorption of toxic analytes have gained more attention over sensory probes only. However, most of the sensors for bisulfites are chemodosimetric probes, which are irreversible and having drawbacks of absolute selectivity, recyclability, and solubility in a pure aqueous system. To address above drawbacks a new nonchemodosimetric probe material with a strong hydrogen bonding pocket for bisulfites is developed. Synthesis of cubic mesoporous silica by a modified Stober process followed by functionalization with 2,2'-(((((3-(triethoxysilyl) propyl)azanediyl)bis(methylene))bis(2,1-phenylene))bis(oxy))bis(N-(4-((E)phenyldiazenyl)phenyl)acetamide) (AZOL) has given a fluorogenic silica probe material SiO<sub>2</sub>@AZOL. This material shows selectivity toward bisulfite anion (limit of detection (LOD): 64 ppb) and Hg<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> cations (LOD: 126, 95, 14, and 27 ppb, respectively) among various analytes. The adsorption studies for these toxic analytes (HSO<sub>3</sub><sup>-</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>) show an extraction efficiency of around 99% and adsorption capacities of 873, 630, 633, 260, and 412 mg g<sup>-1</sup>, respectively. Spectroscopic studies along with adsorption, striping, and regeneration studies reveal that this material is a recyclable sensory cum adsorbent material for these toxic analytes. Moreover, this material can be used as a sensitive probe material for determination of HSO<sub>3</sub><sup>-</sup> levels in various sugar samples.

## 1. Introduction

Selective detection and removal of bisulfites have drawn attraction due to their critical impact on physiological and environmental systems. Though bisulfites are widely used as preservatives for food and beverage industries due to antimicrobial and antioxidant properties,<sup>[1]</sup> they possess a threat to human health and environment. Bisulfites can trigger allergic reactions, breathing problems, and gastrointestinal

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pain.<sup>[2]</sup> Given the deleterious effects of bisulfites and sulfites, the threshold limits in edibles have been limited to 10 ppm  $(125 \times 10^{-3} \text{ M})$  of sulfite by the US Food and Drug Administration (FDA).<sup>[3]</sup> Furthermore, bisulfites are also byproducts of toxic sulphur dioxide gas (SO<sub>2</sub>), which dissolves in water to form an equilibrium mixture of sulfites and bisulfites based on solution pH, which makes their selective detection in the presence of each other a challenging task due to similar reactivity.<sup>[4]</sup> Therefore, an efficient detection and remediation system for sulfites/ bisulfites is desirable. In this regard, many methods have been developed including spectrophotometry,<sup>[5]</sup> titration,<sup>[6]</sup> capillary electrophoresis,<sup>[7]</sup> and electrochemical detection.<sup>[8]</sup> However, most of these methods are time-consuming and involve sample pretreatments, which limit their use in sensory applications. To address these issues, in recent times many homogeneous sensory systems based on organic fluorescent probes have been developed for detection of HSO3<sup>-</sup>/SO3<sup>2-</sup> in aqueous systems. Most of these probes are based

on reactivity of HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> toward various functional groups to constitute chemodosimetric probes<sup>[9]</sup> such as the nucleophilic addition reaction with aldehydes,<sup>[10]</sup> Michael-type additions,<sup>[11]</sup> deprotection of the levulinate group,<sup>[12]</sup> and very rare non-chemodosimetric interaction with amine<sup>[13]</sup> (**Figure 1**).

But most of these chemodosimetric probes are for detection purposes only and lack absolute selectivity. Therefore, only a few pieces of literature show bisulfite selectivity in the presence of sulfites while others have not considered it for sensing studies.<sup>[14]</sup> In addition to that most of the probes need organic solvents such as acetonitrile, *N*,*N*-dimethylformamide (DMF), or dimethyl sulfoxide for preparation of the homogeneous system for sensing studies. Also, their use for bulk applications such as environmental remediation is limited due to irreversible reactions and poor performances in a pure aqueous system. Thus, there is a need for a sensory cum adsorbent material other than chemodosimetric probes for detection and remediation, which can also overcome the above limitations of selectivity, solubility, and recyclability issues. To address these

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Figure 1. Representation of different types of fluorescence probes for  $SO_3^{2-}/HSO_3^{-}$  anions.

problems, recently, the combination of organic-inorganic hybrid materials has emerged as an alternative for the homogeneous sensory system, as they can disperse well in an aqueous system for sensing studies.<sup>[15]</sup> The main advantages of such hybrid materials are that they provide a heterogeneous platform for dual functions of signaling and remediation in the aqueous system which can be easily recovered and recycled.<sup>[16]</sup> Therefore, in recent times many chelating fluorophores appended nanostructured materials reported for detection and removal of toxic analytes.<sup>[17]</sup> Among various porous materials, mesoporous silica materials with different shapes and sizes have drawn attraction due to high surface area and porosity, good thermal and chemical stability, excellent aqueous dispersibility, and ease of functionalization.<sup>[18]</sup> However, the strategy for the development of functionalized materials for both detection and removal purposes is distinct from designing of molecular probes only. Such materials require developing of both solid support and chelating fluorophore ligands with appropriate coordination environments for ion binding to impart dual functions. Apart from that, reversible responses of probes or chelating ionophores are also necessary for recyclability of such materials. Also the stability of these materials during detection and adsorption, striping, and regeneration is also an important aspect of designing such materials. Although such materials for dual functions of detection and removal are known but rare for sulfites or bisulfites.<sup>[19]</sup> Recently Martínez-Máñez and co-workers have well studied a chromo fluorogenic detection system for sulfite anions based on a chemodosimetric probe with MCM-41 mesoporous nanoparticles as solid support.<sup>[20]</sup> But these heterogeneous systems are not studied in the presence of both sulfites and bisulfites. Also, striping and regeneration of probes for recyclability are not considered. However, there is no such report of heterogeneous systems for selective detection of bisulfites in literature comprising above advantages.

In this study, we have synthesized nanocubic mesoporous silica as solid support by a modified Stober process using cetyl pyridinium bromide hydrate (CPB) as structure directing template which is never used before for synthesis of cubic



mesoporous silica.<sup>[21]</sup> Then we have fabricated a new azo derived ligand on the surface of above mesoporous silica to obtain the hybrid material (SiO2@AZOL). Presence of two amide hydrogens (hydrogen bond donor) and one tertiary amine nitrogen (hydrogen bond acceptor) in a triangular binding pocket provides strong hydrogen bonding affinity toward bisulfite anion. Apart from bisulfite, this material also shows coordination driven selectivity toward various toxic metal ions such as  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ . Toxicity of these metal ions is of environmental concern and a subject of many reviews.<sup>[22]</sup> Though various mesoporous materials are known for detection and removal of these toxic metal ions, this material also shows exceptionally high adsorption capacity.

To the best of our knowledge, there is no material based heterogeneous fluorescence probe known for bisulfites. Apart from

that, dual functions of detection and adsorptions, striping, and regeneration are additional advantages of this material for a precise detection and remediation system. Additionally, dual functions of detection and removal of above toxic metal ions with recyclability of material are also other advantages offered by this material.

## 2. Result and Discussion

## 2.1. Synthesis, Structural Characterization, and Porosity Assessment

The synthetic approach to the material SiO<sub>2</sub>@AZOL is briefly depicted in Scheme 1 and the details of the synthetic procedures are given in the Experimental Section. Initially, the solid support cubic mesoporous silica was synthesized by a modified Stober process using Cetyl Trimethylammonium Bromide cetyl trimethylammonium bromide (CTAB) as structure directing template which has yielded high surface area as compared to the original method.<sup>[23]</sup> However, most of the synthetic procedures in literature use either CTAB or triblock copolymers as structure directing template for ordered cubic mesoporous silica.<sup>[24]</sup> Then the surface modifications of above cubic silica were performed through four consecutive steps to yield the final product SiO2@AZOL (Scheme 1D). To confirm the formation of the ligand AZOL on the solid surface an indirect approach was made, where the ligand AZOL was synthesized first and then fabricated on cubic silica surface to generate same product confirmed from characterization data of both methods. In this work, the product from the direct method (Scheme 1D) was used for most of the studies.

