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Functionalized SBA-3 silica: investigation of adsorption performance towards glyphosate herbicide

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INTRODUCTION

Glyphosate (N-(phosphonomethyl) glycine, $C_3H_8NO_5P$) is a very common type of non-selective herbicide, which can inhibit the growth of unwanted plants by controlling enzymatic activity, suppressing the synthesis of aromatic amino acids. Glyphosate creates ecological toxicity through bio-magnification, as it enters the ecosystem. Human exposure to groundwater, surface water, food contamination and bioaccumulation has been associated with negative reproductive outcomes. Toxicological effects include acute poisoning, chronic / subchronic toxicity, genotoxicity, carcinogenicity and nephrotoxicity. The latest data published by the United States Environmental Protection Agency (EPA) set a maximum limit for glyphosate in drinking water of 0.7 mg/L. The toxicity of glyphosate is aggravated by the ability to form complexes with heavy metals. Consumption of pesticides, including glyphosate, is estimated at two million tonnes per year, of which 48% in Europe. A recent study showed a possible link between glyphosate exposure and kidney abnormalities in newborns, infants and young children.

Silica nanoparticles typically create a positive surface charge through the anionic attraction of molecules, which tend to undergo self-aggregation during the adsorption process. The hydrophobic nature of silica limits its ability to attract ions; therefore covalent bond functionalization is used to improve surface affinity.

The objectives of the present study were: (1) synthesis of mesoporous silica nanoparticles with subsequent functionalization and characterization by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), determination of specific surface and pore size; (2) adsorption experiments to determine the removal capacity of the glyphosate herbicide; (3) investigation of the adsorption mechanism by isothermal and kinetic study.

SYNTHESIS

SBA-3 mesoporous silica was prepared using cetyltrimethyl-ammonium bromide and tetraethyl orthosilicate as the template and source of Si, respectively. An aqueous solution of HCl (37%) was added to control the pH of the system reaction. Thus, 2 g of CTAB and 40 mL of HCl (37%) were dissolved in 100 mL of ultrapure water. TEOS (10 mL) was added dropwise to the acidic solution of CTMABr with vigorous stirring at 30 °C. After 2 hours, the white precipitate (precursor SBA-3) was aged at room temperature for 12 hours. The sample was then filtered and dried for 12 hours at 100 °C. SBA-3 was then immersed at reflux in ethanol for 6 hours to extract the surfactant; after that, the precipitate was filtered and washed with ultrapure water. After drying, SBA-3 mesoporous silica was calcined at 550 °C in air for 6 hours.

The support, SBA-3 (1 g), was immersed in anhydrous toluene (25 mL) to which 1 mL of aminopropyltriethoxysilane was added. The obtained mixture was refluxed for 5 h at 120 °C, under stirring, after which it was left only under stirring until the next day. Subsequently, the mixture was centrifuged for 15 minutes at 4500 rpm, washed three times with a minimum amount of ethanol, the alcohol being removed by centrifugation under the same conditions. The resulting white-yellow precipitate was dried in an oven at 80 °C, under vacuum.

ADSOPRTION TESTING

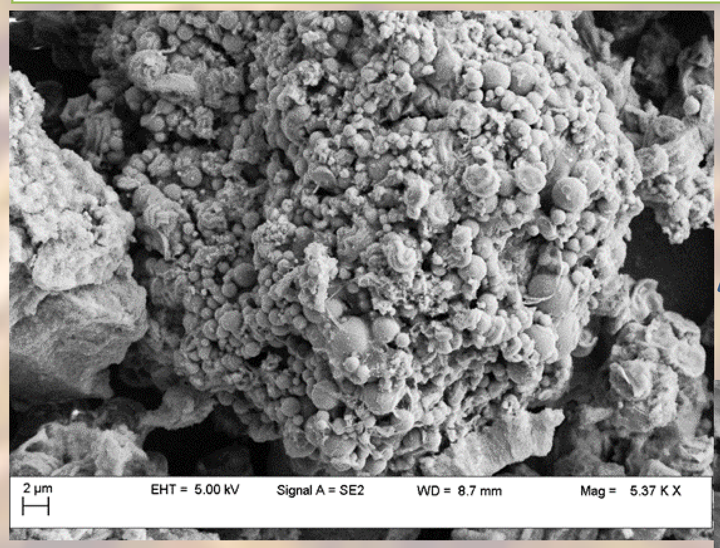
Two solutions of glyphosate in water were prepared, one with a concentration of 5.15 g/L (notation C1), the other with 0.515 mg/L glyphosate (notation C2), starting from a commercial product with an initial concentration of 360 mg/L. A product of Roundup Classic Pro type (Monsanto, Bucharest, Romania) containing potassium glyphosate salt-N-(phosphonomethyl) glycine was used. Reactions were monitored by determining total phosphorus concentration using HACH LANGE LCK 349-350 total phosphorus reagent kits (Hach Lange GmbH, Dusseldorf, Germany) and total organic carbon concentration using HACH LANGE LCK 380-381 TOC kits (Hach Lange GmbH, Dusseldorf, Germany); concentration readings were performed using the visible HACH DR 3900 spectrophotometer (HACH, Loveland, CO, U.S.).

