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Mesoporous silica materials: investigation of catalytic performance towards chlorinated pesticides

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INTRODUCTION

There has been a steady increase in the production and use of chemicals for agricultural activities in the past decades. This trend has generated an increase in public awareness of the effects of these compounds on the earth and in water ecosystems. Due to their chemical characteristics, pesticides, in general, are a type of pollutant that demonstrate variable persistence to photochemical, chemical, and biochemical degradation. The environmental lifetime of some of these pesticides tends to be long. The application of synthetic pesticides to control weeds, insect pests, and fungal diseases has been routine in agriculture for the past century. It has been shown that residues of these synthetic pesticides are the cause of many adverse health effects. Moreover, several kinds of pesticides have been used in many indiscriminate and haphazard ways in the past. The United Nations has reported that from the total amount of pesticides used in agriculture, less than 1% actually contacts the crops. The rest ends up in the soil or in the air, but mostly, in the water. The lack of these pollutants' biodegradability, along with their continuous accumulated use, is a considerable problem and a critical issue with potentially detrimental and unpredictable consequences for the future. Despite the undesirable characteristics of pesticides, the global sale of these products increases each year, and predominantly in developing countries, which contribute to more than 70% of the total pesticide consumption. Included among these developing countries, The widespread presence of these organic chemicals in water has motivated interest to find alternative environmental-friendly solutions for the treatment and/or removal of their residues. Many technologies for pesticide removal have been studied and reported. These include adsorption, filters, biological treatment, and advanced oxidation processes (AOPs). Nevertheless, tertiary treatment of drinking water as done in treatment plants, such as inverse osmosis or adsorption with activated carbon, seems not to be efficient and effective enough for the removal of these highly persistent pollutants. In the last few years, solar photodegradation processes have been proven to be an excellent alternative for pesticide degradation in the field of AOP. This technology degrades the pesticides in polluted water; however, the efficiency of the process is heavily dependent on the chemical nature of the pesticides being treated.

Also, catalytic degradation of chlorinated hydrocarbons is considered as a promising process, resulting potential useful chemicals, such as hydrocarbons or HC1.

SYNTHESIS

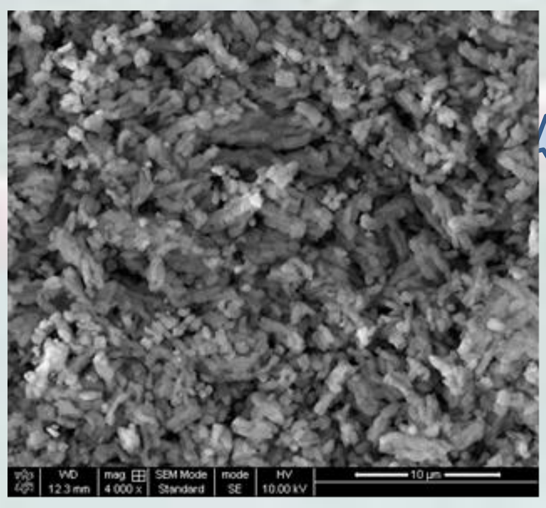
In the typical synthesis, TEOS (tretaethylorthosilicate) purchased from Sigma Aldrich (Steinheim, Germany) was introduced to an aqueous HCl (Sigma Aldrich - Steinheim, Germany) solution containing triblock copolymer Pluronic P123 (EO20PO70EO20) (Sigma Aldrich - Steinheim, Germany) (initially stirred and refluxed for 24 h at 35°°C) and hydrolysed for 24 h under stirring at 35 °C. After this time, the reaction mixture is autoclaved at 120 °C for 24 h, and then it is filtered, washed and dried. The obtained powder is calcined at 60 0°C for 8 h in order to obtain SBA-15 with highly ordered structure.

The synthesis of amino-SBA-15 was carried out in toluene. APTES was added into the SBA-15 – toluene mixture slowly. The resultant mixture was stirred and refluxed at 120 °C for 9 h. The solid product was filtered, washed with toluene and diethyl ether. The solid product was filtered, washed with toluene and diethyl ether and then it was submitted to a continuous extraction with diethyl ether/dichloromethane (1/1, v/v/) using Soxhlet at 100 °C and then it was dried at room temperature overnight. The metallic material was synthesized through mesoporous silica (0.3 g) impregnation with 0.5 mL aqueous solution of $Ni(CH_3COO)_2$ (1 M).

