

# Removal of persistent organic pollutants by mesoporous silica nanocomposites derived from fly ash

**ÅForsk Project 21-353**

Final report

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## **Background/introduction**

The spread and accumulation of persistent organic pollutants (POPs) has become a major concern to human health and surrounding environment [1]. Among the many techniques to remove POPs, adsorption is considered more promising and advantageous, owing to its low cost, environmentally friendly, easy operation and possibilities of recycling the adsorbent materials [2,3].

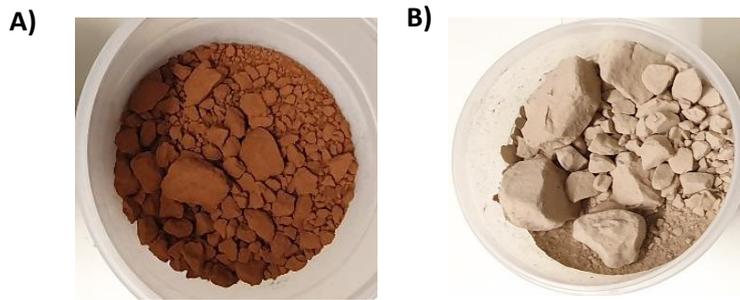
Fly ash, derived from waste incineration, has a great potential in environmental applications, which would solve both disposal problems and serve as a cheaper material for adsorption of water pollutants. Considering the substantial amounts of silicon in fly ash composition, it can be a valuable source for synthesizing mesoporous silica materials, which can surpass the limitations of zeolites when it comes to selectivity and reusability [4]. Having well-ordered and uniform pores with easy adjustable pore size, mesoporous silica found a wide application in diverse fields, such as drug delivery, molecular separation, adsorption and catalysis [5]. Modification of these mesoporous materials by incorporation of organic ligands can further increase the selective adsorption capacity of POPs [6].

In general, mesoporous nanoparticles are synthesized by combining appropriate amounts of silica source (ex. Silicon alkoxides), surfactant, base and water [7–9]. After certain aging time, the template is removed by calcination. To make this process more cost-effective and environmentally friendly, this project aims to develop a new method for grafting and enzyme immobilization using fly ash from waste incinerators as a primary silica source. Main findings of this project can help to design efficient and more sustainable nanocomposites for future applications in industrial levels.

## **Project Results**

### **Extraction of silica from fly ash**

The first step of silica nanoparticles' synthesis involved extraction of silica from fly ash in the form of sodium silicate. Even though the silicates in fly ash are present in both amorphous and crystalline forms [10], only the amorphous forms react with alkali and have a role in silica extraction efficiency. While the crystalline silicates are inert and rarely react with the acids or bases at normal conditions [10]. Fly ash samples that were collected from Easy Mining Company originated from sewage sludge incineration (Figure 1). Sample no 1 is the ash after leaching with mild acid at ambient temperature to dissolve the P, Ca and some other elements. Sample no 2 is derived from sample no 1, after a second acidic leaching step that removes Fe. That is why there was no need for an additional step to remove iron from these samples. Herein we used alkali dissolution method to extract the silica in a form of sodium silicate solution. To do so, 5g of fly ash (sample no 2) was mixed with 5 M NaOH solution and the mixture reacted at 100 °C for half an hour in a condenser. The obtained solution was separated from fly ash by centrifugation and filtered using a filter paper.