RESULTS AND DISCUSSION

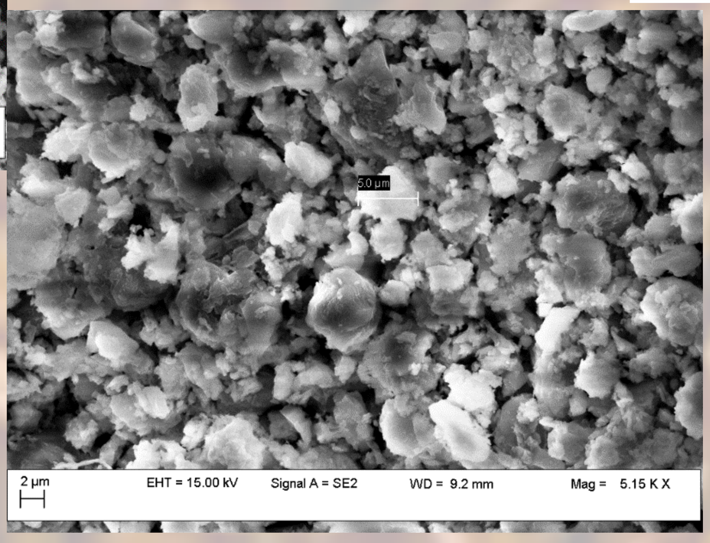
The presence of oxygen, carbon and iron was confirmed by elemental analysis and EDS.

Table. Elemental analysis and EDS

Sample	C (%)	H (%)	O (%)	Si (%)	N (%)
SBA-3	0.40	0.64	50.25	48.71	-
amino-SBA-3	19.88	2.80	36.51	35.01	5.80