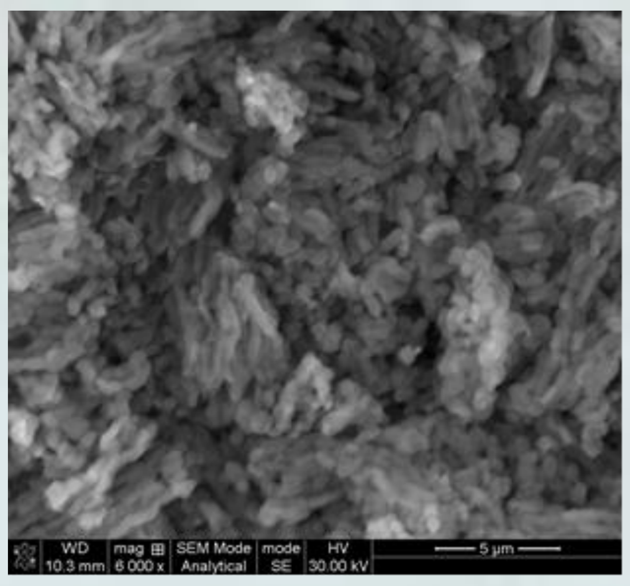
CATALYTIC EXPERIMENTS

Catalytic reactions were carried out in 25 mL stainless steel Anton Paar reactor at ambient temperature and pressure.

