Original Research Article

SYNTHESIS AND CHARACTERIZATION OF A PERIODIC MESOPOROUS ORGANOSILICA MOLECULAR IMPRINTED POLYMER FOR REMOVAL OF DDT

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Abstract: A Periodic Mesoporous Organosilica (PMO) is an organic-inorganic hybrid composition with ordered porous structure on a molecular imprinted polymer (MIP). A triblock copolymer Pluronic F127 poly(ethylene glycol)- poly(propylene glycol)-poly(ethylene glycol) as structure directing agent (SDA) and 1,4-bis(triethoxysilyl)benzene (BTEB) as a precursor were used to synthesis the PMO-MIP using a non-covalent approach. The non-covalent approachshowed a limited number of selective imprinted sites due to the lack of strong intermolecular attractions between DDT template and the BTEB precursor. However, treatment of PMO-MIP with chlorotrimethylsilane (CTMS) significantly reduced the SiO-H and Si-OH resulting in a more non-polar material. The synthesized PMO-MIP was able to recover 106%, 85% and 99% of DDT, DDD and DDE respectively which shows that it can be used not only for extraction of DDT and its metabolites from environmental samples but also as a clean-up for samples.

Keywords: PMO-MIP, BTEB, triblock copolymer F127, removal of DDT and CTMS.

Introduction: Porous materials have attracted scientific and technological interests because of their applications in a variety of fields including catalysis, separations, adsorbents, sensors, drug delivery, optics, and electronics[1]. Periodic mesoporous organosilicas (PMOs) have the organic-inorganic hybrid composition and ordered porous structure that distinguishes them from the traditional organic-inorganic hybrid materials[2].

The PMOs can be synthesized through hydrolysis and subsequent condensation reactions of bridged organosilsesquioxane precursors of the type $(OR')_3Si-R-Si(OR')_3$ with R' being hydrolysable methoxy or ethoxy groups and R being a non-hydrolysable organic bridge group in the presence of cationic, anionic and polymeric surfactants[3]. These PMOs exhibit a distinct advantage over other mesoporous silica materials because there exist a large number of organic functional groups homogeneously distributed throughout the pore wall of the PMOs[4] and they also offer organic

functionalities within the pore wall, increased hydrothermal stability, higher mechanical stability, variable hydrophilic-hydrophobic micro-environments, and myriad pore surface compositions that fine-tune interactions with guest molecules[5].

The unique hydrophilic-hydrophobic framework of PMOs can be easily adjusted through incorporation of different kinds of organic groups in the mesoporous framework without pore blocking. This study examined the treatment of the PMO with chlorotrimethylsilane (CTMS) to create a more non-polar imprinted polymer by significantly reducing the Si-OH and SiO-H. The PMOs were synthesized with 1,4-bis(triethoxysilyl)benzene (BTEB) as a precursor in the presence of triblock copolymer F127 as an SDA and DDT as a template under acidic conditions.

DDT (dichlorodiphenyltrichloroethane) is the best known organochlorinepesticide; it became the most widely used pesticide in agriculture around the world because of its broad-spectrum activity, long-lasting control, inexpensiveness to manufacture and effectiveness[6].However, DDT's environmental and human's effects arise because of two important properties; its persistence in the environment and toxicity due to accumulation in fatty tissues[7]. In Swaziland, DDT is used in Indoor Residual Spraying (IRS) in the Malaria endemic areas. A study of DDT and its metabolites in soils, sediments and cow's milk in the Malaria endemic areas of Eswatinireported p,p-DDT with mean concentration of 0.249 mg/kg in soils, 0.990 ppm in sediments and 70.130 μg/mL in cow's milk[8]. While, another one done to investigated DDT in breast milk of women from Siphofaneni revealed that 83.5%, 76.7% and 47.6% of the samples analyzed had p,p-DDT, o,p-DDT and p,p-DDE respectively[9]. The study concluded that 80% of the breastfeed infants were taking breast milk with DDT residue that amply exceed the acceptable daily intake (ADI) of 0.05 μg/mL as the DDT residue had a mean of 1.66 μg/mL[9].

In a study conducted to investigated the presence of DDT in human breast milk in South Africa in the KwaZulu-Natal Province where they selected the Ubombo and Ngwavuma districts who lies between Swazilandto the west, Mozambique to the north and the Indian Ocean to the east it was reported that Jozini in the Ubombo district had the highest concentrations of DDT in both the whole breast milk and the milk fat from the mothers of 238.23 μg/l and 6237.52 μg/kg respectively and that was 33.74% of the samples had DDT detected. Kwaliweni in the Ngwavuma district had the lowest concentrations of DDT 26.69 μg/l from the whole breast milk and 871.01 μg/kg form the milk fat where only 27.99% had DDT detected and this was because Kwaliweni does not undergo the annual IRS control[10].

