Template-free synthesis of hybrid silica nanoparticle with functionalized mesostructure for efficient methylene blue removal

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HIGHLIGHTS

• Template free route for hybrid silica nanoparticles with ~500 m².g⁻¹ surface area.
• Cocondensation of a nonsilane precursor to achieve phosphonic acid functionality.
• Silica nanoparticles displayed high Methylene blue adsorption (380 mg. g⁻¹).
• This method broaden the precursor selection for mesoporous silica synthesis.

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ABSTRACT

A simple one-pot synthesis process for functionalized mesostructured silica nanoparticles (MSNP) is reported. The novel process demonstrated the possibility to achieve MSNP with a surface area up to 501 m².g⁻¹ using a phosphonate based nonsilane precursor such as N, N’-bis[4,6-bis(diethylphosphono)-1,3,5-triazin-yl]-1,2-diaminoethane (ED). MSNP obtained by using 20 mol% of ED achieved a surface area of 80 m².g⁻¹ and increasing the ED content to 30 mol% resulted in a surface area of 501 m².g⁻¹. Zeta potential of novel MSNPs (−65.5 and 70.0 mV) were much higher than the nanoparticles (NP) prepared from only TEOS (−49 mV), indicating the presence of a large number of −SiOH and phosphonic acid surface functional groups, as confirmed by Fourier-transform infrared spectroscopy (FT-IR) and Nuclear magnetic resonance (NMR) analysis. The functionalized MSNPs were used as an adsorbent for the removal of cationic pollutants like methylene blue (MB). The MSNP with the highest porosity displayed favorable MB adsorption behavior with ~380 mg.g⁻¹ of MB adsorption capacity. Facile regeneration in an acidic medium (~pH 4.5) with easy recyclability (10 cycles) confirmed the practical applicability of this novel functionalized MSNPs.

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1. Introduction

Degradation-resistant dyes present in industrial effluents accumulate in water bodies and have the potential to cause irreversible damage to aquatic ecosystems and also pose a serious threat to human health. For example, high doses of accumulated methylene blue (MB) in water can cause anemia, breathing difficulties, and nausea [1]. Removing these pollutants from water by adsorption is a viable and safer option of pollution control, unlike oxidation or degradation methods, where degradation product of these dyes can lead to secondary pollution. Thus, several adsorbents have been designed for efficient removal of the MB and similar cationic pollutants [2–9]. The use of functionalized hydrogels [3,4], carbon-based adsorbents [5], and mesoporous silica nanoparticles (MSNs) [6,7,10] are extensively investigated because of their high adsorption capacity. Recently adsorbents designed from agricultural wastes have gained interest due to their low cost, although their low adsorption capacity makes them unattractive for commercial exploitation [11,12]. Among adsorbents, MSNs have attracted a lot of attention, owing to their docile nature, high stability, and potential applications in the field of drug delivery [13,14], bio-molecule delivery [15,16], bioimaging [15], and many more areas [17–20].

Even though MSNs are promising candidates in many fields, their preparation is mainly template-directed methods of silane precursors followed by template removal to achieve porosity [21–23]. Ideally, detemplating should ensure unblocked pores with a large number of silanol (–SiOH) groups. Calcination is considered an effective method of detemplatation to achieve the final porosity. However, high temperature (500–600 °C) during calcination leads to the destruction of –SiOH groups due to thermal condensation and resulting in an inert mesoporous surface [24]. Besides, calcination can result in structural shrinkage, agglomeration, and loss in porosity. To avoid agglomeration and maintain the surface –SiOH groups, detemplation via dissolution using an organic solvent [25] or supercritical fluid [26] is followed. The use of relatively lower temperature in the dissolution method makes it more suitable for synthesis of co-condensed MSNs with organic functionalities. However, complete removal of templates by dissolution is quite challenging and can take several days [27].

