

# DIFFERENTIAL PULSE VOLTAMMETRIC STUDIES OF NITROBENZENE ON SILICA NANOPARTICLE MODIFIED ELECTRODES

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## ABSTRACT

Differential pulse voltammetry (DPV) was employed for the sensitive electrochemical detection of nitrobenzene (NB) using a glassy carbon electrode modified with silica nanoparticles derived sustainably from *Zea mays* L. (Poaceae) husk through a simple, template-free, reagent-free combustion process. The synthesized nanoparticles were characterized by FTIR, XRD, EDX, AFM, and TGA, confirming their functional, structural, morphological, elemental, and thermal properties. The mesoporous structure and abundant surface silanol groups facilitated NB interaction and electrochemical reduction. The modified electrode achieved a detection limit of 1.1805  $\mu\text{M}$  with excellent linearity ( $R^2 \approx 0.99$ ), demonstrating the potential of maize husk-derived silica as a simple, cost-effective, and sustainable electrode material for DPV-based NB monitoring.

**Keywords:** electrochemical sensor, silica nanoparticles, maize husk, DPV and nitrobenzene.

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## INTRODUCTION

Differential pulse voltammetry (DPV) is a sensitive electrochemical technique widely used to detect trace amounts of environmental pollutants. By minimizing capacitive current and amplifying the faradaic response, DPV offers high sensitivity, a favorable signal-to-noise ratio, and rapid analysis; consequently, it is well-suited for the detection of nitrobenzene (NB), a toxic and persistent nitroaromatic pollutant. Electrochemical detection represents a rapid, simple, cost-effective, and potentially portable approach for monitoring NB, although sensor performance depends heavily on the material used to modify the electrode<sup>1-3</sup>.

Silica nanoparticles, particularly mesoporous silica nanoparticles (MSNs), exhibit high specific surface area, tunable porosity, good stability, and an abundance of surface silanol groups. These properties provide active sites for analyte interaction and facilitate both mass and electron transfer processes, making silica nanoparticles promising materials for electrochemical detection. Their incorporation into glassy carbon electrodes (GCEs) can enhance the electrochemical response toward target pollutants<sup>4,5</sup>.

Corn husks constitute an abundant, silica-rich agricultural waste product that is typically disposed of via burning or landfilling. Their use as a renewable silica precursor offers a sustainable and cost-effective approach to waste valorization, while

reducing reliance on conventional resources and supporting circular economy principles<sup>1,6-8</sup>.

In this study, silica nanoparticles were synthesized from *Zea mays* L. (Poaceae) husks using an eco-friendly, template-free process and subsequently characterized in terms of their structural, morphological, elemental and thermal properties. The synthesized nanoparticles were used to modify a glassy carbon electrode; Subsequently, its efficacy for the electrochemical detection of nitrobenzene was evaluated using DPV. This work demonstrates a sustainable approach to developing a simple, sensitive, and environmentally friendly sensing platform for monitoring nitrobenzene in aqueous media.

## MATERIALS AND METHODS

### Materials

*Zeamays*L. (Poaceae) husks were collected from an agricultural field in Ketchilapuram, Thoothukudi, while hydrochloric acid (LR grade) was procured from ISOICHEM.

### Synthesis of Silica nanoparticles

Husk of *Zea mays* L. (Poaceae) was thoroughly rinsed with distilled water, oven-dried at 100 °C, pulverized, and subjected to calcination at 550 °C for 8 h to produce silica-enriched ash<sup>1,7,8</sup>. The resulting ash was subsequently purified with concentrated HCl to eliminate metallic contaminants, followed by repeated washing until a

neutral pH was attained. After drying for 2 h, the purified material was finely milled to obtain uniform mesoporous silica nanoparticles (Si-SCH).