In Mozambique, a study was done at Manhica district which is a rural area located in the north of the Maputo province where they investigated the concentration of DDT compounds in breast milk from African women in 2002 and 2006. They concluded the breast milk concentrations of organ chlorines in 2006 were significantly higher than those of 2002, the median of ∑DDT in 2006 being 2.9 times higher than in 2002. IRS with DDT is the main likely cause for the increase of this insecticide in maternal milk samples[11].In another study, assessment of DDT and metabolites exposure after indoor residual spraying through the analysis of thatch material from rural dwellings in Manhica district published that total DDT concentrations ranged between 0.6 and 6100 ng/g in materials collected in 2006. The predominant isomer was p,p-DDT with 49 ng/g followed by p,p-DDD with 5.2 ng/g and lastly p,p-DDE with 2.2 ng/g. The o,p-isomers for DDE, DDD, and DDT (0.2, 1.0 and 7.5 ng/g, respectively) were in lower concentration than the p,p-isomers. Whilematerials sampled in 2007 from sprayed dwellings had total concentrations of DDT ranging between 12 and 29,000 ng/g. The predominant isomer again was p,p-DDT with 150 ng/g followed by p,p-DDD with 23 ng/g and p,p-DDE with 21 ng/g. The concentration of the o,p-isomers for DDE, DDD, and DDT (0.3, 5.4, and 21 ng/g, respectively) were lower than those

among the p,p-isomers. The concentrations of all DDT isomers and their metabolites were higher in thatch samples collected in year 2007 than in 2006[12].The study suggested that DDT exposure through inhalation is a probable mechanism for exposure of their inhabitants. Other exposure routes could be related to dust or particles falling from the treated walls or roofs of the dwellings such that DDT has been found in floor dust[13]. These particles could eventually be inhaled through respiration or ingested if they become mixed with food or water. In this study the synthesized PMO-MIP was used to remove DDT from environmental samples with were the Marula brew and oil. The Marula brew is made from Marula fruits which are collected and kept in the houses which are sprayed through the IRS control in the Malaria endemic areas of Eswatini and the Marula oils are extracted from the oily kernels of the fruits.

Experimental Materials and Methods
Reagent: Pluronic F127 poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol), sodium chloride AR grade, absolute ethanol, hydrochloric acid, 1,4-bis(triethoxysilyl)benzene (BTEB), chlorotrimethylsilane (CTMS), tetrahydrofuran (THF) and acetone were purchased from Sigma Aldrich and Merck. All solvents were HPLC grade and chemicals were used as received. 0.1% (w/v) DDT, DDE and DDD was prepared by dissolving 0.135 g DDT, DDE and DDD in 135 mL ethanol.

Preparation of non-covalently PMO-MIP/NIP
Masses of 5.4 g F127 and 59.7 g NaCl were dissolved in 90 mL distilled water, then 107.3 mL of 0.1% (w/v) DDT, DDD and DDE and 270 mL 2.0 M HCl (32%) solution were stirred into the mixture at room temperature. Lastly, a mass of 21.45 g BTEB was added to the homogenized mixture while stirring at a temperature of 40 ℃ and continued stirring for 24 hours. The mixture was then transferred into a Teflon bottle for hydrothermal treatment under static conditions at a temperature of 90 ℃ for 48 hours. The recovered PMO-MIP was filtered using a nylon membrane filter and then washed with 50 mL distilled water three times before drying at 60 ℃

for 12 hours. A mass of 14.28 g of the PMO-MP was recovered which was then incubated in 50 mL of CTMS for 16 hours there after rinsed with THF for 48 hours and then dried at 60 ℃ for 12 hours. A non-imprinted polymer (NIP) was prepared using the same procedure of polymerization above but in the absence of the DDT template and it was not incubated in CTMS.

Template and surfactant removal: The PMO-MIP and PMO-NIP materials were extracted sequentially with ethanol, acetone and ethanol using the Soxhlet extractor to remove the template in the PMO-MIP and surfactant. Extracts were collected and then analyzed to determine the removal of template using GC/ECD. The complete removal of the surfactant was confirmed by the disappearance of the characteristic IR absorptions of the surfactant.