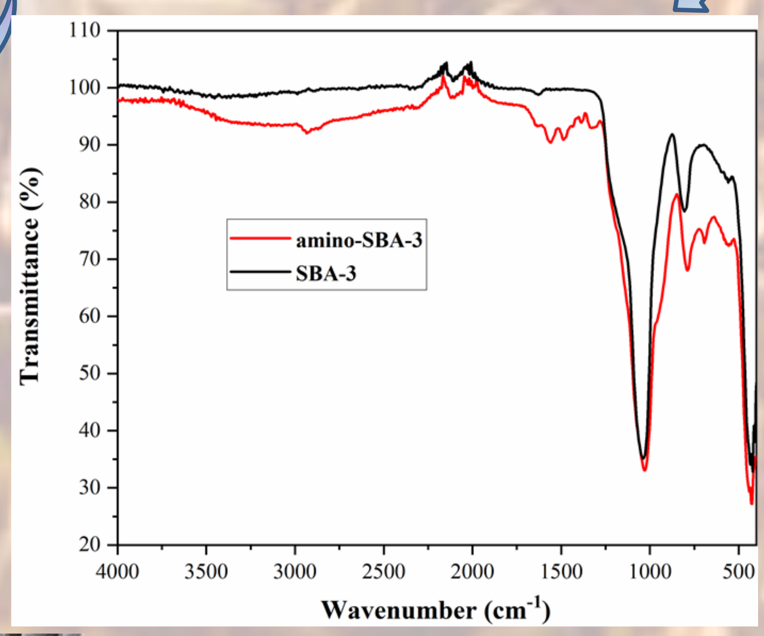


SEM image for SBA-3

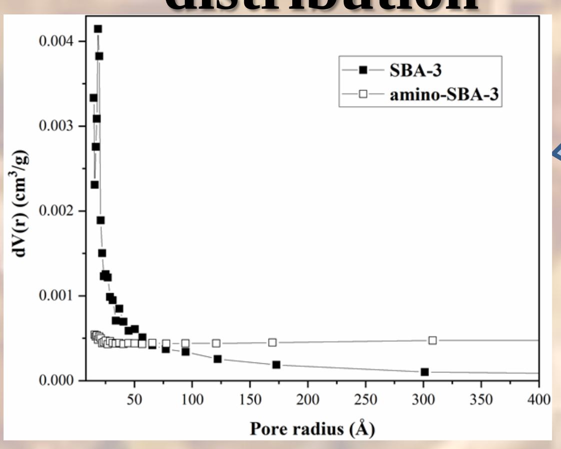


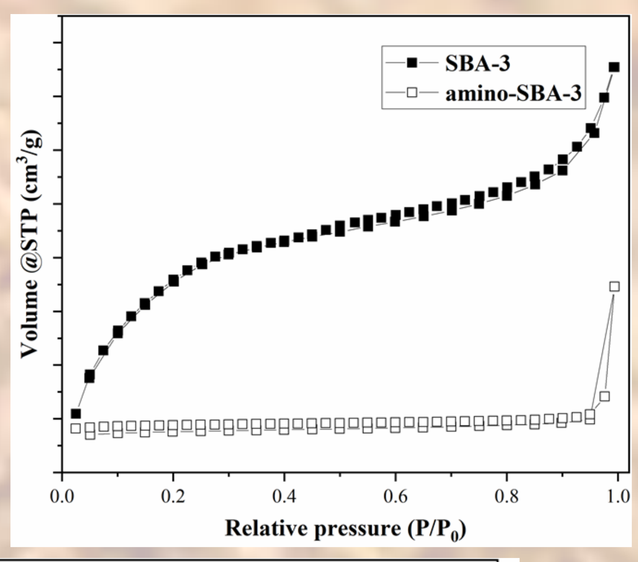
SEM image for amino-SBA-3

FTIR spectra



Adsorption-desorption isotherm and pores distribution