Only a few templateless synthesis methods are reported in the literature for preparation of MSNs. In one such method, nano aggregate of poly(N-isopropylacrylamide) (PNIPAm) above its LCST temperature was used as a template for condensation of TEOS [28]. Later, lowering the temperature below LCST made PNIPAm water-soluble and was easily removed from the silica nanoparticles to achieve porosity. MSN obtained by this method displayed low porosity (245 m².g⁻¹) and the method was found to be unsuccessful in presence of thermoresponsive polymers like poly(vinyl methyl ether). On the other hand, reported template-free methods produced aggregated mesoporous silica with high porosity (537 mg.g⁻¹) [29]. Though both these methods are template free, low porosity [28] and morphology (aggregated) of the material produced [29] ultimately limit their application.

To address aforementioned challenges, this work reports a single-step template free route for preparation of functionalized mesostructured silica nanoparticles (MSNPs) via co-condensation of tetraethyl orthosilicate (TEOS) and a non-silane precursor like N,N´-bis[4,6-bis(diethylphosphono)-1,3,5-triazin-yl]-1,2-diaminoethane (ED, Fig. 1b) [30]. Phosphonate groups in ED prevent a sudden change in pH of the reaction medium. Upon hydrolysis of phosphonate groups under strong alkaline conditions generates multiple phosphonic acid groups (Fig. S3c) which increases the possibility of ED-TEOS co-condensation to form Si-O-P hybrid networks and eventually MSNPs. Formation of MSNPs was confirmed by Electron microscopy, nitrogen adsorption, and Small-angle X-ray scattering (SAXS) analysis. The inclusion of ED in Si-O-Si network and generation of functional mesostructured surface with silanol (–SiOH) and phosphonic acid functionalities was confirmed by nuclear magnetic resonance (NMR) and fourier-transform infrared spectroscopy (FT-IR). Then, decontamination of water by removing cationic pollutants like methylene blue was demonstrated using MSNP as an adsorbent. Apart from pollution control, phosphonic acid functionalized MSNs are used as proton exchange membranes [31,32], active bio-molecule carrier systems [33]. Additionally, materials containing silica and phosphorous hybrid are kown for their improved flame retardancy [34–36].

2. Materials and methods

2.1. Materials

TEOS (99%), NaOH, ethanol (99.8%), diethyl ether (99%), MB, Congo Red (CR), and Brilliant Blue were purchased from Sigma-Aldrich and used as received. N,N´-Bis[4,6-bis(diethylphosphono)-1,3,5-triazin-yl]-1,2-diaminoethane (ED) was synthesized following the procedure given in supplementary information (SI, Fig. S1) [30]. Preliminary in vitro cytotoxicity assessment indicates that ED does not pose a risk for human cells (see Sec. S1.3 for detail).

![Fig. 1. Schematic representation showing (a) condensation of TEOS and (b) co-condensation of TEOS-hydrolyzed ED and creating structural defects in Si-O-Si network with phosphonic acid functionality. (c) Procedure for silica nanoparticle synthesis using different loading of ED.](image-url)
2.2. Synthesis of silica NPs

Silica NPs were synthesized following a modified reported protocol [37,38] using TEOS and ED as precursors (Fig. 1c, Table 1). Typically, a freshly prepared solution of ED and TEOS in 6 mL of ethanol was added dropwise for 1 min to an H2O-ethanol mixture (54 mL, 1.25:1) with the required quantity of NaOH (at 25 °C and 800 rpm). After 2 h of reaction time, 40 mL of diethyl ether was added to the mixture under stirring and centrifuged for 10 min at 7000 rpm to isolate NPs. 15 mL of ethanol-H2O mixture was added to the collected particles and samples were sonicated for 15 min and stirred for 30 more minutes. Then, MSNPs were recovered by centrifugation and washing in ethanol-H2O mixture was repeated four times to ensure removal of unreacted precursors. Finally, collected NPs were dried under vacuum at 75 °C for 48 h.

2.2. Characterization

**NMR** spectra of ED and hydrolyzed ED were recorded on a Bruker Advance III 400 NMR spectrometer (Sec. S12). For Solid-state CP-MAS NMR analysis, a 4 mm CP-MAS probe with 4 mm zirconia rotor was used. CP-MAS NMR spectra were recorded at 162.0 MHz using a 4 mm CP-MAS probe with 4 mm zirconia rotor. The geometries were optimized at the B3LYP level using a 6–31 + G* basis set in gas phase. Chemical shifts were calculated by GIAO method and values are reported relative to H3PO4 (0.00 ppm).