DDT/DDD/DDE extraction with PMO-MIP/PMO-NIP: Masses of 0.09 g of PMO-MIP and PMO-NIP, 0.24 g of anhydrous magnesium sulfate and 0.06 g of sodium chloride were measured into a vial and 2 mL aliquots of 0.2 ppm DDT/DDD/DDE standard were added into the vials. The mixture was thereafter shaken for 12 hours in a shaker, the supernatant was removed using syringes with a glass fiber micro-filter and placed in GC vial. A volume of 3 mL cyclohexane: acetone (7:3) was used to elute DDT/DDD/DDE from the PMO-MIP and PMO-NIP that remained in the syringes with glass fiber micro-filter and extracts were also placed in GC vials for analysis.

The difference between the values obtained of the percent recovery for the PMO-MIP and PMO-NIP give the actual occurrence of selective cavities in the PMO-MIP. Therefore, the selectivity ratio can be calculated using the equation below.

$$Selectivity\ ratio = \frac{\%\ recovery\ MIP}{\%\ recovery\ NIP}$$

Physical Characterization: Fourier-transform Infrared Spectroscopy (FT-IR) was done using an IR Prestige 21 Shamadzu where

AR grade KBr was used to prepare the pellets. Scanning Electron Microscopy (SEM)analyses were performed on a Leo 1430VP and a Cambridge S200 scanning electron microscope after gold sputter coating was applied. Image acquisition conditions were 7 kV accelerating voltage with 150 pA probe current for the former and 10 kV accelerating voltage with 50 pA probe current for the later. Thermo gravimetric Analysis (TGA), a Q500 thermo-gravimetric analyzer in air at 10 °C per min up to 900 °C was used to determine thermal stability of the polymers.

Results and Discussion

FT-IR: The PMO-MIP and PMO-NIP spectra showed similar appearances of major peaks after washing. The intense absorption in the region 1029-1035 cm^{-1} assigned to Si-O-Si vibrations indicated the formation of siloxane bonds (Si-O-Si). The Si-C_6H_4-Si stretching mode at 1140 cm^{-1} indicated that the phenylene bridges in the polymers were intact even after washing and the peak at 770 cm^{-1} is attributable to the symmetric Si-O stretching vibration. The disappearance of the absorptions at 1251-1635 cm^{-1} of the alkyne groups and at 2970 cm^{-1} and 2870 cm^{-1} corroborated by methyl (CH_3) and methylene (CH_2) groups after washing indicated the removal of the surfactant (F127).

After the PMO-MIP was treated with CTMS, two major peaks at 1245 cm^{-1} and 837 cm^{-1} were observed as seen in figure 1 below which resulted from the formation of Si-CH_3 bonds. CTMS treatment also significantly reduced the SiO-H and Si-OH absorbances at 3360 cm^{-1} and 901 cm^{-1} respectively and this was in agreement with Graham report which showed the presence of Si-CH_3 groups at 1252 cm^{-1} and 841 cm^{-1} and the significant decrease in the amount of the SiO-H and Si-OH absorbances at 3360 cm^{-1} and 878 cm^{-1} region[14].
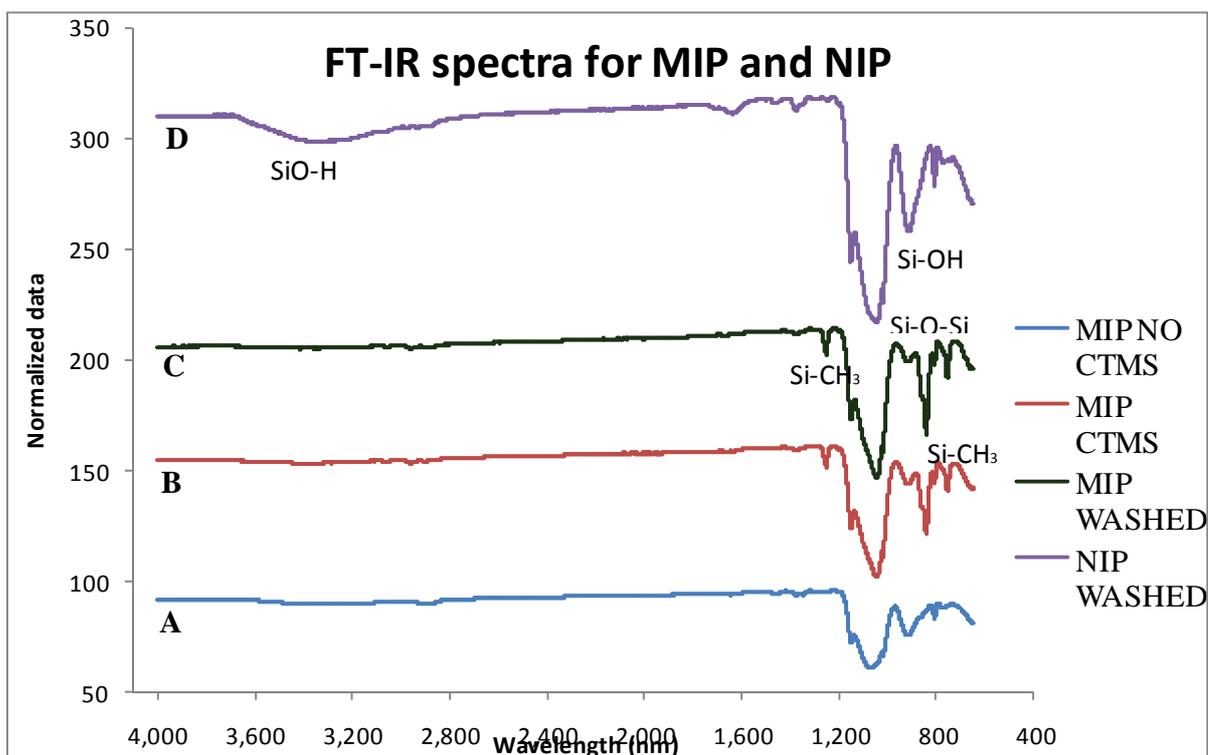
Figure 1:FT-IR spectra for: A-MIP before treatment with CTMS, B-MIP after treatment with CTMS, C-MIP after washing and D-NIP after washing.