The mesoporous structure of modified silica nanoparticles  $(SiO_2)$  and final SiO<sub>2</sub>@AZOL materials is confirmed by highresolution transmission electronic microscopy (**Figure 2**). Evaluation of the Transmission electron microscopy (TEM) images shows that the size of the cubic shaped SiO<sub>2</sub> nanoparticles is in the range of 250–330 nm with uniform pore sizes of ~5 nm SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com



Scheme 1. A-E) Representation of preparation of mesoporous silica, AZOL ligand, and final probe material SiO<sub>2</sub>@AZOL.

(Figure 2B). In case of surface modified SiO<sub>2</sub>@AZOL material also a regular cubic morphology was observed with particle sizes in the range of 280–360 nm and uniform pore sizes of ~2.5 nm (Figure 2D). A decrease in pore width from 5 nm (SiO<sub>2</sub>) to 2.5 nm (SiO<sub>2</sub>@AZOL) may be due to functionalization at mesopores of the SiO<sub>2</sub>.<sup>[25]</sup> Further confirmation of this cubic morphology and particle size of SiO<sub>2</sub>, SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@ AZOL materials was confirmed from field emission scanning electron microscope (FESEM) images (**Figure 3**A–F).

The broad angle X-ray diffraction pattern for porous silica (SiO<sub>2</sub>), SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@AZOL materials (Figure 3G) displays similar broadband at  $2\theta = 22^{\circ}$ , which indicates core silica sphere is unchanged (amorphous nature) before and after AZOL group grafting.<sup>[26]</sup> The small-angle X-ray diffraction pattern for porous silica (SiO<sub>2</sub>), SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@AZOL materials shows one strong diffraction peak at  $2\theta = 1.72^{\circ}$ , and three weak diffraction peaks at  $2\theta = 3.40^{\circ}$ ,  $4.24^{\circ}$ , and  $6.54^{\circ}$ . Based on the Bragg formula, the corresponding crystal plane d-spacings were found to be 5.12, 2.53, 2.08, and 1.34 nm, respectively. These d-spacings can be assignable to the 100, 110,

200, and 210 diffraction of a well-ordered 2D hexagonal structure.<sup>[27]</sup> From these observations it is interpreted that 2D-hexagonal ordering has been unchanged after grafting with the AZOL ligand but a decrease in intensity of all the peaks may be due to the lowering of local mesoporous ordering due to the reduction of pore size after functionalization of sensing probes between the channel walls of the silicate framework.<sup>[28]</sup> Thus, it can be understood as indirect evidence for the successful covalent grafting of sensing probe (AZOL group) on the channels of mesoporous silica.

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The physicochemical parameters derived from the N<sub>2</sub> adsorption/desorption analysis are described in **Table 1** and corresponding values for the specific Brunauer–Emmett–Teller (BET)<sup>[29]</sup> surface area, pore volume, and pore size distribution (PSD) for the modified SiO<sub>2</sub> nanoparticle, SiO<sub>2</sub>@NH<sub>2</sub>, and functionalized SiO<sub>2</sub>@AZOL materials are shown in Figure 3H. Typical type IV isotherms were observed for SiO<sub>2</sub> and SiO<sub>2</sub>@ NH<sub>2</sub>, which is the characteristic of mesoporous materials.<sup>[30]</sup> From these isotherms, the sharp increase in N<sub>2</sub> adsorption at partial pressure *P*/*P*<sub>0</sub> of 0.30–0.45 was observed, indicating the





Figure 2. A) TEM image of cubic SiO<sub>2</sub>. B) Hexagonal arrangement of pores in cubic SiO<sub>2</sub>. C) TEM image of cubic SiO<sub>2</sub>@AZOL material. D) Hexagonal arrangement of pores in cubic SiO<sub>2</sub>@AZOL material.

uniform size of mesopores. On the other hand, type-I isotherm was observed for SiO<sub>2</sub>@AZOL material which did not show any capillary condensation step resulted in a decrease in pore size. The pore size distribution patterns of materials SiO<sub>2</sub>, SiO<sub>2</sub>@ NH<sub>2</sub>, and SiO<sub>2</sub>@AZOL are shown in Figure S1 (Supporting Information). In PSD, peak pore diameters for SiO<sub>2</sub>, SiO<sub>2</sub>@ NH<sub>2</sub>, and SiO<sub>2</sub>@AZOL materials are 4.9, 3.2, and 2.2 nm which are in good agreement with TEM pore sizes. The BET surface areas were found to be 939.3827, 334.3625, and 13.6571 m<sup>2</sup> g<sup>-1</sup> with pore volumes of 1.0781, 0.3807, and 0.0920 cm<sup>3</sup> g<sup>-1</sup>, respectively. A gradual decrease of surface area, pore volume, and pore diameter from SiO<sub>2</sub> to SiO<sub>2</sub>@NH<sub>2</sub> to SiO<sub>2</sub>@AZOL materials suggests that the functionalization of azo group happened inside the mesopores.<sup>[31]</sup>

#### 2.1.1. Surface Characterization

To confirm the covalent attachment of the ligand AZOL on SiO<sub>2</sub> surface, solid state NMR, fourier-transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis were carried out. The <sup>13</sup>C solid state NMR spectrum of SiO<sub>2</sub>@NH<sub>2</sub> (**Figure 4A**) shows that three peaks for the methylene carbons in the aminopropyl group<sup>[32]</sup> linked to the silica surface, denoted as a star (\*), are also present in intermediates and final product SiO<sub>2</sub>@AZOL material (Figure 4B,C). Successful formation of



intermediates and SiO2@AZOL material is characterized by the presence of additional peaks for methylene carbon (50-60 ppm, black square), arene carbon (92-165 ppm),<sup>[33]</sup> ethereal methylene (68 ppm),<sup>[34]</sup> and carbonyl carbon (180 ppm).<sup>[35]</sup> Similarly, the covalent attachment of the (3-aminopropyl) triethoxysilane (APTES) on surface of silica was further confirmed by <sup>29</sup>Si MAS NMR which shows only three signals at -94, -102, and -110 ppm ( $Q_n$ ) for surface silanol groups in SiO<sub>2</sub> and additional three signals between -50 and -70 ppm ( $T_n$ ) for SiO<sub>2</sub>@ NH<sub>2</sub> originated from silicon atom of organic linker 3-aminopropyl triethoxysilane<sup>[29,35c]</sup> (Figure S2, Supporting Information).

FT-IR spectrum for SiO<sub>2</sub> (Figure 5A) shows bands at 3432, 1640, 1062, and 793 cm<sup>-1,[36]</sup> whereas for SiO<sub>2</sub>@NH<sub>2</sub> bands it appears at 3438, 2930, 2880, 1631, 1560, 1333, 1062, 793, and  $694 \text{ cm}^{-1}$ . The new bands at 694, 1631, and 1560 cm<sup>-1</sup> for the  $SiO_2@NH_2$  are due to N-H stretching and bending vibrations.<sup>[37a]</sup> The band at 1333 cm<sup>-1</sup> is due the C–N vibration of primary alkyl amine.[37b] The bands at 1489, 2930, and 2880 cm<sup>-1</sup> are due to the C-H stretching and bending vibrations from APTES group.<sup>[38]</sup> This gives solid evidence of 3-APTES functionalization on silica surface. To confirm formation of SiO<sub>2</sub>@ AZOL material, comparison of FT-IR spectrum (Figure 5B-D) shows that new peaks at 3080, 1665, 1595, 1460, 1305, 826, 766, and

686 cm<sup>-1</sup> appear in SiO<sub>2</sub>@AZOL material due to presence of =C-H group (3080 cm<sup>-1</sup>), -CONH- (amide I, 1665 cm<sup>-1</sup>) group,<sup>[39]</sup> N=N vibration (1595 cm<sup>-1</sup>) in azo group,<sup>[40]</sup> vibration of C–N–C bond (1460 cm<sup>-1</sup>),<sup>[41]</sup> aromatic C–N (1305 cm<sup>-1</sup>), and other characteristic peak of 4-aminoazobenzene<sup>[40]</sup> at 826, 766, and 686 cm<sup>-1</sup>. Similarly, comparison of FT-IR spectrum of AZOL ligand with SiO<sub>2</sub>@AZOL material (Figure 5D; Figure S3 of Supporting Information) shows that all the bands for ligand are present in SiO<sub>2</sub>@AZOL material, which provides a strong evidence of AZOL framework existing on SiO<sub>2</sub>@AZOL material.