**FT-IR** spectra were recorded in a Bruker FT-IR (TENSOR 27, Switzerland), under transmission mode using MSN-KBr pallets and analyzing by OPUS™ 7.2 software.

**Scanning electron microscopic (SEM)** images were recorded on a Hitachi S-4800 SEM operating at 20 kV. Before SEM analysis, NP dispersion in ethanol was casted on a silicon wafer and dried for 4 h under the atmospheric condition, and coated with 7 nm Au/Pd coating.

**TEM** analysis was carried out in TEM, JEOL JEM2200FS microscope operating at 200 kV. For TEM analysis, the sample was prepared by putting a drop of NP dispersion (0.5 mg in 1 mL ethanol) on a Lacey carbon TEM grid and dried overnight under atmospheric conditions.

**ζ-potentials** of NPs dispersed in water (pH 7, sonicated 2 min) was measured at 25 °C by a Malvern Zetasizer ZS equipment using DTS 1070 folded capillary cells.

**N2 adsorption and desorption isotherms** were recorded at 77 K on a Tristar 3020 (Micromeritics, US) with 15 s equilibration time. The specific surface areas (SBET, uncertainty ~20 m²/g) were obtained using the Brunauer–Emmett–Teller (BET) method [39], and the pore volume (Vp) and average pore size (Dh) were calculated using Barrett–Joyner–Halenda (BJH) model [40].

**Small-angle X-ray scattering (SAXS)** analyses were performed on a NanoStar (Bruker AXS GmbH) with a 2D Xe-based gaseous avalanche detector (VANTEC-2000). A micro-focused Cu-Kα Nancor beam stops was used for background subtraction. Quartz capillaries (Ø 1.5 mm, −10 μm wall, Hilgenberg GmbH, Germany) with NPs were placed in the sample chamber under ~10−2 mbar vacuum to reduce the scattering due to air, and Silver benenate was used for calibration. 1D radial profiles were extracted from DIFRACEVA software (Bruker AXS, Germany). The scattering patterns were simulated using a model with the Porod function and the Guinier approximation. The former simulates the scattering from large polydispers NPs (≥100 nm) while the latter takes into account the scattering from small particles (herein the pores). The total scattering function is given in Eq. (1), where, a, R, and b are the Porod slope, radius of gyration of the pores, and a background correction constant respectively.

\[
I(q) = \frac{1}{q^a} + \exp \left( -\frac{q^2 R^2}{3} \right) + b
\]

**Elemental analysis** of the nanoparticles was done using the inductively coupled plasma optical emission spectrometry (ICP-OES), on a 7110 ICP-OES apparatus (Agilent Switzerland AG, Basel). Prior to analysis, ~15 mg of NPs were dissolved in 3 mL HNO3 using a microwave.

**MB adsorption** was carried out by putting 30 mg of MSNPs in 3 mL MB solutions (200 rpm, 25 °C, pH 7) and stirring for desired time. Then, MSNPs were isolated by centrifugation (7500 rpm, 1 min) and UV–vis intensity of residual MB (at 665 nm) was recorded by a Cary 50 Bio UV–vis spectrophotometer after required dilution. Concentration of MB was determined by using the MB calibration curve (Fig. S12) and adsorption characteristics were studied by Langmuir [41] and Freundlich isotherms [42]. For MB release study, MB containing NPs (5 mg) were dispersed in 25 mL of water (200 rpm, at 25 °C) and MB release was monitored using a UV–vis spectrophotometer.

3. Result and discussion

Solid silica NPs synthesized from TEOS (1.12 g, 90 mmol/L) and NaOH (42 mg, 18.0 mmol/L) achieved a uniform size of 401 ± 21 nm (SiO2, Fig. 2a) [37,38]. On the contrary, no NPs were formed at the same NaOH concentration in presence of ED (20.0 mol%). It can be attributed to the rapid decrease in pH of the medium (Fig. S10) due to the formation of phosphonic acid groups after hydrolysis of ED. Following which, a higher concentration of NaOH was used (Table 1) and the yield of NPs (SiO2) increased (Table S1). At 72 mg of NaOH in 60 mL of the mixture, SiO2 NPs with rough surfaces were formed (Fig. 2b, S5b). Further increasing the NaOH concentration resulted in an extensive cluster formation with a decrease in the surface roughness (Fig. S5c).