SEM: The morphologies of the MIP and NIP after removal of template are shown in figure 2 below. The images of the MIP illustrate that the PMO-MIP had almost cubic particle morphology similar to the prepared BTEB-SBA 16 reported by Nohair and his colleagues[15]. Zang and companions concluded that large caged cubic PMO could be prepared easily by using F127 in the presence of acetone or tetrahydrofuran instead of ethanol which is why it is believed that the polymer had large domains of well-ordered cage like mesostructure[16]. However, the PMO-NIP images appeared to be smooth and flaky because there were no specific binding sites created as no DDT template was used.
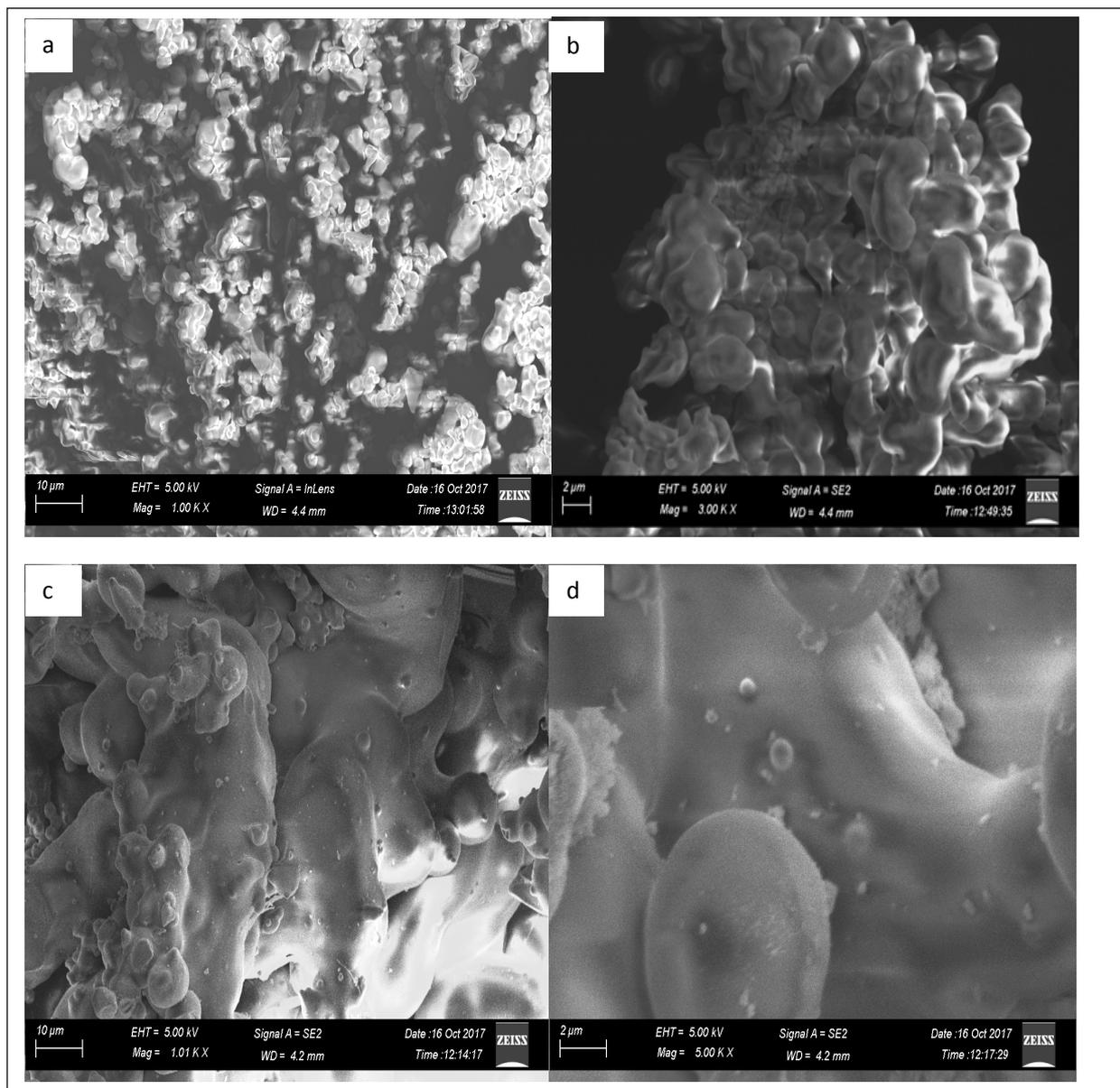
Figure 2: Images of SEM of the synthesized polymers; a) MIP at 10μm, b) MIP at 2μm, c) NIP at 10μm and d) NIP at2μm.

