Smart Synthesis of Trimethylethoxysilane (TMS) Functionalized Core – Shell Magnetic Nanosorbents Fe₃O₄@SiO₂ for Removal of Pesticides: A Full Factorial Design – Assisted Statistical Approach

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BACKGROUND

Stöber Method

Hydrolysis

\[ \text{Si} = \text{OR} + \text{H₂O} \leftrightarrow \text{Si} = \text{OH} + \text{ROH} \]

Condensation (Alcohol)

\[ \text{Si} = \text{OR} + \text{Si} = \text{OH} \rightarrow \text{Si} = \text{O} - \text{Si} = \text{O} + \text{ROH} \]

Condensation (Water)

\[ \text{Si} = \text{OH} + \text{Si} = \text{OH} \rightarrow \text{Si} = \text{O} - \text{Si} = \text{O} + \text{H₂O} \]

Overall Reaction

\[ \text{Si} = \text{OR} + 2 \text{H₂O} \rightarrow \text{SiO}_2 + 4\text{ROH} \]

Scheme 1. Hydrolysis and condensation of TEOS.

Design of Experiments (DoE):

- Full Factorial Design (FFD)
- 2 – 15 Factors.
- \(2^k\) Number of Runs: \(k\) is the number of variables.

GOALS & OBJECTIVES

- Synthesize Trimethyl-functionalized Core – Shell Magnetic Nanoparticles (mcSNPs) with the following Properties:
  - Magnetic Properties
  - Uniform PS
  - Homogenous PSD
- Magnetic Solid Phase Extraction (MSPE) of Pesticides.
- Synthesis:
  - Modified Mössbauer Method
  - Stöber Method
- FFD Advantages:
  - Saving time and resources;
  - Data obtained can be treated with inevitability.

MATERIALS & METHODS

Chemicals

- Ammonium hydroxide (22% W/V) *TEOS
- *TMS
- *Iron (II) and Iron(III)
- *Carbamate/OP Pesticides

Software

- Minitab*18
- ZEN* 2.3 Blue Edition

Synthesis Procedure

Design of Experiments (DoE)

- Pareto Chart of Standardized Effects (response in Magnetic Properties, \(n = 8\) FFD)

Figure 1: Pareto Chart of Standardized Effects

Figure 2: 2D Contour Plots (Left) and 3D Surface Plots (Right).

Figure 3. SEM Micrographs of Well-Defined mcSNPs

Figure 4. TGA curve of sample 1 (22 nm) and sample 2 (100 nm).

RESULTS and DISCUSSION

Table 1: Numerical factors for FFD

<table>
<thead>
<tr>
<th>Assessed Variables</th>
<th>Code</th>
<th>Low ((x))</th>
<th>High ((x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS (TEOS, M)</td>
<td>A</td>
<td>0.01</td>
<td>0.50</td>
</tr>
<tr>
<td>Concentration of Ammonia (Ammonia, M)</td>
<td>B</td>
<td>2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Dose of Fe₃O₄ (Dose, mg/25 ml)</td>
<td>C</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Addition Mode</td>
<td>D</td>
<td>One time</td>
<td>Gradually</td>
</tr>
<tr>
<td>Responses</td>
<td></td>
<td>Highest magnetic properties, Smallest PS (monodisperse), Narrowest MSD (uniform distribution).</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: The recovery concentrations of the carboxylates pesticides by using TMS grafted samples

<table>
<thead>
<tr>
<th>Carboxylates pesticides (stock 40 ppm)</th>
<th>R. (nm.)</th>
<th>Control</th>
<th>Recovered (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alicarb</td>
<td>0.091</td>
<td>35.90</td>
<td>87.75</td>
</tr>
<tr>
<td>Diazinon</td>
<td>14.06</td>
<td>19.77</td>
<td>49.42</td>
</tr>
<tr>
<td>Methiocarb</td>
<td>15.71</td>
<td>28.98</td>
<td>72.94</td>
</tr>
<tr>
<td>Propoxur</td>
<td>16.52</td>
<td>34.80</td>
<td>86.95</td>
</tr>
<tr>
<td>Promecarb</td>
<td>22.47</td>
<td>34.92</td>
<td>87.06</td>
</tr>
<tr>
<td>Carbarylcarb</td>
<td>18.01</td>
<td>42.27</td>
<td>89.57</td>
</tr>
<tr>
<td>Diazinon</td>
<td>23.85</td>
<td>73.36</td>
<td>183.2</td>
</tr>
<tr>
<td>3-Hydroxydiazinocarb</td>
<td>19.63</td>
<td>73.94</td>
<td>184.8</td>
</tr>
<tr>
<td>Methiocarb</td>
<td>20.14</td>
<td>46.78</td>
<td>116.9</td>
</tr>
<tr>
<td>TGA of Sample 1</td>
<td>0.440</td>
<td>35.90</td>
<td>87.75</td>
</tr>
<tr>
<td>TGA of Sample 2</td>
<td>0.182</td>
<td>20.14</td>
<td>46.78</td>
</tr>
</tbody>
</table>

SIGNIFICANCE

- Green and Smart Synthesis of Functionalized Nanosorbents for Wastewater Treatment from Pesticides.
- Novel Approach Using Factorial Design.

POST-PROJECT PLANS

- We have already started testing other functionalization strategies and for removal of other water contaminants, e.g. antimicrobials.
- Synthesis of polymethacrylate – functionalized silica nanoparticles has already been done in our labs.

CONCLUSION

- Fe₃O₄@SiO₂@TMS nanosorbents were successfully prepared using Massart method (magnetite core) followed by Stöber synthesis (silica coat).
- Optimum conditions for coating were obtained using a smart statistical approach; full factorial design (2⁴ – FFD).
- TMS-Functionalized mcSNPs were further applied as nanosorbents for MSPE of pesticides.