The thermogravimetric measurements for SiO<sub>2</sub>@NH<sub>2</sub> and SiO2@AZOL materials show three major weight losses between 33 and 220 °C, 220 and 550 °C, and 550 and 800 °C. The first region exhibits a weight loss of 17.29% for SiO<sub>2</sub>@ NH2 and 11.69% for SiO2@AZOL materials due to the desorption of physically adsorbed water on the surface of the materials.<sup>[42]</sup> From the above results, it can be assumed that more water molecules are adsorbed on the SiO2@NH2 surface due to the presence of the hydrophilic NH2 group. The second region represents the decay of organic contents, which shows a weight loss of 7.01% for SiO<sub>2</sub>@NH<sub>2</sub> as compared to17.64% for SiO<sub>2</sub>@ AZOL due to high organic loading in the SiO<sub>2</sub>@AZOL material. The weight loss in the last region represents dehydroxylation of surface silanol groups, which shows similar weight losses for SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@AZOL materials (1.52% and 1.51%, respectively) as expected, Figure 6.







**Figure 3.** A,B) FESEM image of cubic SiO<sub>2</sub>. C,D) FESEM image of cubic SiO<sub>2</sub>@NH<sub>2</sub>. E,F) FESEM image of cubic SiO<sub>2</sub>@AZOL. G) Low angle and broad angle PXRD of SiO<sub>2</sub>, SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@AZOL. H) N<sub>2</sub> adsorption/desorption isotherms of SiO<sub>2</sub>, SiO<sub>2</sub>@NH<sub>2</sub>, and SiO<sub>2</sub>@AZOL.

#### 2.2. Sensing Properties of SiO<sub>2</sub>@AZOL

Since the SiO<sub>2</sub>@AZOL material is acid sensitive due to presence of the tertiary amine group and amide NH, the stability of material at different pH ranges was studied by UV–Vis absorption studies in the pH range of 1.5–10 in aq. buffer medium (**Figure 7A**). The pH-dependent absorption studies show that the material is stable within the pH range of 5–10 with two absorption bands observed at 372 and 262 nm. At lower pH (<5) the above bands vanish and two new bands appear at 328 and 255 nm due to protonation at tertiary nitrogen and hence the appearance of new bands for SiO<sub>2</sub>@AZOL-H<sup>+</sup> material. Though at higher pH (>8) the material is stable but the formation of metal hydroxides is well known. So, based on above observations, neutral pH ( $\approx$ 7) was chosen as the analytical condition for the detection and removal of various analytes in these studies. To study the selective sensing properties

 Table 1. Surface areas, pore volumes, and pore diameters of the synthesized materials.

| Sample name                       | Surface area<br>[m <sup>2</sup> g <sup>-1</sup> ] | Pore volume<br>[cm³ g <sup>-1</sup> ] | Pore diameter<br>[nm] |
|-----------------------------------|---|---------------------------------------|-----------------------|
| SiO <sub>2</sub>                  | 939.3827  | 1.0781                                | 4.9                   |
| SiO <sub>2</sub> @NH <sub>2</sub> | 334.3625  | 0.3807                                | 3.2                   |
| SiO <sub>2</sub> @AZOL            | 13.6571   | 0.0920                                | 2.2                   |

of above material SiO2@AZOL toward different anions and cations both UV-Vis absorption and fluorescence emission studies were carried out in aqueous buffer system in suspended form at pH 7 (K<sub>2</sub>HPO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub> buffer). The UV/Vis spectrum of SiO<sub>2</sub>@AZOL shows two absorption bands at 372 and 262 nm due to  $\pi$ - $\pi$ \* transition corresponding to the transisomer of AZO group and electronic transitions of aromatic rings, respectively.<sup>[43]</sup> These bands undergo blue shifts (329 and 256 nm) with decrease in absorbance in presence of bisulfite (HSO<sub>3</sub><sup>-</sup>) anion, whereas no changes are observed with other anions (HPO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>,  $CH_3COO^-$ ,  $HCOO^-$ ,  $Ph-COO^-$ ,  $S^{2-}$ ,  $CN^-$ ,  $SO_3^{2-}$ ,  $SO_4^{2-}$ ) under similar conditions (Figure 7B). Similarly, among various metal ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>) only Cu<sup>2+</sup> (268 and 371 nm), Zn<sup>2+</sup> (256, 329, and 378 nm), Hg<sup>2+</sup> (254 and 326 nm), and Cd<sup>2+</sup> (256, 329, and 374 nm) show changes in UV/Vis spectrum while no change was observed with other cations (Figure 7C). The UV/Vis titration profile for one of the representative cases with Hg<sup>2+</sup> shows a gradual change in spectrum pattern with increasing concentration of Hg<sup>2+</sup> (Figure S4, Supporting Information), whereas Figure 7A shows a sudden change in spectrum pattern once the pH reaches below 5 which suggests that the changes with above metal ions are not due to change in pH.

Similarly, the fluorescence emission spectra of suspended  $SiO_2@AZOL$  material in aqueous buffer medium exhibit a strong band at 510 nm upon excitation at 390 nm which







Figure 4. A) <sup>13</sup>C solid CP NMR for SiO<sub>2</sub>@NH<sub>2</sub>. B) <sup>13</sup>C solid CP NMR for SiO<sub>2</sub>@TEPABMD. C) <sup>13</sup>C solid CP NMR for SiO<sub>2</sub>@AZOL.



Figure 5. A–D) Comparision of FT-IR spectra of SiO<sub>2</sub>, SiO<sub>2</sub>@NH<sub>2</sub>, AZOL, and SiO<sub>2</sub>@AZOL.

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Figure 6. TGA of SiO<sub>2</sub>@NH<sub>2</sub> and SiO<sub>2</sub>@AZOL material.

quenched dramatically upon addition of bisulfite anion, whereas no changes were observed with other anions including sulfite (Figure 8A). As both sulfite and bisulfite can exist in an equilibrium mixture<sup>[4,44]</sup> at neutral pH, as discussed earlier the pH-dependent fluorescence sensing studies were also carried out. For this pH 5.0 and pH 9.0 were chosen where bisulfites and sulfites predominate, respectively. It has been observed that there was no change in fluorescence spectra with sulfites at pH 9.0 (Figure 8C), whereas with bisulfite at pH 5.0 (Figure 8B) a distinct turn-off response was observed which provides strong evidence in favor of bisulfite which is responsible for quenching of emission spectra at neutral pH. Hence this material shows selectivity toward bisulfite even in the presence of sulfite. To add further, we did a competitive fluorescence study by taking an excess of other competing anions along with bisulfite anion in the same solution which shows similar quenching effect that of control experiments with bisulfite anion (Figure 8F).