With the increase in the ED loading to 30 mol%, a higher NaOH concentration was required for synthesis of NP. 105 mg of NaOH in 60 mL of ethanol-H2O mixture achieved cluster free NPs with rough surface (SiO2, Fig. 2c and Fig. S6a, b). Increasing the NaOH concentration further, clusters with decreased surface roughness were obtained. Additionally, on increasing the ED loading to 40 mol% (SiO2), very small NPs (Fig. S7a) and two different particle population (Fig. S7b) with a very low yield were obtained (Table S1). An attempt to improve the yield by increasing NaOH concentration (125 mg, Table 1) led to cluster formation (Fig. S7). It is clear from these observations that at higher NaOH concentration, TEOS condensation is faster than ED-TEOS codensation. This leads to clusters formation with a smoother surface resembling SiO2. Small particle size of SiO2 can be challenge for recovery and reuse. Additionally, uncontrolled particle growth and low yield of SiO2 can limit its applications. Therefore, SiO2 was not considered for further study.

| Entry | TEOS (g) | ED (g) | ED/TEOS molar ratio | NaOH (mg) | Sample name |
|-------|----------|--------|---------------------|-----------|-------------|
| 1     | 1.12     | 0      | 0                   | 42        | 0SiO2       |
| 2     | 1.12     | 0.82   | 0.2                 | 42, 60, 72, 78 | 1SiO2      |
| 3     | 1.12     | 1.23   | 0.3                 | 90, 105, 110 | 2SiO2      |
| 4     | 1.12     | 1.64   | 0.4                 | 110, 117, 125 | 3SiO2      |
3.1. Physical characterization of nanoparticles

Although the condition mentioned in entry 2 (72 mg NaOH) and entry 3 (105 mg NaOH) of Table 1 achieved the highest quantity of cluster free silica NPs, the overall yield remains lower than $\text{SiO}_2$ (Table S1). ~9% of $\text{SiO}_2$ NPs have a hole in the center (Fig. 2b) and no such particles were formed in the case of $\text{SiO}_2$ (Fig. 2c). The average size of NPs decreased with an increase in the concentration of ED (Fig. S6d). TEM analysis of $\text{SiO}_2$ revealed the presence of a darker core and lighter shell of few nanometers (Fig. 3a), indicating a denser core. On the other hand, the TEM image of $\text{SiO}_2$ was uniform without any sign of density change within NPs (Fig. 3b).

$\text{SiO}_2$ showed a type IV isotherm with H4 hysteresis, highlighting the presence of both meso- and micro-pores (pore width ~5.5 nm) with a surface area and BJH pore volume of 80 m$^2$.g$^{-1}$ and 0.13 cm$^3$.g$^{-1}$ respectively (Fig. 3d, S8a). In $\text{SiO}_2$, significant improvement in porosity and a type IV isotherm with H1 hysteresis was observed (Fig. 3e), indicating a homogeneous mesoporous structure (pore size ~7 nm, Fig. S8). $\text{SiO}_2$ also displayed a high surface area of 501 m$^2$.g$^{-1}$ and BJH volume of 0.74 cm$^3$.g$^{-1}$ (Table 2).

Unlike template-directed MSNs [43,44], no pore boundaries were observed during TEM analysis of $\text{SiO}_2$ despite high porosity (501 m$^2$.g$^{-1}$), indicating a random pore orientation. SEM analysis of ball-milled $\text{SiO}_2$ confirmed the presence of randomly interconnected pores formed due to aggregation of nano-domains of ~6 nm (Fig. S9) and similar observation can also be found in the literature [28]. In SEM image of ball-milled $\text{SiO}_2$, flaking-off of the porous layer from the top exposed a denser core (Fig. S9a), which is in agreement with the TEM analysis (Fig. 3a).