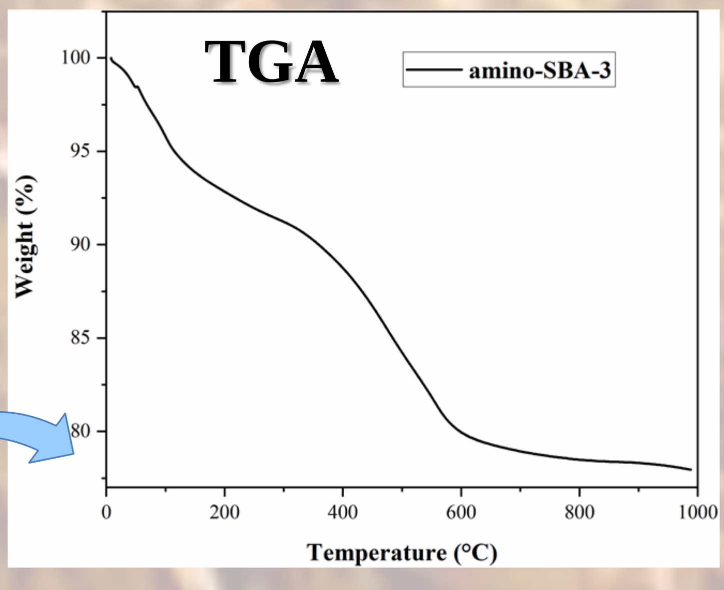
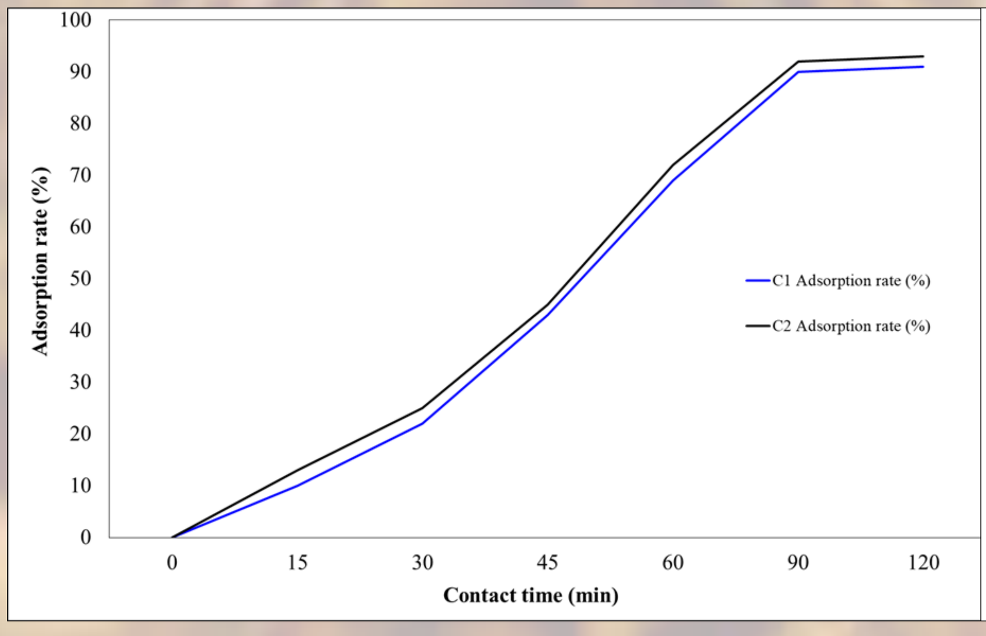


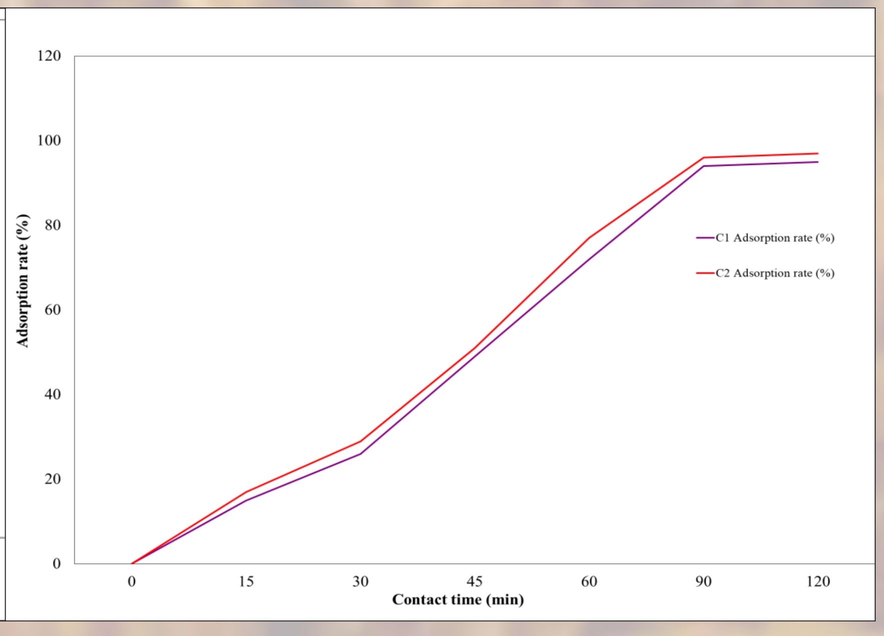
Table. Textural properties of silica nanomaterials

Sample	S_{BET} (m^2/g)	d_{pBJH} (nm)	V_{mp} (cm^3/g)
SBA-3	600	3.8	0.127
amino-SBA-3	14	3.2	0.081