TGA: The TGA curves for the NIP and MIP before and after washing are shown in figure 3 below. The TGA curves were divided into three steps. The first step at the temperature range 20 - 100 ºC was due to physisorbed water. The NIP unwashed showed weight loss of 2% while the NIP washed showed a sharp significant weight loss of 8% at this step. Before the MIP was treated with CTMS the weight loss of 16% was observed, however, after the MIP was treatment with CTMS there was no weight loss due to water and this showed that treatment of MIP with CTMS resulted in an MIP which had no water molecules.

The second step at temperature range of 100 - 400 ºC indicated a weight loss of 5% in the NIP washed from 10% in NIP unwashed but only 2% weight loss was observed in the MIP washed while the MIP unwashed showed 8% weight loss which was due to surfactant decomposition. So the weight loss can be attributed to molecules of surfactant residues which remained in the NIP

even after solvent extraction procedure but in the MIP washed the weight loss at this step was due to the methyl in the $Si-CH_3$ after treatment with CTMS.

The phenylene bridge was still stable before 400ºC temperatures. Weight losses of 50% and 40% observed in the NIP unwashed and washed respectively and 31% and 40% in the MIP unwashed and MIP washed in the temperature range 400-800 ºC was due to the benzene framework decomposition which was the last step. The high thermal stability of the PMO material can be attributed to the aromatic system in the BTEB precursor. Similary, Rebbin and colleagues synthesized a polymer with P123, CTAB and BTEB where TGA results showed a total mass loss is 40%. The drying step from 20-200 °C had mass loss 1% while at200-450 °C a mass loss of 9% occurred and at 450°C the organic bridge started to decompose. The decomposition was completed at a temperature of 650 °C[17].
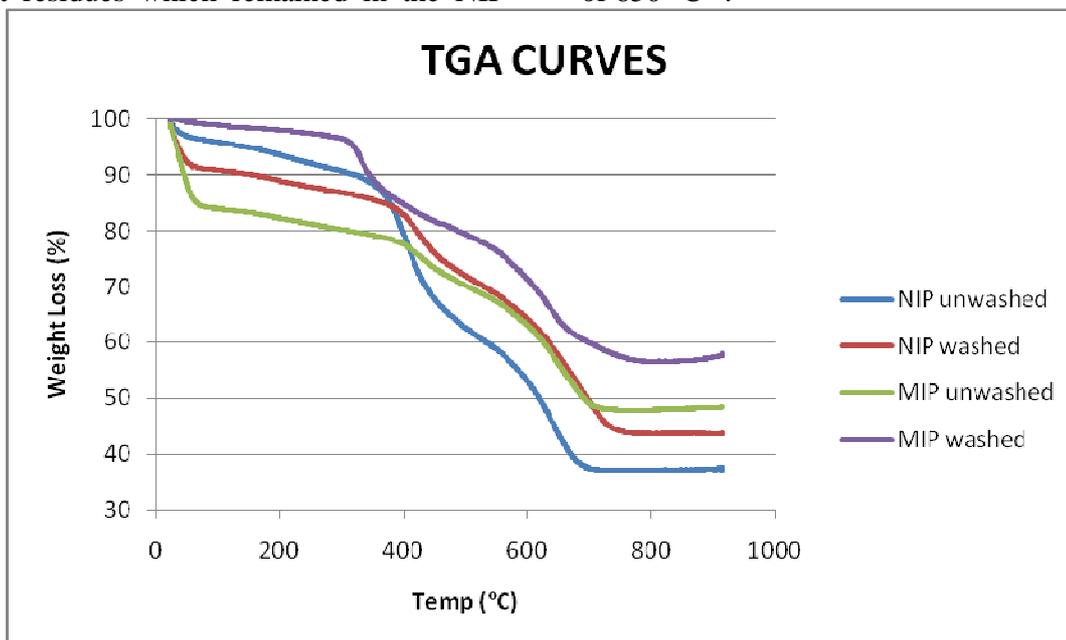
Figure 3: TGA curves for the NIP before and after washing and the MIP before treatment with CTMS and washing and then after washing.