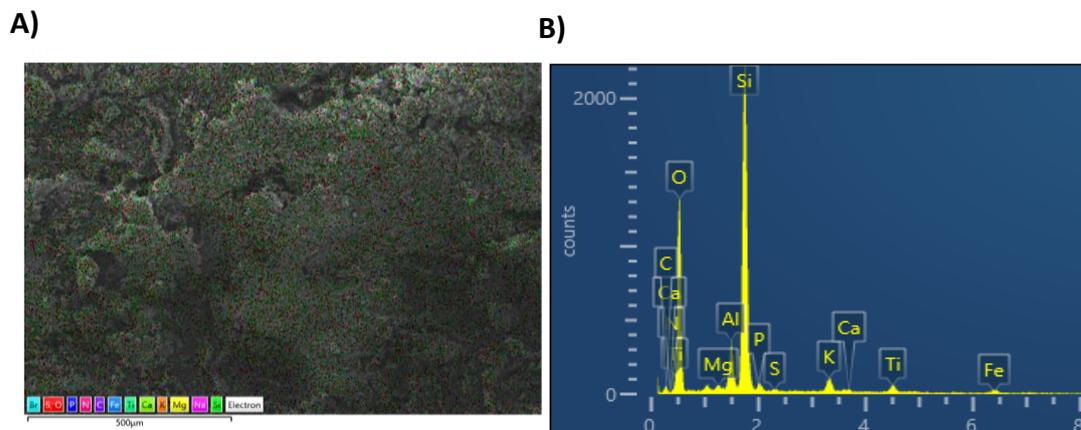


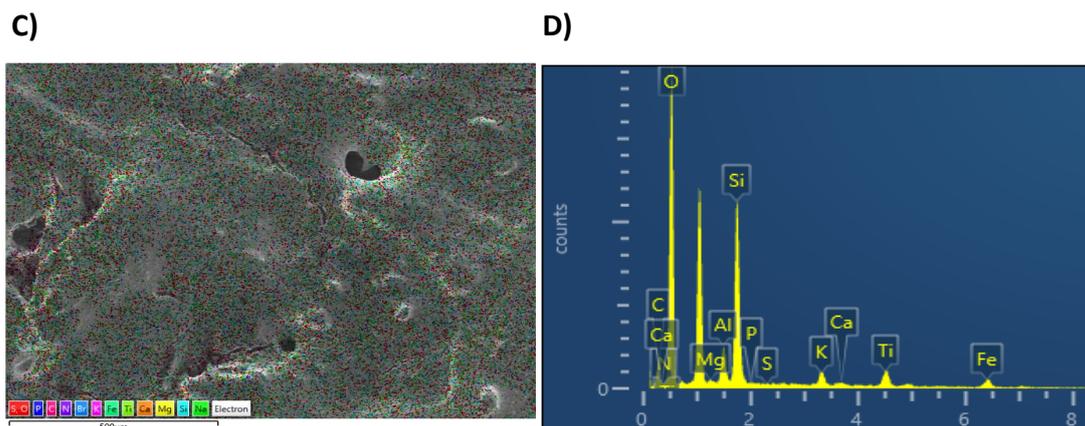
**Figure 1.** Fly ash samples collected from Easy Mining: A) sample no 1, B) sample no 2.

To measure silica extraction rate, fly ash samples before and after desilication process were analyzed by energy-dispersive X-ray spectroscopy (EDS) for elemental mapping. The results are summarized in table 1 and figure 2. Approximately 50-60% desilication rate was achieved after one step basic treatment with NaOH.

**Table 1.** Elemental mapping of fly ash before and after desilication (numbers represent molar percentage of each element).

Element	Before desilication	After desilication
O	60.05	57.12
Na	0.40	13.47
Si	17.97	7.63
Al	2.29	1.67
Ti	0.90	1.22
K	0.96	0.69
Fe	0.75	1.12
C	15.06	15.86
Mg	0.33	0.19
Ca	0.13	0.14
N	0.42	0.85
P	0.61	0.02
S	0.13	0.00
Total	100.00	100.00