To confirm the role of ED on the porosity of MSNPs, SAXS experiments were carried out. The $\text{SiO}_2$ demonstrated a decay in the intensity over $q$-range of 0.09 nm$^{-1}$ and 0.5 nm$^{-1}$ (Fig. 4a). This decay is simulated using the only first part of the Eq. (1) ($1/q^4$) to deduce the Porod exponent. Porod decay rate of nearly ~4 indicates a smooth surface of $\text{SiO}_2$. The increase in surface roughness leads to high fluctuations in lateral electron density profiles and deviates from the decay.
rate of $-4$. For extremely rough surfaces, an exponent close to $-3$ can be obtained [45]. A decrease in Porod exponent for $1\text{SiO}_2$ and $2\text{SiO}_2$ (Fig. 4) is the signature for higher surface roughness and agrees with SEM observation (Fig. 2). The scattering from $1\text{SiO}_2$ and $2\text{SiO}_2$ displayed a broad hump at a high $q$ region (arrow in Fig. 4b, c), and its intensity increased with the increase in ED concentration. This hump also moved towards lower scattering angles for $2\text{SiO}_2$. These observations indicate the growth of pores size within MSNPs. Pore size determined using the Guinier approximation (Eq.(1), exp ($-q^2R^2/3$)) was found to be 2.2 and 11.3 nm for $1\text{SiO}_2$ and $2\text{SiO}_2$ respectively (Table 2). This implies that ED influences the surface morphology and porosity. Similar findings have also been reported for other morphogenic agents used in MSN preparation [46].

To confirm the incorporation of ED into NPs, P-content of $1\text{SiO}_2$ and $2\text{SiO}_2$ was determined by ICP-OES analysis. P-content in $1\text{SiO}_2$ (0.1%) and $2\text{SiO}_2$ (0.7%) are lower than the calculated value of ~13.0 and ~15.5% for $1\text{SiO}_2$ and $2\text{SiO}_2$ respectively. It can be attributed to the slow co-condensation of ED-TEOS compared to the condensation of only TEOS and partial hydrolysis of Si-O-P link [47]. Although there was a difference in P-content and porosity between $1\text{SiO}_2$ and $2\text{SiO}_2$, $\zeta$-potential of both MSNPs were similar ($-65.5$ and $-70.0$ mV, Fig. 5a) and higher than $0\text{SiO}_2$ ($-49$ mV), indicating the presence of similar functionality (–SiOH and –PO(OH)₂) on both the MSNPs.

### Table 2
Composition and properties of silica NPs synthesized.

| Sample | BET area (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | BET pore size (nm) | SAXS pore size (nm) | P-content (%) | $\zeta$-potential (mV) |
|--------|------------------|----------------------|-------------------|-------------------|--------------|---------------------|
| $0\text{SiO}_2$ | 22 | 0.05 | – | – | – | $-49.0$ |
| $1\text{SiO}_2$ | 81 | 0.13 | 5.5 | 2.5 | 0.12 | $-65.5$ |
| $2\text{SiO}_2$ | 501 | 0.75 | 6.5 | 11.5 | 0.70 | $-70.0$ |

* Phosphorous content (P-content) determined by ICP-OES analysis.

As mentioned earlier, P-content and porosity of $1\text{SiO}_2$ were low as compared to $2\text{SiO}_2$ (Table 2). Therefore, $1\text{SiO}_2$ was excluded from further detailed study. In the FT-IR spectra of both $0\text{SiO}_2$ and $2\text{SiO}_2$ (Fig. 5b), intense bands of Si-O-Si skeleton (1088 cm⁻¹) and Si-O-Si bending vibration (799 cm⁻¹) were observed [23,48]. The appearance of a shoulder around 1200 cm⁻¹ in the case of $2\text{SiO}_2$ can be attributed to P=O groups [49,50]. Moreover, the intensity of the peak for –SiOH symmetric stretching (961 cm⁻¹) was found to be higher in $2\text{SiO}_2$ [51]. The increased intensity of the band at 1635 cm⁻¹ can be attributed to the adsorption of H₂O by P=O functionality in $2\text{SiO}_2$ via H-bonding [23,48]. The broad shape of this band can arise due to overlapping of the band at 1635 cm⁻¹ arising from –NH of ED [52,53]. The combined effect of absorbed H₂O by P=O functionality and a higher number of –SiOH significantly increased the intensity of the band at 3000–3700 cm⁻¹ [48,54]. These FT-IR observations highlight the incorporation of ED in the Si-O-Si network.
29Si NMR spectra of both 0SiO2 and 2SiO2 showed the presence of Q4 and Q3 peak (Fig. 6a) [55,56]. However, the intensity of the Q3 peak was higher in the case of 2SiO2 along with a new peak of Q2 (Fig. 6a). Higher amount of Q2 and Q3 in 2SiO2 can be due to the disruption in Si-O-Si network during the inclusion of ED. It was difficult to resolve Si-O-P signals that appear between −110 to −120 ppm [55,56], possibly due to the lower number of Si-O-P links compared to Q4 and Q3.