Performance of PMO-MIP in DDT removal

The PMO-MIP materials were said to be highly selective and specific after they were treated with CTMS to remove the –OH thus resulting in the PMO-MIP being more lipophilic for maximum

adsorption of DDT[14].This was concluded because the percent recovery for DDT increased from 61.5% before the PMO-MIP was treated with CTMS to 80.6% after treatment with CTMS. To the PMO-MIP treated with CTMS,

15% NaCl was added to increase the ionic strength of the PMO-MIP[18]and anhydrous $MgSO_4$was also added to remove any polar matrix from samples and that showed improved recoveries of DDT, DDD and DDE to 106%, 85% and 99% respectively.

The binding studies were carried out in parallel to PMO-NIP which had no specific binding sites as there was no template in its preparation. The PMO-NIP showed poor recoveries for all three analyses as only 47% was recovered for DDT, 30% for DDD and 18% for DDE.

The selectivity ratio for DDT when the PMO-MIP was not treated with CTMS was calculated to be 1.31 which was a lower value compared to 1.50 Graham and his colleagues[14] obtained when they also used a non-covalent molecular imprinting without treatment with CTMS. However, treatment of the PMO-MIP with CTMS improved the selectivity ratio to 1.72 which was then observed as an improved value compared to the value obtained after a covalently prepared molecular imprinted polymer combined with CTMS of 1.35 from 1.29 before it was combined with CTMS. Finally addition of NaCl and anhydrous $MgSO_4$to the PMI-MIP after treatment with CTMS proved to increase the selectivity of the PMO-MIP materials, as the selectivity ratio was 2.26 for DDT, 2.8 for DDD and 5.50 for DDE.

Conclusion: The main objective was to synthesize and use a non-covalent molecular imprinted polymer on a periodic mesoporousorganosili causing BTEB as a precursor to extract p,p'-DDT, DDE and DDD from environmental samples. The PMO-MIP was successfully synthesized because the FT-IR spectra indicated the formation of the siloxane bonds (Si-O-Si) at 1020-1161 cm^{-1} and the Si-C_6H_4-Si stretching mode at 1240 cm^{-1} that indicated the phenylene bridges in the polymers were intact even after washing. Treatment of the PMO-MIP with CTMS was evident as two major peaks at 1253 cm^{-1} and 842 cm^{-1} were observed as a result of the formation of $Si-CH_3$ bonds and CTMS significantly reduced the SiO-H and Si-OH absorbances at 3360 cm^{-1} and 810 cm^{-1}

respectively. The images from SEM illustrate that the PMO-MIP had a large caged-like mesostructures which suggested that the polymer had a large pore *Im3m*mesostructure in an armopholous silica layer. The TGA showed the high thermal stability of the PMO-MIP material which can be attributed to the aromatic system in the organ silica precursor. In conclusion the synthesized PMO-MIP was able to recover 106%, 85% and 99% of DDT, DDD and DDE respectively which shows that it can be used not only for extraction of DDT and its metabolites from environmental samples but also as a clean-up for samples.

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