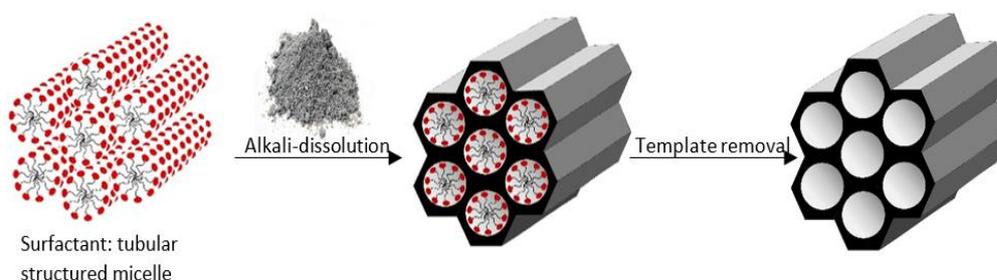


**Figure 2.** EDS elemental mapping and spectrum of fly ash sample before A) B) and after desilication C) D).

### Synthesis of silica nanocomposites

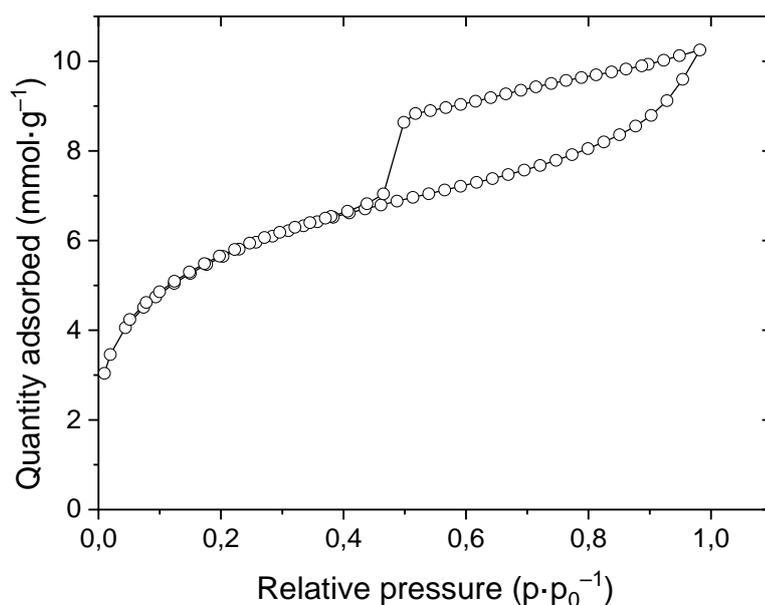
Different synthesis approaches were used to synthesize silica nanoparticles from extracted sodium silicate solution (SSS). In the first approach SSS was mixed with ethanol (30 mL each) and heat at 50 °C in the water bath. Afterwards, concentrated nitric acid was added dropwise until the pH of the solution was dropped to 7. Silica nanoparticles were formed after few minutes of adding the nitric acid. The reaction was left for an hour and the nanoparticles were collected afterwards by centrifugation and washed 3 times with ethanol and 3 times with water to get rid of excess SSS. SEM images showed that synthesized nanoparticles have round shape and the size is ranging between 160-190 nm.

In the second approach mesoporous silica nanoparticles were synthesized using previously established method with some alterations [7,9] (Figure 3). 4 g of surfactant Pluronic 123 was dissolved in 60 mL of water and 38 mL of concentrated HCL was added afterwards. The mixture was put in water bath under continuous stirring at 40 °C. After 30 min, SSS solution (40mL) was added slowly and let under the same conditions for 2 h. The particles that were formed immediately after adding SSS were left for 20 h at 80 °C. To remove the template the synthesized nanoparticles were centrifuged and boiled in acidified ethanol for 3 hours, 4 times (changing the ethanol each time). Afterwards, the particles were vacuum dried for 30 min at room temperature, 30 min at 50 °C and 3 hours at 100 °C.