#### Preparation of silica modified glassy carbon electrode

The glassy carbon electrode (GCE, 3 mm) was polished with 0.05  $\mu\text{m}$  alumina, ultrasonically cleaned in ethanol and deionized water for 10 min, and subsequently dried. 5 mg of Si-SCH were dispersed in 10 mL of deionized water, and the mixture was subjected to ultrasonic treatment for 20 min. Next, 10  $\mu\text{L}$  of the suspension were deposited onto the GCE using the drop-casting technique and dried at room temperature to obtain the GCE/Si-SCH electrode.

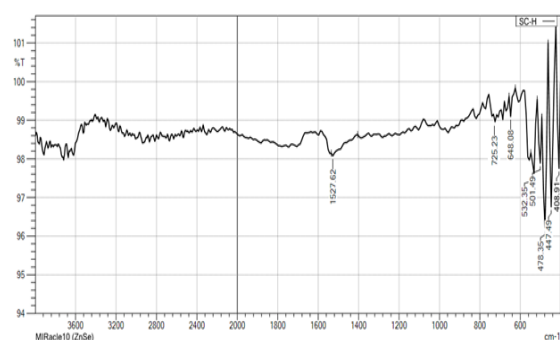
#### Characterization techniques

Si-SCH nanoparticles were characterized using FTIR, AFM, EDX, XRD and TG/DTA to evaluate their functional groups, morphology, elemental composition, crystallinity, and thermal stability, respectively. Electrochemical measurements were performed at 25  $^{\circ}\text{C}$  using a glassy carbon electrode (GCE, 0.07  $\text{cm}^2$ ) modified with Si-SCH, employing Ag/AgCl and Pt electrodes as the reference and counter electrodes, respectively.

### RESULTS AND DISCUSSION

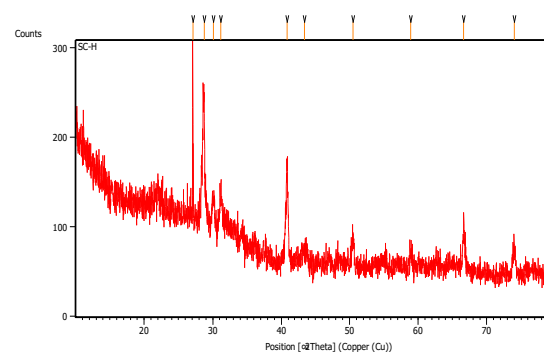
#### FT-IR Analysis

The FTIR spectrum of the synthesized  $\text{SiO}_2$  nanoparticles (400–3800  $\text{cm}^{-1}$ ; Fig. 1) shows the characteristic vibrations of silica. The band at 1527  $\text{cm}^{-1}$  corresponds to the O–H stretching of adsorbed water<sup>5,8</sup>, indicating moisture physisorption through the porous network<sup>1,5</sup>. The band at approximately 725  $\text{cm}^{-1}$  is attributed to symmetric Si–O stretching, with possible residual Si–Si and C–H contributions<sup>8,9</sup>. The bands at 648.08, 532.35 and 501.49  $\text{cm}^{-1}$  originate from Si–O–Si<sup>1,8</sup> bending and rocking vibrations, while the peaks at 478.35, 447.49 and 408.91  $\text{cm}^{-1}$  correspond to O–Si–O bending vibrations<sup>9,11,12</sup>.



**Fig 1:** FT-IR spectrum for Si-SCH nanoparticles

The structural characteristics of the synthesized silica nanoparticles were analyzed using X-ray diffraction (XRD) (Fig. 2). The average crystallite size was calculated using the Scherrer equation ( $D = k\lambda/\beta\cos\theta$ ), yielding a value of 5.8069 nm.