To get more information, 31P CP-MAS solid NMR spectra (15 and −10 ppm) was deconvoluted and six resonances were observed (Fig. 6b). 31P CP-MAS NMR chemical shifts have been simulated using GIAO method according to the change in the chemical environment around the phosphonate groups at each side of the organic precursor (Fig. 6c) [30]. The chemical shift at 4.8 ppm is due to the monodentate binding and at 2.67 ppm is associated with the physiosorption of −P(O)(OH)₂ groups with −SiOH. This explains the presence of the Q2 peak in 2SiO2 compared to 0SiO2 (Fig. 6a). That’s to say, the hydrolysis of the phosphoester forms the phosphonic acid, which can be physiosorbed to the −SiOH group, mitigating the transformation of Q2 to Q3 and Q3 to Q4. The resonance at 11.1 ppm is assigned to the presence of two bidentate bindings on the same side. The resonance at 8.4 ppm can be attributed to bidentate binding of the phosphonate group, which is present next to a physiosorption mode of binding. The NMR resonances between −0.71 to −5.5 ppm are attributed to the overlapping of physiosorbed −P(O)OH on the same side of bonded phosphonate to −SiOH. Unhydrolyzed phosphoester also appears within the same region.

### 3.3 Mechanism of MSNP formation

Based on the different analysis, a simplified mechanism of MSNP formation is proposed in Fig. 7. The presence of very small primary particles (PPs) of ~6 ± 1 nm size (Fig. S9) observed during SEM analysis were formed in Stage-2, right after the hydrolysis and condensation of precursors in a highly alkaline medium (Stage-1). High alkalinity at Stage-1 facilitates the hydrolysis and co-condensation of ED with TEOS (Fig. S10). However, incomplete hydrolysis of ED results in the presence of a small fraction of residual phosphorous groups in the final 2SiO2, which is confirmed by NMR analysis (Fig. 6b) [57]. A higher concentration of ED and NaOH during the synthesis of 2SiO2 (Table 1) led to a higher ED incorporation in the PPs, which is reflected in the measured P-content of 2SiO2.

The initial stage marked by the rapid decrease in pH in the case of 1SiO2. 2SiO2 compared to 0SiO2 is attributed to the hydrolysis of phosphoester of ED to phosphonic acid (Fig. S10) and decrease in the co-condensation rate of ED-TEOS. The pH of the medium remains high enough for TEOS condensation which leads to the formation of secondary particles by aggregation of PPs (Fig. 7) [28,58]. Low ED content in PPs and a higher pH at Stage-1 of 1SiO2 synthesis results in compact secondary particles by incorporation of a higher amount of TEOS (Stage-3). Conversely, a higher amount of ED in PPs and a lower pH of the medium in the case of 2SiO2 prevented the formation of compact secondary particles. The size of the secondary particles grew via the incorporation of the PPs. However, lowering the pH due to the formation of phosphonic acid group results in a more open and porous structure (Stage-4). This difference in TEOS condensation in 1SiO2 synthesis is visible as a denser core during TEM analysis (Fig. 3a). On the contrary, low incorporation of TEOS Stage-3 and 4 produces porous 2SiO2 (Fig. 3e). The removal of co-condensed ED due to partial hydrolysis of Si-O-P bond [47] during synthesis also improves the porosity of 2SiO2 to achieve a surface area of 501 m².g⁻¹. A lower pH during the synthesis of 2SiO2 (Fig. S10) reduces the amount of of PPs that can be incorporated, which ultimately decreases the size of 2SiO2 compared to 1SiO2 (Fig. 2).