**Figure 3.** Synthesis of mesoporous silica nanoparticles from fly ash

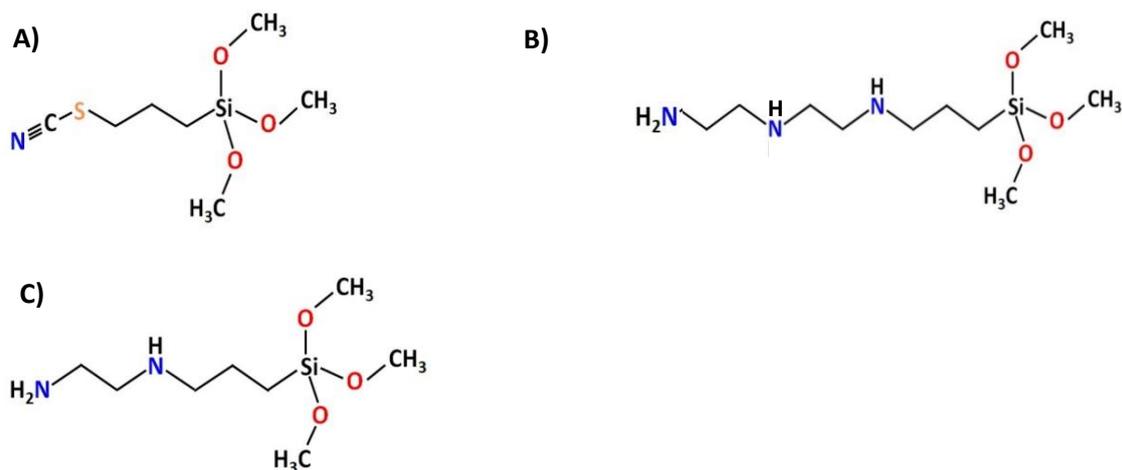
To measure the surface area and confirm porosity of synthesized nanoparticle, nitrogen adsorption and desorption isotherms were obtained at  $-196\text{ }^{\circ}\text{C}$  (Micromeritics ASAP 2020 Surface Area and Porosity analyser). The samples were degassed at  $120\text{ }^{\circ}\text{C}$  for 3 hours before the measurements. The nitrogen adsorption/desorption isotherms for the SSS NPs sample are presented in Figure 4. The shape of the isotherms corresponds to characteristic type IV which is common for mesoporous materials. In general, it is widely accepted that there is a correlation between the shape of the hysteresis loop and the texture (e.g., pore size distribution, pore geometry, and connectivity) of a mesoporous material [11]. An empirical classification of hysteresis loops was given by IUPAC, which is based on an earlier classification of hysteresis by de Boer [12]. The hysteresis loop of isotherms belongs to type H4 which is associated with narrow slit pores. Brunauer–Emmett–Teller specific surface area (SBET) was found to be  $462\text{ m}^2\cdot\text{g}^{-1}$  for the SSS NPs sample. Barrett-Joyner-Halenda (BJH) desorption cumulative surface area and volume of pores between 1.7 nm and 300 nm with were found to be  $311.3\text{ m}^2\cdot\text{g}^{-1}$  and  $0.284\text{ cm}^3\cdot\text{g}^{-1}$ , respectively, whereas average pore width was 3.6 nm.



**Figure 4.** The nitrogen adsorption/desorption isotherms for SSS NPs.

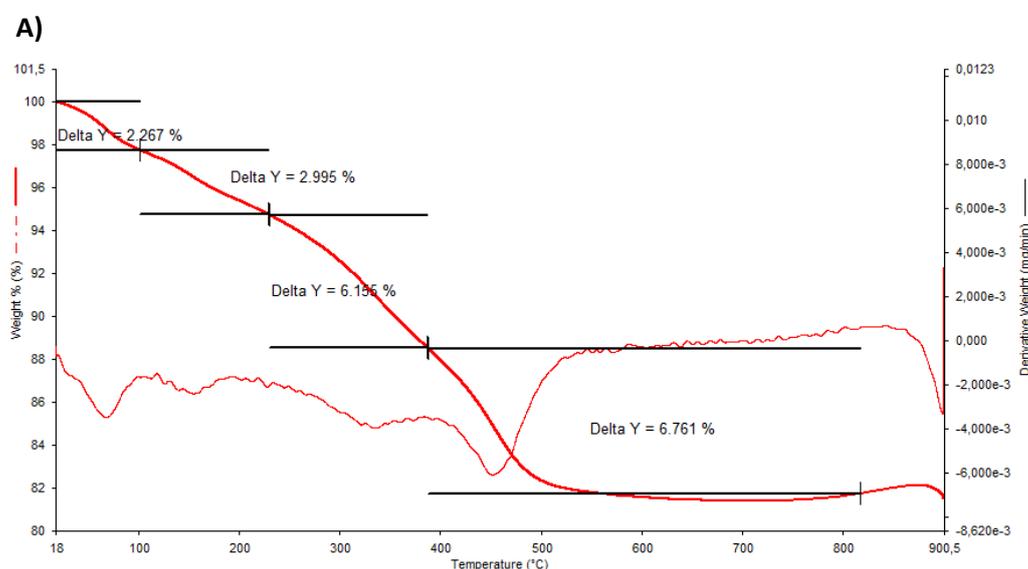
#### **Functionalization of silica nanoparticles**

Three different ligands were tested to graft the surface of silica nanoparticles. The names and structures of the ligands are presented in figure 5. Surface functionalization with different ligands was performed in a one-step reaction according to a procedure that was established in our group previously [13]. Typically, 500 mg SSS nanoparticles were dispersed in 20 mL toluene to which 1 mL corresponding ligand was added. The reaction mixture was refluxed for 24 h under inert atmosphere, and afterwards, the nanoparticles were separated by centrifugation (10,000 rpm, 15 min), washed twice with toluene and twice with ethanol, and dried under nitrogen atmosphere.