Similarly, the fluorescence emission band at 510 nm gets quenched in the presence of only  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$ ,  $Cd^{2+}$  metal ions among various other relevant metal ions under similar conditions (**Figure 9**). A similar competitive

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fluorescence study in the presence of large excess of other metal ions with either of the above metal ions in the same solution shows similar quenching effect that of control experiments (Figure S5, Supporting Information). So, this material shows selective sensing properties toward bisulfite among various anions and Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup> metal ions among different cations.

To determine the quenching constant  $(K_{sv})$  of SiO<sub>2</sub>@AZOL material toward HSO<sub>3</sub><sup>-</sup> anion and heavy metal ions (Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>), fluorescence titration was carried out with incremental addition of above analytes to the SiO2@AZOL material with a saturation concentration  $160\times 10^{-6}$  m. It has been observed that the Stern-Volmer plots for HSO3- anion and Zn<sup>2+</sup> obey linear fitting while a nonlinear fitting was observed for Cu<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup> (Figure 10). A linear fitting suggests a static mechanism<sup>[16a]</sup> where the quencher binds with the probe in the ground state forming a nonfluorescent complex or "dark" state also supported by UV-Vis spectral changes due to the ground state charge transfer complex formation. A positive deviation of the Stern-Volmer plot from linearity for Cu<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup> indicates that quenching mechanism is either static or combination of both static and dynamic.<sup>[45]</sup> Therefore, an exponential quenching equation  $F_0/F = A \cdot e^{K[m]} + B$  was used to the nonlinear Stern-Volmer curve and a linear quenching equation  $F_0/F = K_{sv}[M] + 1$  was used for the linear Stern-Volmer curve, where  $F_0$  is the initial fluorescence intensity of the SiO<sub>2</sub>@AZOL material, F is the fluorescence intensity of the SiO<sub>2</sub>@AZOL with incremental addition of analytes, [M] is the concentration of analytes, A, B, and K are constants,  $K_{sv}$ is the Stern-Volmer constant which is the slope of the linear plot, the quenching constant for nonlinear curve is the product of constants A and K.<sup>[45]</sup> The calculated linear quenching constants for HSO<sub>3</sub><sup>-</sup> anion and Zn<sup>2+</sup> are found to be  $5.784 \times 10^3$  M<sup>-1</sup> and  $4.1494 \times 10^4$  M<sup>-1</sup>, respectively. Similarly, the calculated nonlinear quenching constants for Cu<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup> are found to be 2.4856  $\times$  10<sup>4</sup>  $_{\rm M}$ <sup>-1</sup>, 5.7842  $\times$  10<sup>3</sup>  $_{\rm M}$ <sup>-1</sup>, and 3.619  $\times$  10<sup>3</sup>  $_{\rm M}$ <sup>-1</sup>, respectively. To calculate the limit of detection (LOD) for all the analytes (HSO<sub>3</sub><sup>-</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup>) incremental amounts of above solutions (10–70  $\times$  10<sup>-6</sup> M) were added to a suspension of SiO2@AZOL material in an aqueous medium and fluorescence quenching was recorded (Figures S6-S10, Supporting Information). Plot of intensity versus concentration



**Figure 7.** A) UV–Vis spectra of SiO<sub>2</sub>@AZOL at different pH range. B) UV–Vis spectra of SiO<sub>2</sub>@AZOL with all anions. C) UV–Vis spectra of SiO<sub>2</sub>@ AZOL with all metal ions. Buffers used:  $pH \le 5$ : Na<sub>2</sub>HPO<sub>4</sub>/citric acid; neutral pH (7): K<sub>2</sub>HPO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub>; pH (8–10), KH<sub>2</sub>PO<sub>4</sub>·NaOH.







**Figure 8.** A) Fluorescence spectra of SiO<sub>2</sub>@AZOL in presence of various anions in aqueous medium at neutral pH ( $K_2HPO_4/KH_2PO_4$  buffer) with an excitation at 390 nm. B) Fluorescence spectra of SiO<sub>2</sub>@AZOL in presence of only HSO<sub>3</sub><sup>-</sup> anion at pH 5.0 (Na<sub>2</sub>HPO<sub>4</sub>/Citric acid buffer). C) Fluorescence spectra of SiO<sub>2</sub>@AZOL in presence of NH 9.0 ( $KH_2PO_4$ -NaOH buffer). D) Fluorescence titration profile with increasing concentration of HSO<sub>3</sub><sup>-</sup> anion. E) Relative emission intensity with various anions. F) Competitive fluorescence intensity in presence of all coexisting anions.

of analytes revealed linear relationship with a slope, *S*, and correlation factor ( $R^2$ ) using the equation LOD = 3 × (SD/*S*),<sup>[46]</sup> Where SD is the standard deviation of the initial intensity of

 $SiO_2@AZOL$  without analytes and *S* is the slope obtained from the linear plot. The LOD and correlation factors of  $SiO_2@AZOL$  toward heavy metal ions and anions are described in **Table 2**.



Figure 9. A) Fluorescence spectra of SiO<sub>2</sub>@AZOL in presence of various metal ions in aqueous medium at neutral pH (7.0) with an excitation at 390 nm. B–E) Fluorescence titration with increasing concentration of Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, respectively. F) Relative emission intensity with various metal ions.







Figure 10. A-C) Nonlinear Stern-Volmer plot for Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> ions. D,E) Linear Stern-Volmer plots for Zn<sup>2+</sup> and HSO<sub>3</sub><sup>-</sup> anions.

#### 2.3. Adsorption Studies

Since the SiO<sub>2</sub>@AZOL material is pH sensitive, protonation and deprotonation also affect the adsorbent surface charges and hence adsorption capacities. So, the zeta potential of SiO<sub>2</sub>@ AZOL adsorbent was measured at different pH values<sup>[47a]</sup> which shows that, at neutral conditions (pH 7), zeta potential value of SiO<sub>2</sub>@AZOL material is found to be –40.6 mV due to presence of electronegative donor atoms (N,O) which did not change much at higher pH range (8–10) but at lower pH range 4–2 a more positive value was observed due to protonation of AZOL ligand (**Figure 11**A). Similar observations were made from pH-dependent absorption studies also. So, based on above observations adsorption studies were also carried out at neutral pH ( $\approx$ 7).

To evaluate the effect of treatment times on the adsorption process, one of the representative studies with  $Zn^{2+}$  shows that the adsorption capacity increases with time which gets saturated after 2 h (Figure 11B). So, based on above observations the equilibrium adsorption time was kept at a little higher side for 3 h for all adsorption experiments.

| Table 2. | Some | detection | parameter, | K <sub>sv</sub> , | LOD, | and | $R^2$ of | analyte | s. |
|----------|------|-----------|------------|-------------------|------|-----|----------|---------|----|
|----------|------|-----------|------------|-------------------|------|-----|----------|---------|----|

| K <sub>sv</sub>                  | Limit of detection  | R <sup>2</sup>  |
|----------------------------------|---|---|
| $2 \times 10^{3} \text{ m}^{-1}$ | 126 ppb   | 0.9693  |
| $0 \times 10^{3}  \text{m}^{-1}$ | 95 ppb  | 0.9940  |
| $5	imes 10^4~{ m M}^{-1}$        | 14 ppb  | 0.9840  |
| $1 \times 10^4 \text{ m}^{-1}$   | 27 ppb  | 0.9996  |
| $7 	imes 10^4 \text{ m}^{-1}$    | 64 ppb  | 0.9966  |
|                                  | $\frac{K_{sv}}{2 \times 10^3 \text{ m}^{-1}}$ $\frac{1}{2 \times 10^3 \text{ m}^{-1}}$ $\frac{1}{2 \times 10^4 \text{ m}^{-1}}$ $\frac{1}{4 \times 10^4 \text{ m}^{-1}}$ $\frac{1}{7 \times 10^4 \text{ m}^{-1}}$ | $K_{sv}$ Limit of detection           2 × 10 <sup>3</sup> m <sup>-1</sup> 126 ppb           0 × 10 <sup>3</sup> m <sup>-1</sup> 95 ppb           5 × 10 <sup>4</sup> m <sup>-1</sup> 14 ppb           4 × 10 <sup>4</sup> m <sup>-1</sup> 27 ppb           7 × 10 <sup>4</sup> m <sup>-1</sup> 64 ppb |