### 3.4 Dye removal from water

High surface area with −SiOH and −P(O)(OH)₂ functionalities make 2SiO2 an ideal adsorbent. Hence, the adsorption behavior of 2SiO2 was investigated using pollutants like CR, BB, and MB (Fig. 8). Equilibrium adsorption of CR was low (10%, Fig. S11a), due to competing CR-2SiO2 and CR-H₂O interactions (Fig. S11d). Higher adsorption of BB (~38%, Fig. S11b) is the result of slightly stronger BB-2SiO2 interaction, owing to more number of amino groups than sulfonic acid groups in BB (Fig. S11e). Nearly complete adsorption of MB within 10 min (Fig. 8c, 8d) is due to the strong interaction between MB with −PO(OH)₂ and −SiOH groups (Fig. S11f).

Considering a fast adsorption of MB by 2SiO2 detailed adsorption study was carried out (Fig. 8d, e) to predict MB distribution between H₂O or solid phase (2SiO2) using Langmuir [41] and Freundlich models.
Fig. 7. Schematic representation showing MSNP formation at 20% ($1\text{SiO}_2$) and 30% ED ($2\text{SiO}_2$). Hydrolysis of Si-O-P can also take place at Stage-3, for simplicity it is shown at Stage-4 only.

Fig. 8. (a) CR, (b) BB and (c) MB adsorption from 3 mL aqueous solutions (0.25 g/L, pH 7) by 30 mg of $2\text{SiO}_2$. (d) Effect of MB concentration on absorption behavior of $2\text{SiO}_2$. (e) Adsorption isotherms of MB at equilibrium concentration. (f) Langmuir and (g) Freundlich model of MB absorption by $2\text{SiO}_2$. 

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[42]. In Langmuir isotherm (Eq. (2)), \( C_e \) and \( q_e \) refers to the equilibrium MB concentration in H2O (mg L\(^{-1}\)) and 2SiO\(_2\) (mg g\(^{-1}\)) respectively. \( Q_{\text{max}} \) is the maximum MB that can be adsorbed on a monolayer (mg g\(^{-1}\)). Similarly, \( K_L \) (mg g\(^{-1}\)) and \( n \) are constants in Freundlich model (Eq. (4)) for adsorption capacity and adsorption favorability respectively.

\[
\text{Langmuir model: } \frac{q_e}{C_e} = \frac{1}{Q_{\text{max}}} K_L + \frac{1}{Q_{\text{max}}} \\
\text{Freundlich model: } \log q_e = \log K_F + \frac{1}{n} \log C_e
\]

From correlation coefficients (\( R^2 \), Table 3) it is clear that both Langmuir (Fig. 8f) and Freundlich model (Fig. 8g) provides a good fit with the experimental data. However, higher accuracy in Langmuir model describes better the absorption of MB. Based on Langmuir model, the maximum MB adsorption capacity of 2SiO\(_2\) (\( Q_{\text{max}} \)) was calculated to be ~380 mg g\(^{-1}\). \( R_L \) value derived by Eq. (3) signifies, if the isotherm is favorable (0 < \( R_L < 1 \)), linear (\( R_L = 1 \)), irreversible (\( R_L = 0 \)) or unfavorable (\( R_L > 1 \)) [53,59]. In this work, \( R_L = 0.95 \) indicates favorable adsorption of MB. Heterogeneity factor (\( n \)), calculated from Freundlich model shows if the adsorption follows a linear (\( n = 1 \)), chemical (\( n < 1 \)) or physical (\( n > 1 \)) process. The value of \( n = 2.5 \) shows some degree of physical adsorption of MB (Fig. 8g, Table 3), and the value of \( n \) also shows a favorable adsorption of MB by 2SiO\(_2\) [60].