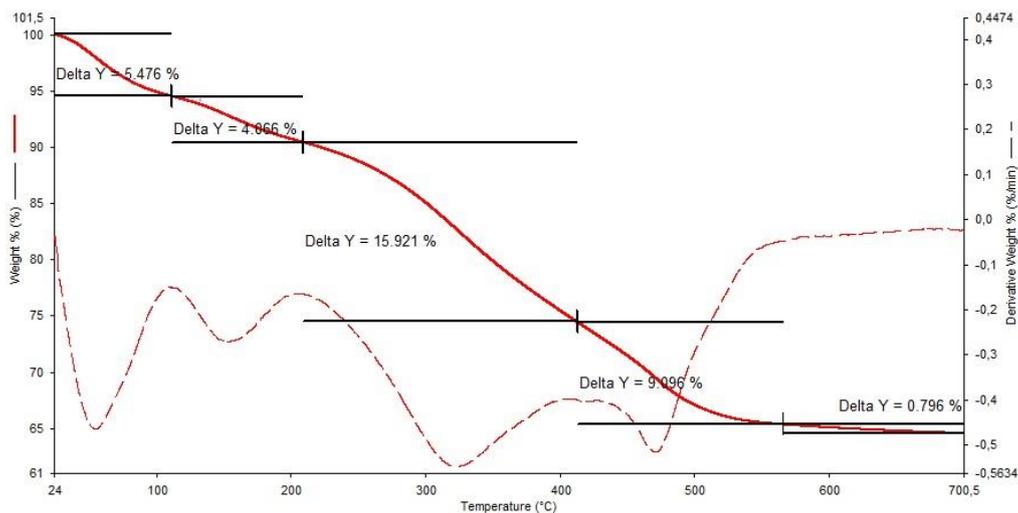


**Figure 5.** Chemical structure of selected ligands: A) **L1**-triethoxy (3-isothiocyanatopropyl) silane, (B) **L2**-N1-(3-Trimethoxysilylpropyl)diethylenetriamine, (C) **L3**-N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane

Since all three ligands contain organosilane groups, the grafting was achieved in one-pot reaction where the bond occurs between the organosilane group of the ligand and active sites of nanoparticles such as hydroxyl groups. TGA analysis were performed to confirm the successful functionalization and calculate the amount of the ligand that was grafted on SSS NPs' surface (Figure 6). The calculated grafted amount of the ligands were 0,93 mmol/g, 1,6 mmol/g and 2,2 mmol/g for ligands 1, 2 and 3 respectively.



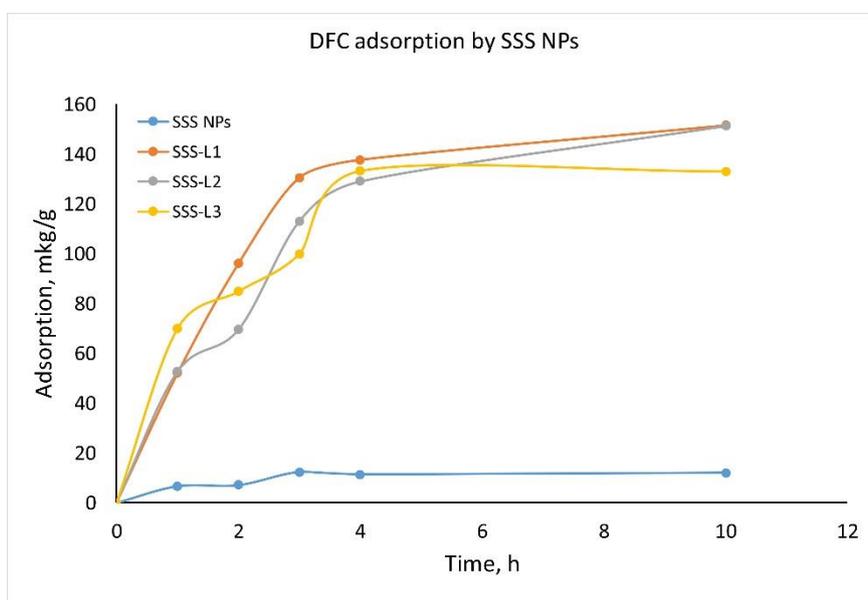
B)