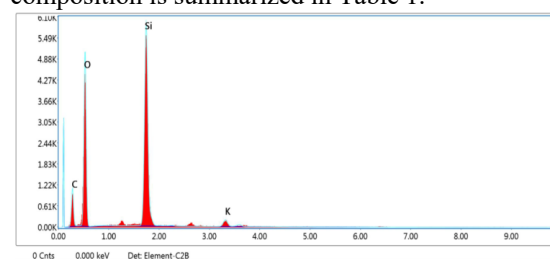


**Fig 2:** XRD Spectrum of Si-SCH nanoparticles

The XRD pattern ( $2\theta = 20\text{--}70^{\circ}$ ) showed peaks at  $21\text{--}22^{\circ}$ ,  $26\text{--}27^{\circ}$ ,  $36\text{--}38^{\circ}$ ,  $50^{\circ}$ ,  $60^{\circ}$ , and  $68\text{--}75^{\circ}$ , corresponding to the (100), (101), (111), (202), (220), and (213) planes of trigonal  $\alpha$ -quartz  $\text{SiO}_2$ , consistent with JCPDS 46-1045 and COD 96-810-3514<sup>13,14</sup>. The pattern confirms predominantly amorphous silica with minor crystalline features and partial long-range order.

#### EDAX Analysis

The EDAX spectrum of  $\text{SiO}_2$  nanoparticles (Fig. 3) displays characteristic O K $\alpha$  ( $\sim 0.5$  keV) and Si K $\alpha$  (1.7–2.0 keV) peaks, confirming silica formation. Minor C and K signals are attributed to the mounting tape and residual biomass components<sup>15</sup>, respectively. The elemental composition is summarized in Table 1.



**Fig 3:** EDAX Spectrum of Si-SCH nanoparticles

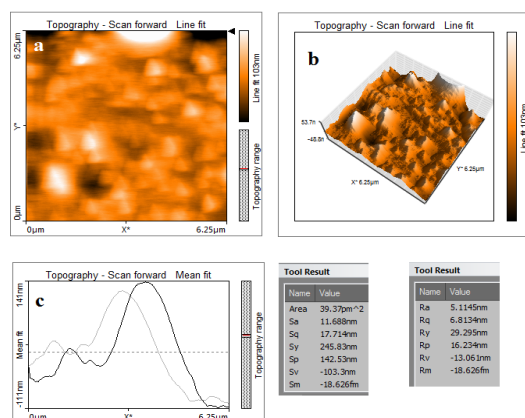
**Table 1:** Elemental Composition of Si-SCH nanoparticles

| Element | Atomic % | Weight % |
|---------|----------|----------|
| Si      | 32.8     | 47.1     |
| O       | 67.0     | 52.4     |
| C       | 0.2      | 0.3      |
| K       | 0.0      | 0.2      |

#### Atomic Force Microscopy (AFM)

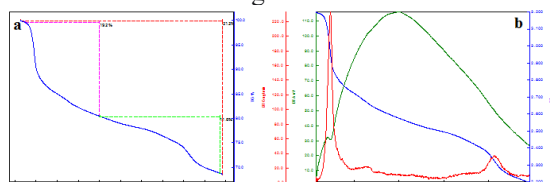
Atomic Force Microscopy (AFM) analysis was performed over a  $6.25 \times 6.25 \mu\text{m}^2$  scan area to investigate the surface topography and nanoscale roughness of the synthesized silica shown in fig 4. The 2D and 3D images (fig 4(a) & (b)) revealed a heterogeneous surface with uniformly distributed nanoscale grains and distinct elevations and depressions. The cross-sectional profile (fig 4(c)) showed height variations from approximately  $-111$

to +141 nm. The areal roughness parameters,  $S_a = 11.688$  nm,  $S_q = 17.714$  nm, and maximum peak-to-valley height ( $S_y = 245.83$  nm), together with linear parameters  $R_a = 5.1145$  nm and  $R_q = 6.8134$  nm, confirmed a moderately rough and well-defined nanostructured surface. Such surface heterogeneity can enhance the accessibility of active sites and promote surface interactions, making the synthesized silica suitable for adsorption and catalytic applications.