RESULTS AND DISCUSSION



SEM image for SBA-15



SEM image for Ni-amino-SBA-15

FTIR spectra

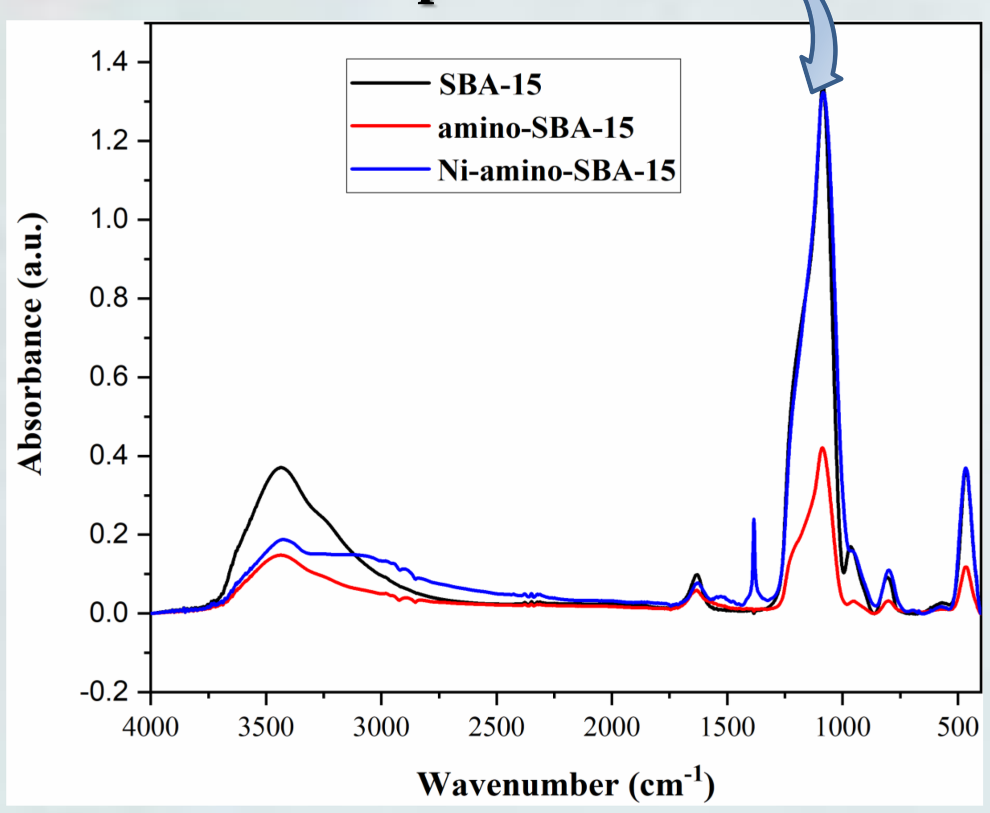
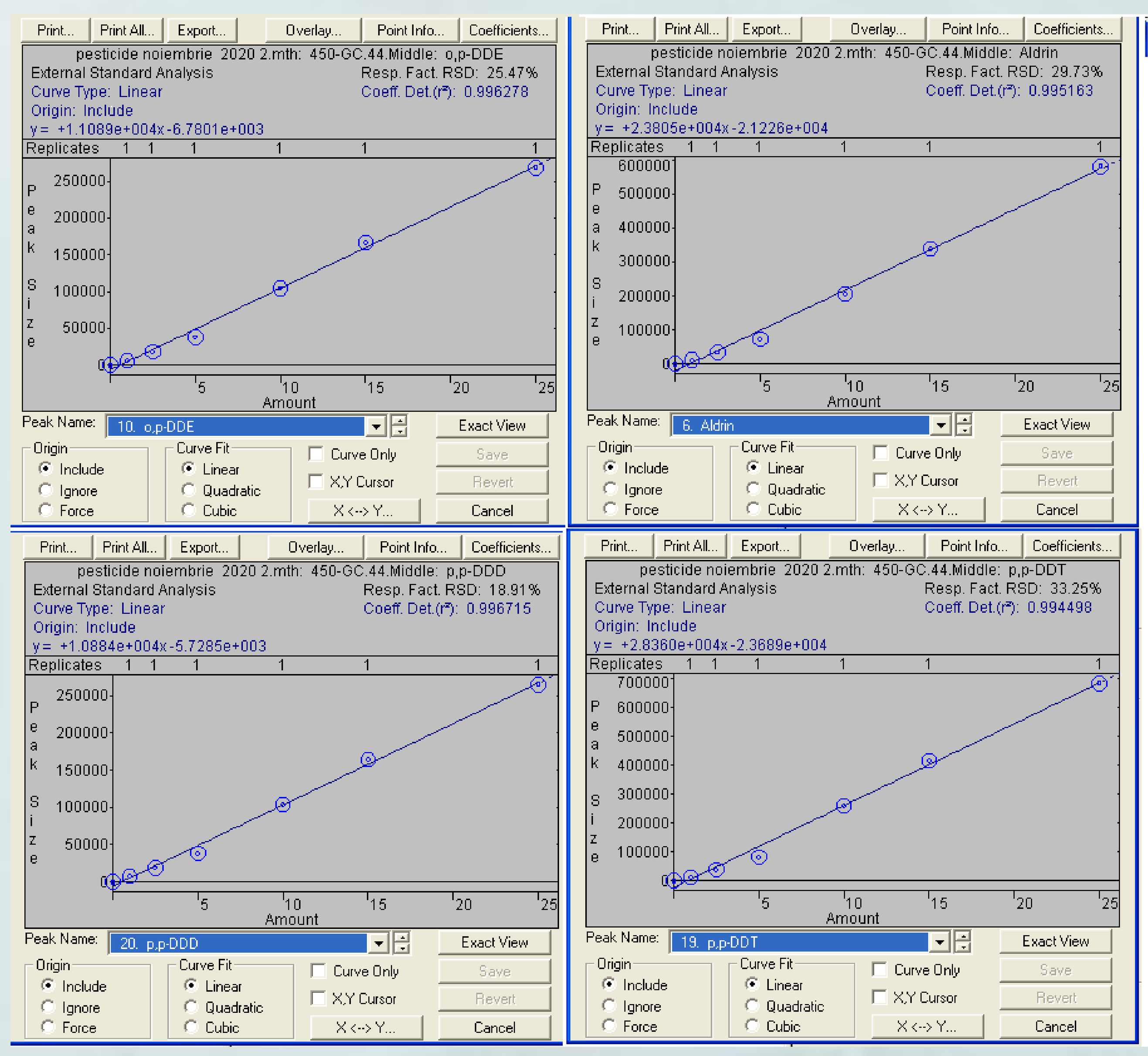
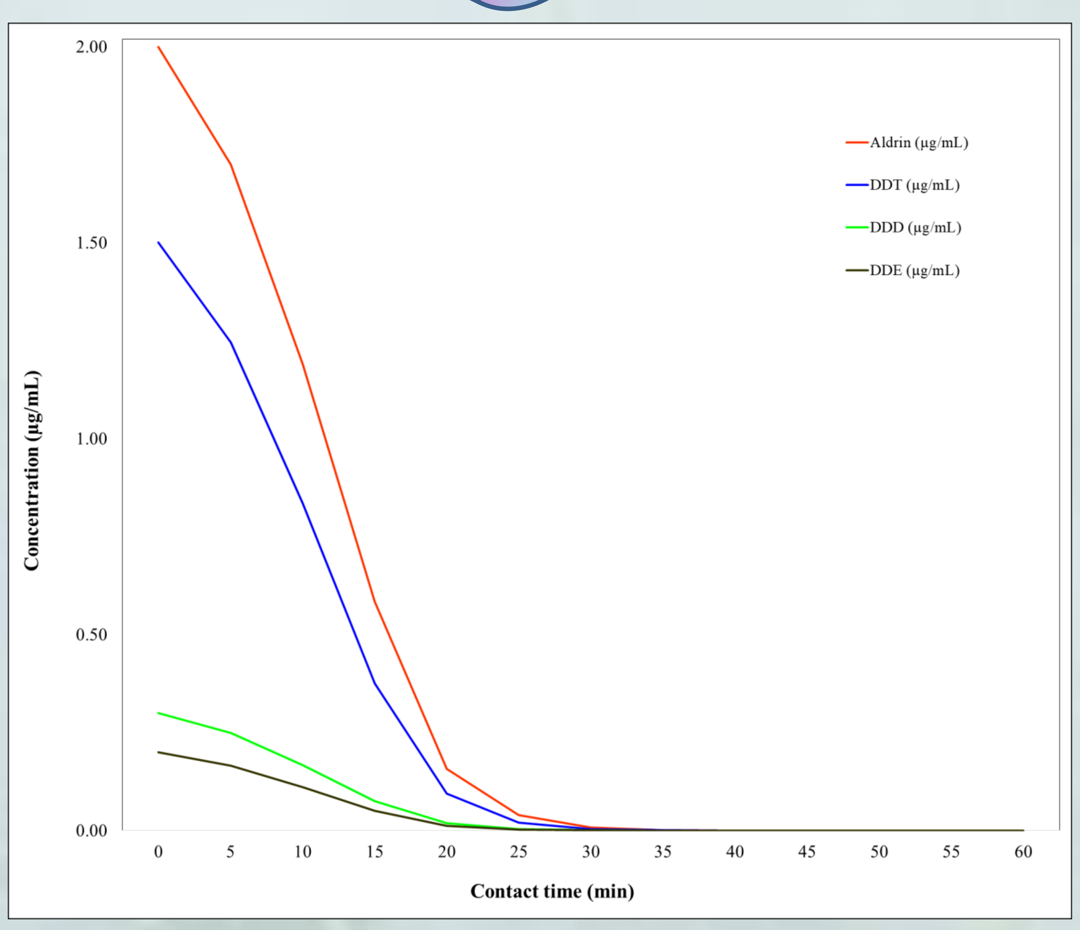