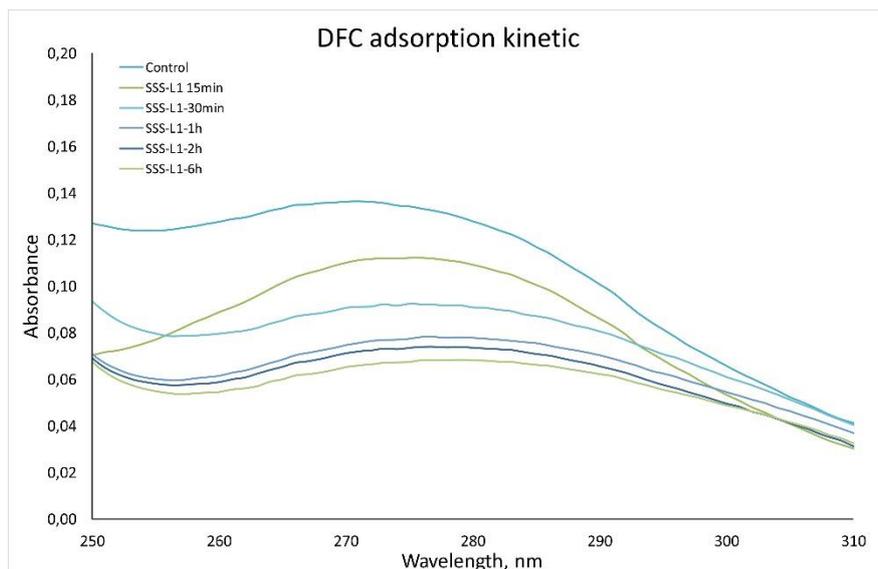


**Figure 6.** TGA curves of functionalized SSS nanoparticles with ligand 1 **A)** and ligand 2 **B)**

### Adsorption of diclofenac by functionalized silica nanoparticles

For the adsorption experiments 100 mg of adsorbent was shaken with 10 mL of diclofenac solution at room temperature for 24 h. Afterwards the solution was separated from the sorbent by centrifugation and the residual diclofenac concentration was measured by UV-VIS spectrometer at 273 nm with a standard quartz cuvette (Figure 7 A). For adsorption kinetics samples from the mixture were taken every set interval of times and measured by UV-VIS (Figure 7 B). For a comparison the SSS NPs without any ligands were also tested for DFC adsorption.





**Figure 7.** Adsorption kinetics of DFC on SSS NPs with and without ligands: A) kinetic curves, B) adsorption spectra of SSS-L1 derived from UV-VIS measurements

From the results it was evident that bare silica nanoparticles did not contribute to diclofenac adsorption. Previous researches showed that adsorption of different drugs on functionalized silica adsorbents is highly dependent on solution pH [14]. At pH lower than 4, diclofenac is hardly soluble in water, and at higher pH values the silica surface becomes more and more negatively charged which can cause repulsive interactions. At pH 5 diclofenac has a net negative charge, while the silica surface has a net positive charge. This could contribute to a better adsorption process due to the enhanced electrostatic interactions and hydrogen bonds [14,15].

### Summary

A total of 500 000 SEK was received from ÅForsk foundation for a research project with a duration of 6 months. During this time we investigated silica extraction from a cheap source fly ash to synthesize mesoporous silica nanoparticles. The extraction was successful and reached 50-60% from the fly ash samples that we got from Easy Mining company. Next step was the synthesis of silica nanoparticles from sodium silicate solution derived from the fly ash. Two different nanoparticles were synthesized and one of them showed good mesoporosity and high surface area. These samples were chosen for the functionalization of three different ligands containing amino and thiocyanate functional groups. Grafting the silica surface was performed with already established methods in our lab and high functionalization rates were obtained ranging between 0,9-2,2 mmol/g for the different ligands. In the last step of the project a model pollutant diclofenac was chosen for adsorption experiments and adsorption capacities were established. The next step could be optimizing the silica extraction and nanoparticle synthesis by tuning the reaction parameters and trying the grafted nanoparticles on POPs which can be done with the help of HPLC.

### Acknowledgments

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