Since the SiO2@AZOL materials show selectivity toward bisulfite anion and heavy metal ions ( $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$ , and  $Cd^{2+}$ ), the equilibrium adsorption capacity  $(Q_e)$  was calculated from the plot of adsorption isotherm as described in the Experimental Section. For bisulfite anion, as it is impossible to quantify its concentration by inductively coupled plasma optical emission spectrometry (ICP-OES) or ion chromatography analysis an indirect approach was made. As bisulfite anion adsorption is accompanied by simultaneous intake of sodium ion to maintain charge neutrality by the neutral SiO2@AZOL material and the material does not show adsorption affinity toward sodium ion itself, Na<sup>+</sup> ion concentration was considered for quantification of the equivalent concentration of bisulfite from ICP-OES analysis. As the sodium or potassium phosphate buffer will complicate the actual concentrations in the indirect method, no buffer was used for adsorption studies for bisulfites. Figure 12A shows the equilibrium adsorption isotherm for bisulfite anion with adsorption capacity of 873 mg g<sup>-1</sup> (equivalent to 248 mg g<sup>-1</sup> for Na<sup>+</sup> ions). Figure 12B shows the equilibrium adsorption isotherms for Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup> with adsorption capacities of 260, 412, 630, and 633 mg g<sup>-1</sup>, respectively. The experimental data for these analyte adsorptions onto SiO2@AZOL material were analyzed by using the Langmuir and Freundlich adsorption isotherm model, which applies to heterogeneous surfaces. The Langmuir adsorption isotherm is represented in the equation  $C_e/q_e$ (Langmuir) =  $C_e/q_{max} + 1/q_{max} \times k_L$ <sup>[48]</sup> where  $C_e$  is the equilibrium concentration of analytes (mg L<sup>-1</sup>),  $q_e$  is the equilibrium adsorption capacity (mg g<sup>-1</sup>),  $q_{max}$  is the adsorption capacity of analytes onto adsorbent (mg  $g^{-1}$ ), and  $K_L$  is the Langmuir adsorption constant. The Freundlich adsorption isotherm is represented in the equation,  $\ln q_e = \ln K_f + 1/n \ln C_e$ ,<sup>[48]</sup> where  $q_{\rm e}$  and  $C_{\rm e}$  are the equilibrium adsorption capacity and the





**Figure 11.** A) Change of zeta potential value of SiO<sub>2</sub>@AZOL surface with change in pH of solution. B) Change in adsorption capacity of SiO<sub>2</sub>@AZOL towrad  $Zn^{2+}$  with time (one of the representative cases for equilibrium time).

equilibrium concentration of analytes, respectively.  $K_f$  and n are Freundlich constants. The Langmuir and Freundlich adsorption isotherms for Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup> are illustrated in Figures S11–S16 of the Supporting Information and adsorption parameter is described in **Table 3**, which shows that Langmuir model shows a better agreement with the experimental data. The dual functions of both detection (LOD) and adsorption (adsorption capacity) of this material are comparable to similar kind of materials known in the literature and an advantage over either of the functions (Table S1, Supporting Information).

In an attempt to study the selectivity of the SiO<sub>2</sub>@AZOL material toward various metal ions competitive adsorption studies were carried out in the presence of relevant other metal ions at neutral pH. In competitive adsorption/extraction experiment 100 mg SiO<sub>2</sub>@AZOL material was treated with  $\approx$ 20 ppm of all mixed metal ions in 100 mL aqueous solution. After equilibrating the mixture for 3 h in a vibrating mixture, the mixture was filtered and analyzed by ICP-OES analysis to calculate the final concentration of metal ions and adsorption/removal percentage was calculated from the equation  $R\% = C_I - C_f/C_I \times 100$ ,<sup>[16a]</sup> where  $C_I$  and  $C_f$  are the initial and final concentrations of metal ions, respectively, R% is the removal percentage (Table S2, Supporting Information). It is observed that other than these metal

ions [Cu<sup>2+</sup>(81%), Zn<sup>2+</sup>(87%), Hg<sup>2+</sup>(97%), and Cd<sup>2+</sup>(96%)] the extraction percentage for other metal ions was negligible. It is observed that under similar experimental conditions the removal percentage for these individual metal ions is found to be within 98-99%. As an additional proof, energydispersive X-ray spectroscopy (EDXs) were used to track the adsorption process for the analytes. The materials obtained from competitive adsorption experiments were analyzed by EDX. Figure 13B shows the presence of signals for Cu, Zn, Hg, and Cd elements along with C, O, Si, N, and Cl elements in the above material indicates adsorption of above metal chlorides. Similarly, Figure 13A shows that the presence of signals for S and Na along with C, O, Si, and N elements in material obtained after competitive anion adsorption experiments indicates adsorption of the whole NaHSO3. This also shows that as such this material does not adsorb sodium ion but to maintain the charge neutrality sodium ion is present.

## 2.4. Possible Binding Mechanism of SiO $_2$ @AZOL Material toward Analytes

Though it is hard to provide any direct evidence for the binding mode of bisulfite and other toxic metal ions on the material



Figure 12. A) Equilibrium adsorption capacity of SiO<sub>2</sub>@AZOL material toward bisulfite. B) Equilibrium adsorption capacity of SiO<sub>2</sub>@AZOL material toward toxic metal ions (Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, and Cd<sup>2+</sup>).



| Analytes          | Experimental<br><i>q</i> e | Langmuir linear isotherm               |                                  |                | Freundlich linear isotherm |        |                |
|-------------------|----------------------------|--|----------------------------------|----------------|----------------------------|--------|----------------|
|                   |                            | Q <sub>max</sub> [mg g <sup>-1</sup> ] | $K_{\rm L}$ [L g <sup>-1</sup> ] | R <sup>2</sup> | K <sub>F</sub>             | n      | R <sup>2</sup> |
| Hg <sup>2+</sup>  | 630                        | 775                                    | 0.0423                           | 0.9918         | 55.5827                    | 1.7408 | 0.9771         |
| Cd <sup>2+</sup>  | 633                        | 714                                    | 0.06845                          | 0.9990         | 235.1689                   | 4.6895 | 0.9292         |
| Cu <sup>2+</sup>  | 260                        | 269                                    | 0.1829                           | 0.9989         | 125.8577                   | 6.4053 | 0.9840         |
| Zn <sup>2+</sup>  | 412                        | 526                                    | 0.0334                           | 0.9523         | 31.0670                    | 1.7519 | 0.9525         |
| HSO3 <sup>-</sup> | 873                        | 1136                                   | 0.0051                           | 0.9893         | 29.2819                    | 1.8660 | 0.8939         |

Table 3. Langmuir and Freundlich adsorption parameter for analytes at 25 °C.