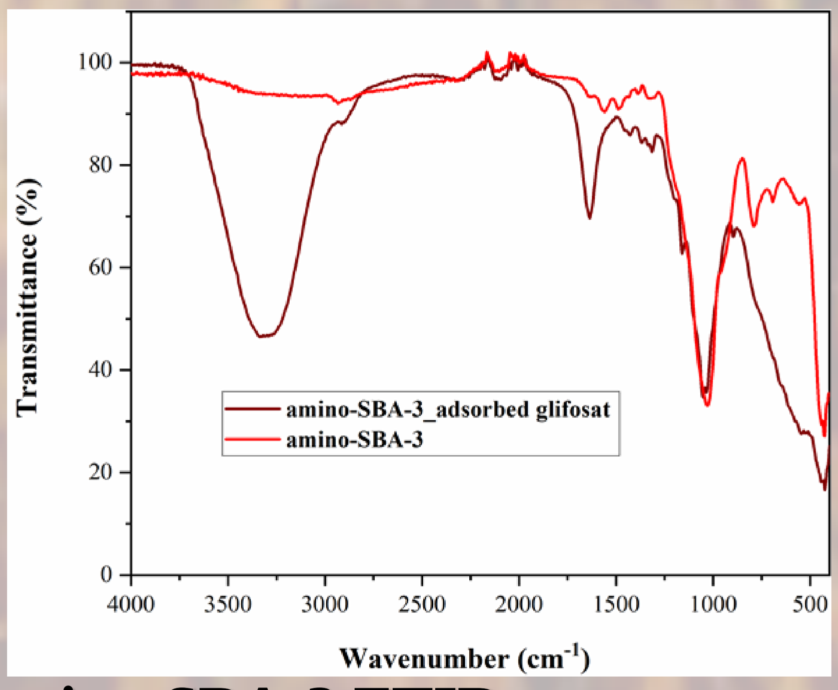
In the case of amino-SBA-3, three weight loss ranges were visible: 30-115 °C - attributed to water loss, 115-330 °C - attributed to fragmentation of APTES attached to the surface of silica, and 330-630 °C - attributed to the disturbance of the remaining mesoporous structure. The total weight loss was approximately 20.5%.



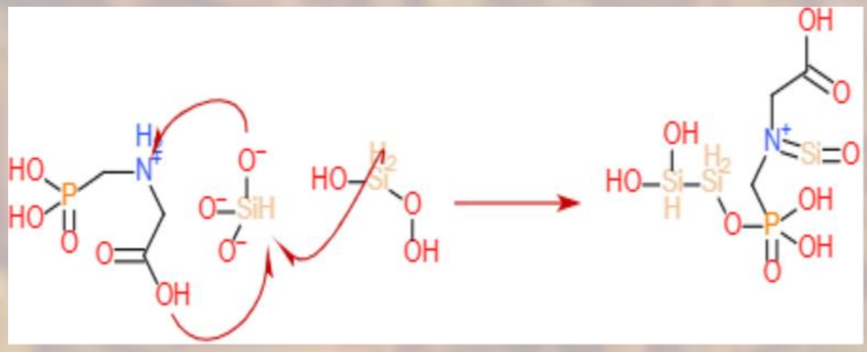
Degree of organic phosphate elimination depending on the total phosphorus content



Degree of organic phosphate elimination depending on the total organic carbon content



Amino-SBA-3 FTIR spectrum after glyphosate adsorption



Potential mechanism for the interaction between amino-SBA-3 and glyphosate

CONCLUSIONS

Amino-functionalized silica nanoparticles were successfully synthesized by post-synthesis grafting of amino groups. The material was characterized by SEM-EDS, FTIR, adsorption-desorption of N2, the results showing the obtaining of a material with ordered structure and high adsorption capacity.

This study showed that amino-SBA-3 mesopic silica can be used as a suitable adsorbent for the removal of phosphates from water. The results showed that mesopic silica was better suited for glyphosate adsorption following the Henry isotherm model and that the reaction was spontaneous and feasible. It can be concluded that amino-SBA-3 could be recommended as an adsorbent for the removal of organic phosphates from aqueous solutions. Next, the study will look at the use of other synthesized nanomaterials in reducing the concentration of phosphates in water, as well as testing them in the removal of inorganic phosphates.

Acknowledgements

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