### 3.5. Regeneration and reuse of 2SiO\(_2\)

To validate the practical application potential of 2SiO\(_2\), MB release, and reusability was studied. ~37.0 wt% MB containing 2SiO\(_2\) obtained after 2 h adsorption was used for the release study (Fig. 9a, Fig. S13). In neutral pH, equilibrium MB release of within 20% (after 6 h) suggests the release of only physio-adsorbed MB, which is in good agreement with the Freundlich isotherm model. Decreased solubility of MB and increase in the number of negatively charged sites in the 2SiO\(_2\) at alkaline pH lowered the MB release to only 7% (Fig. S14) [61,62]. On the contrary, at pH 4.5 nearly 96% MB was released within 2 h. It can be due to the increased solubility of MB and the formation of positively charged sites in 2SiO\(_2\) at this pH (Fig. S14) repels MB out of the NPs [61]. Competition between H-ion and MB prevents further readsorption of MB into 2SiO\(_2\). Complete desorption of MB at pH 4.5 (within 2 h) regenerated the 2SiO\(_2\) for subsequent reuse. \( \zeta \)-potential of 2SiO\(_2\) at different stages of the adsorption-desorption cycle also confirmed its regeneration (Fig. S15). Negative \( \zeta \)-potential of 2SiO\(_2\) approached isoelectric point after the adsorption of MB at the anionic sites in 2SiO\(_2\) [63]. After desorption of MB, negatively charged sites were free and \( \zeta \)-potential was close to the pristine 2SiO\(_2\). Reusability of 2SiO\(_2\) was investigated using 10 adsorption-desorption cycles (Fig. 9b) showed only a marginal decrease in adsorption capacity (~8%) after the tenth cycle. P-content of
$2\text{SiO}_2$ after the tenth cycle (~0.7%) was similar to the pristine $2\text{SiO}_2$ (~0.8%), which minimizes the risk of secondary pollution due to ED release.

The MB adsorption capacity ($Q_{\text{max}}$) of the novel MSNP ($2\text{SiO}_2$) was compared with the recently reported silica-based adsorbents (Table 4). The $Q_{\text{max}}$ of MSNPs (entry 9) was found to be superior to most of the listed adsorbents, except for entry 5 and 7. In these two cases, the adsorption experiments were carried out in an alkaline medium (pH 9) and as discussed earlier, alkaline medium favors adsorption of MB [61]. From the adsorption isotherm data, it can be said that $Q_{\text{max}}$ of $2\text{SiO}_2$ is comparable to the adsorbents listed in entry 5 and 7. Based on the preparation method and adsorption capacity, we can conclude that $2\text{SiO}_2$ is more potent than recently reported silica adsorbents.

4. Conclusion

In summary, a single-step and template-free synthesis method has been developed for the preparation of phosphonic acid-functionalized mesosstructured silica nanoparticles with high surface area (501 m$^2$. g$^{-1}$). $2\text{SiO}_2$ using a nonsilane precursor. Elimination of template removal and post functionalization steps simplified the process, protected the surface functionalities, and reduced the processing time to 2 h, otherwise difficult in state of art template-directed methods. NMR and FT-IR analysis confirmed the presence of $\text{SiOH}$ and $\text{PO(OH)}_2$ functionalities in on MSNPs. Unlike, SBA-15 and MCM-41 type material, randomly oriented pores with uniform pore width were formed within synthesized MSNPs. With the help of physical and chemical analysis, the mechanism of MSNP formation was postulated. The synergy of high porosity and functionality achieved high MB adsorption capacity (380 mg.g$^{-1}$) with excellent reusability of MSNPs (up to 10 recycling), which demonstrates its practical application potential in the field of pollution control. This novel MSNP can also be an ideal candidate for drug delivery and flame retardant applications. Additionally, the successful synthesis of MSNP using a nonsilane molecule broadens the precursor selection. Therefore, research is underway using different multifunctional nonsilane molecules at different synthesis conditions to improve the porosity and yield.

Author contribution

DambaruDhar Parida: Conceptualization; Methodology; Investigation; Data curation; Formal analysis; Supervision; Validation; Visualization; Writing - original draft; Writing - review & editing.

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Shanyu Zhao: Investigation; Formal analysis; Writing - review & editing.

Anjani K. Maurya: Investigation; Software; Formal analysis.

Khalil El Assaf: Investigation; Software; Formal analysis.

Eva Moreau: Investigation.

Sandro Lehner: Investigation.

Milijana Jovic: Investigation.

Hirsch Cordula: Investigation; Formal analysis; Writing - review & editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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