surface, an indirect approach was made by mass spectral analysis of complexation product of ligand with different analytes. For this individually all the analytes were taken acetonitrile and reacted with the chloroform solution of ligand AZOL which gives precipitates immediately after the reactions but soluble in DMF which is used for mass spectral analysis. For the ligand-bisulfite adduct [AZOL-HSO3]<sup>-</sup> peak around 988.3730 (calc. mass: 988.3735) was observed for [C<sub>51</sub>H<sub>58</sub>N<sub>7</sub>O<sub>10</sub>SiS]<sup>-</sup> species in highresolution mass spectrometry (HRMS) spectrum (Figure 14A) suggesting 1:1 binding mode. In order to support the above results and to determine the number of binding sites of SiO<sub>2</sub>@ AZOL material toward HSO3<sup>-</sup> anion, the Scatchard equation<sup>[47b]</sup> was used as  $\text{Log} \{(F_0 - F)/F\} = \text{Log} K_b + n \text{Log} [Q]$ , where  $F_0$  and F are the values of fluorescence intensity of aqueous suspended SiO<sub>2</sub>@AZOL material before and after addition of HSO<sub>3</sub><sup>-</sup> anion (Q) (value taken from SiO2@AZOL verses HSO3<sup>-</sup> titration, Figure 8D).  $K_{\rm b}$  is the observed binding constant to a site and "n" is the number of the binding site of SiO<sub>2</sub>@AZOL material for HSO<sub>3</sub><sup>-</sup> anion. The plot of Log  $\{(F_0 - F)/F\}$  verses Log [Q] in Figure 14B is linear with the slope equal to the value of "n"



**Figure 13.** A) EDX spectrum showing bisulfite adsorption. B) EDX spectrum showing adsorption of metal chlorides (Cu, Zn, Hg, and Cd).

and Log  $K_b$  is fixed on the ordinate. From the above plot, the binding constant K<sub>b</sub> and binding site "n" were calculated to be  $1.419 \times 10^4 \ \mbox{m}^{-1}$  and 1.04 with good correlation coefficient value  $R^2 = 0.9965$ . This shows that one binding site for bisulfite offered by the ligand for a strong hydrogen bonding between two donor amide hydrogens and one acceptor tertiary nitrogen in a triangular pocket of AZOL ligand and one donor hydrogen of bisulfite (OHSO2-) anion. Similarly, the mass spectral analysis of ligand-metal chloride adducts shows the formation of metal complexes. For AZOL-CdCl<sub>2</sub> adduct, peaks at 1056 for  $[C_{51}H_{57}N_7O_7SiCdCl]^+$  and 1130 for  $[C_{51}H_{57}N_7O_7SiCdCl_2 + K]^+$ were observed (Figure S17, Supporting Information). For AZOL-ZnCl<sub>2</sub> adduct, peaks at 1006 for [C<sub>51</sub>H<sub>57</sub>N<sub>7</sub>O<sub>7</sub>SiZnCl]<sup>+</sup> and 1064 for [C<sub>51</sub>H<sub>57</sub>N<sub>7</sub>O<sub>7</sub>SiZnCl<sub>2</sub> + Na]<sup>+</sup> were observed (Figure S18, Supporting Information). For AZOL-CuCl<sub>2</sub> adduct peak at 1041 for  $[C_{51}H_{57}N_7O_7SiCuCl_2 + H]^+$  was observed (Figure S19, Supporting Information). For AZOL-HgCl<sub>2</sub> adduct peaks at 1202 for [C51H57N7O7SiHgCl2 + Na]+ and at 1348 for  $[C_{51}H_{57}N_7O_7SiHgCl_2.2DMF + Na]^+$  were observed (Figure S20, Supporting Information). So based on coordination chemistry of these analytes and mass spectral analysis AZOL-analyte adduct the binding modes are proposed in Figure 15.

#### 2.5. Striping and Recyclability Study

Reusability of material is one of the most important factors which drastically reduces the overall cost of adsorbent. A good adsorbent shows higher adsorption capacity as well as also shows better desorption property. To evaluate the recyclability nature of the SiO<sub>2</sub>@AZOL material qualitative UV-Vis absorption studies and zeta potential measurements were performed to examine the reversibility nature of adsorption and desorption processes. It has been observed that suspended SiO<sub>2</sub>@AZOL material exhibits two absorbance peaks at 372 and 262 nm. When dilute HCl solution (0.1 N) was added to the above suspended material, two new bands appear at 328 and 255 nm due to the protonation at nitrogen sites which vanishes upon addition of dilute NaOH solution (0.1 N) and the band position shifted back to the original SiO2@AZOL material due to the deprotonation (Figure 16A,B). This simple acid-base treated reversibility studies were also carried out for all analytes (HSO3<sup>-</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>) after adsorption process and similar observations made for these analytes suggesting reversibility nature of adsorption and desorption processes (Figure S21, Supporting Information). Recyclability







Figure 14. A) HRMS showing formation of [AZOL-HSO<sub>3</sub>]<sup>-</sup> adduct. B) Scatchard plot showing one binding site for bisulfite.

of SiO2@AZOL material through acid-base treatment was also carried out by measuring the zeta potential of isolated material after treatments which shows similar zeta potential values for SiO2@AZOL materials before and after regeneration (-40.7 and -42.8 mV) due to presence of electronegative donor atoms, whereas for acid treated material (SiO2@AZOL-H<sup>+</sup>) a more positive value of +13.8 mV was observed due to protonation of material (Figure 16C). We also investigated the adsorption/desorption behavior of SiO2@AZOL material toward Cd<sup>2+</sup> as one of the representative case by acid-base treatments for four cycles by measuring the equilibrium adsorption capacity. After every treatment, SiO2@AZOL material was washed with deionized water and repeated thrice to decrease the experimental error. It was observed from the Figure 16D as one of the representative cases with Cd<sup>2+</sup>; the adsorption capacity falls by 1.27% after 1st cycle, whereas after the 2nd cycle, it falls by 2.54%, after that adsorption capacity of the following cycle remains constant. Initial fall

in adsorption capacity may be due to the little destruction of the binding site of functional  $SiO_2@AZOL$  material but latter constant adsorption capacity shows that the resulting  $SiO_2@$ AZOL material is stable enough to resist consecutive acidic stripping steps (Figure S22, Supporting Information). Similar cycles of reusability of materials with all analytes were also performed as shown in Figure S23, Supporting Information.

#### 2.6. Bisulfite Analysis of Real Samples

To demonstrate the application of these probe materials in real samples, the levels of bisulfite in sugar samples were examined. For this purpose, two samples of granulated and crystal sugars were obtained from local super markets for investigation. The sample solutions were prepared by dissolving 5 g of sugar in phosphate buffer (pH 7) under similar conditions and diluted to 10 mL. These sugar sample



Figure 15. Possible binding modes of analytes by the material.

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**Figure 16.** A) Reversible absorption studies of SiO<sub>2</sub>@AZOL material with acid-base treatments. B) Reversible absorption studies with one of the representative cases (Cd<sup>2+</sup>) for adsorption, striping, and regeneration. C) Reversible zeta potential with acid-base treatment. D) Adsorption capacity of SiO<sub>2</sub>@AZOL material toward Cd<sup>2+</sup> up to four cycles.

solutions were treated with 3 mg SiO<sub>2</sub>@AZOL material and after equilibrating, the mixture for 30 s in a vibrating mixture the emission intensity at 510 nm upon excitation at 390 nm was recorded. Aliquots of both the sugar samples were also spiked with  $HSO_3^-$  (8, 16, and 24 µm) that had been accurately prepared and emission intensities were recorded. The concentrations of bisulfite were estimated from the calibration curve which was obtained from fluorescence titration of bisulfite with the material (3 mg of material in 10 mL of phosphate buffer; pH 7). The results in **Table 4** and Figure S24 (Supporting Information) show that the recoveries are good enough for practical use. Through this method, the  $HSO_3^-$  levels in granulated and crystal sugar samples were calculated to be 5.82 and 3.95 µmol L<sup>-1</sup>.<sup>[49]</sup>

## 3. Conclusion

In summary, we synthesized a silica supported functional material for dual functions of sensing and removal of bisulfite and various toxic metal ions from aqueous system. The solid support cubic mesoporous silica with high surface area was synthesized by a modified Stober process using cetyl pyridinium bromide hydrate as structure directing template. Then functionalization with 3-APTES followed by grafting with a fluorescent chromophore 2-bromo-N-(4-phenylazo-phenyl)acetamide has given a new fluorogenic silica probe material SiO<sub>2</sub>@AZOL, which is well characterized. N<sub>2</sub> sorption studies show a gradual decrease of surface area, pore volume, and