**Fig 4:** AFM of Si-SCH nanoparticles  
**Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA) of Si-SCH (Fig. 5a) reveals a total mass loss of 31.39%, of which 19.2% occurs below 380 °C and 11.6% between 380 and 970 °C. The initial loss (< 150 °C) is due to physically adsorbed moisture, followed by the removal of water hydrogen-bonded to the silanol groups (150–450 °C) <sup>1,9</sup>. The final loss (450–900 °C) results from the condensation of Si–OH bonds into Si–O–Si bonds and the densification of the network <sup>1,9</sup>. The negligible mass loss above 950 °C confirms high thermal stability. The TGA-DTG-DTA curves (Fig. 5b) corroborate these three stages of thermal transformation, with the corresponding endothermic and exothermic DTA signals.

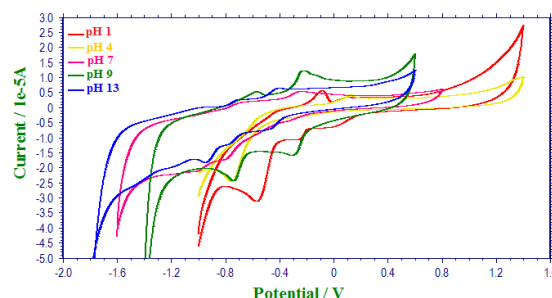


**Fig 5:** (a) TGA Curve (b) Combined TG, DTG and DTA curves for Si-SCH

## Electrochemical Studies

### Effect of pH

The effect of pH on the electrochemical reduction of nitrobenzene (80  $\mu$ M) was investigated via cyclic voltammetry using a GC/Si-SCH electrode in buffer solutions at pH 1, 4, 7, 9 and 13.

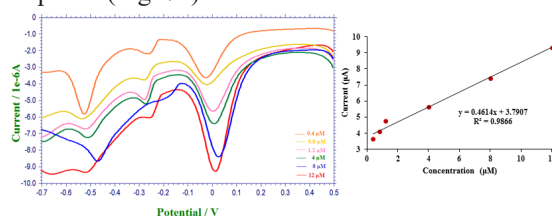


**Fig. 6:** CV of nitrobenzene reduction at GC/Si-SCH at various pH values (50 mV/s)

Increasing the pH caused a shift in the reduction peak toward more negative potentials, confirming the involvement of protons and electrons in the reduction process<sup>16</sup>. The highest reduction current (31.47  $\mu$ A) was obtained at pH 1 at a potential of approximately  $-0.05$  V (Fig. 6); consequently, pH 1 was selected for subsequent detection studies. This enhanced response was attributed to surface silanol (–OH) groups, which facilitate the adsorption and reduction of nitrobenzene. All subsequent measurements were performed at pH 1 with a scan rate of 50 mV s<sup>–1</sup>.

### Effect of Concentration by DPV

Figure 7a shows the DPV responses of the GC/Si-SCH electrode to nitrobenzene (0.4–12  $\mu$ M) at pH 1, using a potential increment of 4 mV, a pulse amplitude of 25 mV, and a frequency of 15 Hz. Three distinct cathodic peaks, located at approximately +0.01,  $-0.25$ , and  $-0.50$  V, correspond to the successive reductions (involving, in each case, two electrons and two protons) of nitrobenzene to nitrosobenzene, phenylhydroxylamine and aniline, respectively. The increase in peak intensity with NB concentration indicates a diffusion-controlled process<sup>16</sup>. The calibration curve was established based on the peak located near 0 V, which exhibited the highest current response (Fig. 7b).



**Fig7:** (a) DPV of nitrobenzene reduction at GC/Si-SCH at various concentrations  
(b) Current vs. nitrobenzene concentration using DPV at GC/Si-SCH.