Table. Textural properties of silica nanomaterials

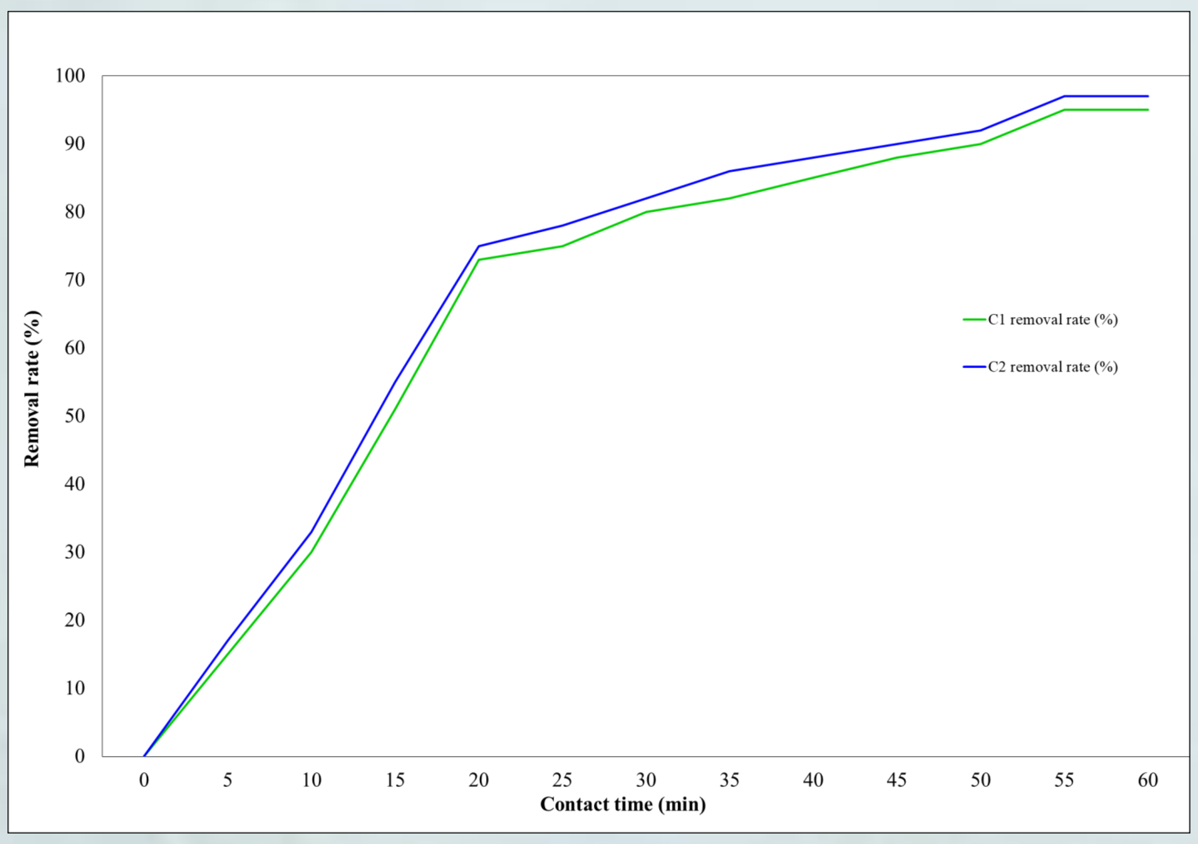
Material	S_{BET} (m^2/g)	V_{mp} (cm^3/g)	d_p (nm)
SBA-15	1108	0.99	6.1
Amino-SBA-15	499	0.94	3.4
Ni-amino-SBA-15	378	0.14	3.2



GC-MS calibration curves



Concentration variation after catalysis



Degree of pollutants elimination

Contact time (min)	Aldrin (μg/mL)	DDT (μg/mL)	DDD (μg/mL)	DDE (μg/mL)
0	2.0000000000	1.5000000000	0.3000000000	0.2000000000
5	1.7000000000	1.2450000000	0.2490000000	0.1660000000
10	1.1900000000	0.8341500000	0.1668300000	0.1112200000
15	0.5831000000	0.3753675000	0.0750735000	0.0500490000
20	0.1574370000	0.0938418750	0.0187683750	0.0125122500
25	0.0393592500	0.0206452125	0.0041290425	0.0027526950
30	0.0078718500	0.0037161383	0.0007432277	0.0004954851
35	0.0014169330	0.0005202594	0.0001040519	0.0000693679
40	0.0002125400	0.0000624311	0.0000124862	0.0000083241
45	0.0000255048	0.0000062431	0.0000012486	0.0000008324
50	0.0000025505	0.0000004994	0.0000000999	0.0000000666
55	0.0000001275	0.0000000150	0.0000000030	0.0000000020
60	0.0000000064	0.0000000004	0.0000000001	0.0000000001

CONCLUSIONS

In summary, ordered mesoporous silica nanomaterials with different surface properties have been successfully synthesized. The obtained nanosilica catalysts have ordered hexagonal mesostructures, uniform pore size distributions, and high surface areas for removal pf organochlorine pesticides from waters.

Acknowledgements

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