Table 4. Results for detection of bisulfite in sugar samples.

| Sample           | $HSO_3^-$ level [ $\mu$ mol L <sup>-1</sup> ] | Added<br>[µmol L <sup>-1</sup> ] | Found<br>[µmol L <sup>-1</sup> ] | Recovery<br>[%] |
|------------------|---|----------------------------------|----------------------------------|-----------------|
| Granulated sugar | 5.89  | 8                                | 13.80                            | 99.3            |
|                  |   | 16                               | 21.98                            | 100.4           |
|                  |   | 24                               | 29.70                            | 99.6            |
| Crystal sugar    | 4.42  | 8                                | 12.30                            | 99.0            |
|                  |   | 16                               | 19.92                            | 97.5            |
|                  |   | 24                               | 27.64                            | 97.2            |



FUNCTIONAL MATERIALS

pore diameter from SiO<sub>2</sub> to SiO<sub>2</sub>@AZOL materials suggesting that functionalization of ligand is mostly located inside the mesopores. This material represents a non-chemodosimetric fluorescence probe material for bisulfite anion among various anions based on strong hydrogen bonding affinity proved by both absorption and fluorescence studies and supported by adsorption studies. Apart from that this material also shows coordination driven selectivity toward several toxic metal ions  $(Hg^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+})$  with very high adsorption capacity. The binding modes of material toward above analytes were anticipated based on EDX analysis and mass spectral analysis of ligand-analyte adducts. Reversibility of material upon acidbase treatments is supported by absorption studies and surface zeta potential measurements show recyclability nature of the material. This material represents the first example of material based recyclable sensory cum adsorbent material for bisulfite. This material can be used as a fluorescence probe to determine the HSO<sub>3</sub><sup>-</sup> levels in real samples.

## 4. Experimental Section

*Materials*: All chemicals and reagents used here were of analytical standards. In all experiments, deionized water was used. Solvents were further dried in the laboratory before use. Tetraethyl orthosilicate (TEOS), APTES, CPB, 4-aminoazobenzene, citric acid, salicylaldehyde, sodium borohydride (NaBH<sub>4</sub>), bromoacetyl chloride were purchased from TCI chemical Private Ltd. The chemicals which were used for preparation of various buffer solutions like disodium hydrogen phosphate/citric acid used for pH 2–5, potassium dihydrogen phosphate/dipotassium hydrogen phosphate buffer used for pH 5–7, potassium dihydrogen phosphate/sodium hydroxide buffer used for pH 8–10 were purchased from Merck group private Ltd. All metal chlorides and Salts of different anions were purchased from Spectrochem private Ltd. and HPLC private Ltd. INDIA. Anhydrous potassium carbonate, dry toluene, dry methanol, dry acetonitrile, sodium hydroxide pellets, hydrochloric acid (37%), dry triethyl amine were purchased from s.d fine chemical private Ltd.

Instrumentation: <sup>29</sup>Si and <sup>13</sup>C solid CP NMR spectra were recorded on a Bruker Advance 500 MHz NMR. UV-Vis spectra of suspension were measured on Shimadzu UV 3101PC spectrophotometer. All emission spectra of suspensions were recorded on Edinburgh Instruments model Xe-900 and reported after applying emission correction. FT-IR spectra (4000–400 cm<sup>-1</sup>) were recorded on a Perkin-Elmer GX spectrophotometer (U.S.A.) using KBR disks. All mass-spectrometric analysis was collected on a Q-TOF Micro TM liquid chromatography-mass spectrometry (LC-MS) instrument. To determine metal ion concentrations in an aqueous system, ICP-OES analyses were performed on Perkin Elmer instrument (Optima 2000DV) and repeated thrice. The zeta potentials were recorded using a Malvern instrument (Zetasizer, Nano series, Nano-ZS90) and dynamic light scattering measurements were performed at 298.15 K on Spectro SizeTM 300 (NaBiTec, Germany) light scattering apparatus with a He-Ne laser at a wavelength of 660-670 nm, and power 4 mW at an angle of 90°. Thermogravimetric analysis (TGA) was determined by using a Mettler-Toledo (TGA/SDTA 851e) in the air at a heating rate 10° C min<sup>-1</sup>. Elemental analyses (C, H, and N) and powder X-ray diffraction (PXRD) measurements were performed on a model 2400 Perkin-Elmer elemental analyzer and a Miniflex-II (FD 41521) powder diffractometer (Rigaku, Japan), respectively. A SEM (Leo series 1430 VP) equipped with INCA was used to determine the morphologies of samples. TEM was performed using a JEOL JEM 2100 microscope.

Synthesis of Ordered Cubic Shape Mesoporous Silica  $(SiO_2)$ : The cubic-shaped mesoporous silica was prepared by a modified Stöber process.<sup>[23,50]</sup> In a typical synthetic procedure (Scheme 1A), 4 g of CPB was dissolved in 800 mL of deionized water under 30 min constant stirring. Then 35 mL of ammonia solution (28 wt %) was added

slowly for 30 min to the above mixture. After forming a clear solution, a homogeneous mixture of *n*-hexane (100 mL) and TEOS (20 mL) was added dropwise for 45 min under continuous stirring. The above mixture was stirred further at 45 °C for 12 h, after which the product was collected by filtration. The solid white precipitate was washed with deionized water and methanol 2–3 times. To remove the CPB template, the above product was dispersed in a mixture of 100 mL methanol 35 mL HCl (1 M) and refluxed for 8 h at 70° C. This solvent extraction process was repeated thrice and sample was collected by filtration, residue was washed with methanol 3–4 times, and dried under hot air at 70° C for 24 h.

Preparation of 3-APTES Functionalized Silica (SiO<sub>2</sub>@  $NH_2$ ): Functionalization of cubic mesoporous silica with 3-aminopropyltriethoxysilane was done by refluxing 2 g of SiO<sub>2</sub> with 5 mL of APTES (21.36 mmol) in 150 mL of dry toluene in an inert atmosphere for 24 h following a literature procedure.<sup>[45a]</sup> After cooling to room temperature, the solid product was filtered, washed thoroughly with toluene, ethanol, and finally with hot chloroform three times to remove excess unreacted APTES and dried at 70 °C overnight in air.

Synthesis of 2-Bromo-N-(4-phenylazo-phenyl)-acetamide (BPPA): This compound was synthesized from 4-amino azobenzene and bromoacetyl chloride (Scheme 1B) in the presence of triethylamine according to a literature procedure and confirmed from HRMS analysis (Figure S25, Supporting Information).<sup>[51]</sup>

In Situ Step by Step Synthesis of  $SiO_2@AZOL$  (Scheme 1D; Direct Method): The above synthesized APTES-functionalized silica (SiO2@ NH<sub>2</sub>) (3.5 g) was refluxed with salicylaldehyde (2.3 g, 18.83 mmol) within dry methanol (100 mL) for 12 h at 70° C. After cooling to room temperature the solid supported Schiff base product was filtered, and washed with methanol and chloroform. The above yellow solid was taken in dry methanol (50 mL) and treated with excess sodium borohydride (4.80 g, 34.78 mmol,) for 12 h at  $45^{\circ}$  C under argon atmosphere. Then the above material was filtered, washed with water, methanol, and chloroform, and dried under vacuum. This material was again reacted with salicylaldehyde (2.3 g, 18.83 mmol) in dry methanol (100 mL) in the presence of 1-2 mL glacial acetic acid (used as catalyst) for 6 h, at room temperature after which excess of sodium borohydride (4.80 g, 34.78 mmol) was added into this mixture and refluxed for 24 h, at 50° C temperature. Then the above material was filtered off washed with methanol, chloroform, and finally with water and dried under vacuum. In the final step, the above solid material (2 g) was refluxed with BPPA (1 g, 3.15 mmol) in the presence of  $K_2 \text{CO}_3$  for 96 h in dry acetonitrile in an inert atmosphere. Final product SiO2@AZOL was filtered off and washed with chloroform, methanol, and water and dried at 70° C overnight in air. During synthesis, various colors from white to yellow and finally brown color for the material was observed (Figure S26, Supporting Information). This final material SiO<sub>2</sub>@AZOL was characterized through solid <sup>13</sup>C NMR, FT-IR, TGA, PXRD, SEM, TEM, and BET surface area measurements.

Synthesis of Ligand AZOL (Scheme 1C): To a 500 mL round bottom flask, APTES (3.96 g; 17.8 mmol) and salicylaldehyde (2.3 g; 18.8 mmol) were taken in 100 mL of dry methanol and stirred for 3 h at room temperature. To the above solution, NaBH<sub>4</sub> (4.80 g; 34.78 mmol) was added under argon and stirred for 30 min till yellow color solution turned colorless. Then methanol was removed by rotary evaporator and the crude product was extracted in the chloroform-water mixture and finally, chloroform extract was collected and dried under vacuum. This crude product was taken in dry methanol and again another equivalent of salicylaldehyde (2.3 g; 18.8 mmol) was added and stirred for 3 h followed by addition of NaBH<sub>4</sub> (4.80 g; 34.78 mmol) and stirred until colorless. The work-up procedure is similar to above step where the chloroform extract was evaporated to give the desired product 2,2'-(((3-(triethoxysilyl)propyl)azanediyl)bis(methylene))diphenol (TEPABMD) (5.86 g; Yield: 76%) confirmed from HRMS (Figure S27, Supporting Information). Then the above product (1 g; 2.3 mmol), 2-bromo-N-(4-phenylazo-phenyl)-acetamide (2.18 g, 6.92 mmol) and K<sub>2</sub>CO<sub>3</sub>(0.96 g, 6.94 mmol) were taken in 100 mL of dry acetonitrile and refluxed for 5 d under argon atmosphere. The progress of the reaction



was monitored with time with LCMS spectra and thin layer chromatography (TLC) spotting which confirms completion of reaction and formation of double substitution product AZOL. After completion of the reaction, the solvent was removed under rotary evaporator, extracted with the chloroform-water mixture, and finally the chloroform extract was dried under vacuum to get the crude ligand AZOL. This crude compound was washed with methanol and recrystallized from the chloroform-hexane mixture to get the brown colored AZOL ligand characterized from HRMS (Figure S28, Supporting Information), which was used as such without any purification for preparation of SiO<sub>2</sub>@AZOL.

Synthesis of SiO<sub>2</sub>@AZOL from AZOL Ligand (Scheme 1E; Indirect Method): In the indirect method, the above synthesized crude ligand AZOL (1.5 g, 1.65 mmol) and the cubic silica (3 g) were taken in 50 mL of dry toluene and refluxed for overnight (12 h) under argon atmosphere. The resulting SiO<sub>2</sub>@AZOL material was filtered off and washed with chloroform thrice to remove unreacted AZOL ligand and then washed with deionized water twice and dried under vacuum for 24 h.

UV–Visible and Fluorescence Studies: For UV–Visible and fluorescence studies, 2 mL suspended SiO<sub>2</sub>@AZOL material (0.5 mg per 2 mL, suspended in aqueous medium) was mixed with various analytes aqueous buffer solution individually and shaken well in a vortex shaker for 1 min. This shaking process was repeated after every spectrophotometric/fluorescence reading. The UV–Vis spectra were recorded in the range between 200 and 800 nm, whereas fluorescence spectra was recorded in the range of 425–675 nm with excitation wavelength 390 nm. For LOD calculations, 0–70  $\times$  10<sup>-6</sup> M solution of analytes were gradually added to the SiO<sub>2</sub>@AZOL suspension (0.5 mg per 2 mL) and fluorescent intensity was recorded. By plotting fluorescence intensity with increasing concentration of analytes, slope (S) of the graph was found. Standard deviation (SD) was calculated from three blank measurements. The detection limit was calculated according to the formula: LOD = (3SD/S).

Adsorption Experiments: Batch adsorption experiments were carried out in an aqueous system to determine several adsorption parameters like equilibrium adsorption time  $(Q_t)$ , equilibrium adsorption capacity  $(Q_e)$ , Langmuir and Freundlich adsorption isotherms. In a typical adsorption experiment 5 mg of adsorbent (SiO<sub>2</sub>@AZOL) was treated with 50 mL of various concentrations of analytes (Hg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>,  $Cd^{2+}$ , and  $HSO_3^{-}$  ions) at room temperature (25 ± 2°C). The initial concentrations of analytes varied from 20 to 200 ppm and the pH of the solution was maintained around 7 (neutral pH) with a buffer solution except for bisulfites. After equilibrating the mixture for 3 h in a vibrating mixture, the mixture was filtered through a polypropylene syringe filter with a pore size of 0.45  $\mu$ m. The concentrations of analytes in the filtrate were analyzed by ICP-OES analysis to get the equilibrium concentration  $(C_e)$ . To quantify HSO<sub>3</sub><sup>-</sup> anion, the equivalent concentration of Na<sup>+</sup> was considered which was measured by ICP-OES analysis as the adsorption of bisulfite anion accompanied by simultaneous adsorption of Na<sup>+</sup> to maintain charge neutrality. The amounts of analytes adsorbed by SiO<sub>2</sub>@ AZOL material were then determined as the difference between the initial and equilibrium concentrations of analytes in the solutions and the adsorption capacity ( $Q_e$ , mg g<sup>-1</sup>) of the analytes adsorbed onto SiO<sub>2</sub>@AZOL was obtained from the equation  $Q_e = (C_1 - C_e)V/W_{ads}$ . In this formula,  $Q_e$  is the equilibrium adsorption capacity (mg g<sup>-1</sup>),  $C_1$  and  $C_{e}$  are the initial and equilibrium concentrations of analytes (mg L<sup>-1</sup>), respectively, V is the volume of analyte solution (L), and  $W_{ads}$  is the weight of adsorbent (g). All the adsorption experiments were repeated thrice to remove the experimental error. To evaluate the effect of treatment times on the adsorption process, 5 mg of SiO<sub>2</sub>@AZOL material was mixed with 50 mL of 200 mg  $L^{-1}$  of analyte solution. The solutions were filtered immediately when the reaction times were reached to 30, 60, 120, 180, and 240 min, respectively. The analyte concentrations in the filtrate were analyzed for equilibrium adsorption time calculations.

Striping/Reusability Studies: The striping of adsorbed analytes and regeneration of  $SiO_2@AZOL$  material for reusability was done by simple acid-base treatments. Initially, adsorption of various concentrations of analytes (20 to 200 ppm) took place in plastic centrifuge tubes (10 nos.) as described above for 3 h at pH 7. Then the mixture in each tube was

filtered separately through polypropylene syringe filter and the filtrate was analyzed by ICP-OES analysis to determine the amounts of analytes that were adsorbed onto the sorbent. Then the adsorbents were washed thoroughly with water to remove noncomplexed metal ions. Then the adsorbents were treated with 0.1 N HCl (5 mL aq.) under vigorous shaking conditions for 5 min and again filtered and the filtrate was analyzed to determine the stripped ions. Then again the adsorbents were treated with 0.1 N NaOH (5–6 mL aq.) under vigorous shaking and then filtered, washed, and dried for reuse. Each centrifuge tube content materials undergo similar adsorption, desorption, and regeneration for four cycles. Adsorption capacity from each cycle was calculated separately from the plot of adsorption isotherms.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

bisulfite detection, cubic mesoporous silica, fluorescence probes, nonchemodosimetric probes, toxic metal ions

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