A strong linear relationship was observed between the cathodic peak current ( $I_p$ ) and nitrobenzene concentration, with  $R^2 = 0.9866$ , confirming good sensor linearity [28,29]. The LOD and LOQ, calculated using  $3.3\sigma/S$  and  $10\sigma/S$ , were 1.1805  $\mu$ M and 3.5774  $\mu$ M, respectively. The GC/Si-SCH electrode showed a sensitivity of 14.6955  $\mu$ A  $\mu$ M<sup>–1</sup>, attributed to its enhanced electroactive surface area and efficient electron transfer, which promote the electrochemical reduction of nitrobenzene. Table

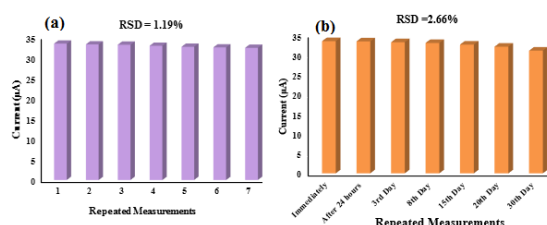
2 compares its performance with previously reported nitrobenzene sensors.

**Table 2:** LOD of the sensor in comparison to previously reported NB sensors.

| Electrode Material                                          | Analytical Technique | Detection Limit | References   |
|-------------------------------------------------------------|----------------------|-----------------|--------------|
| GC/EDAS/(g-C <sub>3</sub> N <sub>4</sub> -Ag) <sub>NC</sub> | SQW                  | 2 $\mu$ M       | [17]         |
| OMC/DDAB/GC                                                 | LSV                  | 10 $\mu$ M      | [18]         |
| Ag/ATP/GCE                                                  | LSV                  | 1.1 $\mu$ M     | [19]         |
| GC/Au MOF-5                                                 | CV                   | 1.0 $\mu$ M     | [20]         |
| C60/CPE                                                     | SDCV                 | 30 $\mu$ M      | [21]         |
| GC/Si-SCH                                                   | DPV                  | 1.1805 $\mu$ M  | Present Work |

#### Repeatability Study

The repeatability of the GC/Si-SCH electrode was evaluated by seven successive nitrobenzene DPV measurements at 80  $\mu$ M and pH 1 (Fig. 8a). Virtually identical reduction peaks were obtained, with a coefficient of variation (CV) of 1.19%, confirming excellent repeatability, reproducibility, and reliability.



**Fig 8: (a)** Repeatability (b) Stability of GC/Si-SCH for 80  $\mu$ M nitrobenzene at pH 1 by DPV.

#### Stability Study

The stability of the GC/Si-SCH electrode was evaluated for 30 days using an 80  $\mu$ M nitrobenzene solution at pH 1 (Fig. 8b). The electrode showed stable current responses, with minimal variation and a coefficient of variation (CV) of 2.66%, confirming its excellent stability and suitability for long-term nitrobenzene detection.

#### CONCLUSION

Differential pulse voltammetry (DPV) confirmed the efficacy of the GC/Si-SCH electrode for nitrobenzene detection. Silica nanoparticles derived from *Zeamays*\*L. (*Poaceae*) husks were prepared using a simple, reagent-free combustion process. The electrode exhibited a limit of detection of 1.1805  $\mu$ M, a sensitivity of 14.6955  $\mu$ A  $\mu$ M<sup>-1</sup>, good linearity and selectivity, as well as excellent repeatability (RSD = 1.19%) and stability (RSD = 2.66%). Compared to nitrobenzene sensors described in the literature, the GC/Si-SCH electrode offers a competitive limit of detection using only biomass-derived silica as a modifying agent, without noble metals, dopants, or complex compounds. Overall, it constitutes a simple, cost-effective, and sustainable platform for nitrobenzene monitoring via DPV.

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#### REFERENCES

1. Rachel DCJ, Vedhi C, Sivagami S, Vimala P, Subramanian S. Electrochemical Studies of Nitrobenzene using Novel Mesoporous Silica Nanoparticles as Working Electrode, Synthesised from Silk of Zea mays L. (*Poaceae*) Waste. *International Journal of Drug Delivery Technology*. 2026;16(6):1319-1337. DOI: 10.25258/ijddt.16.6.169.
2. Lailiyah NTE, Darmayanti MR, Mulyana N, Nuryatin N, Hapiddin A, Basuki B, Zuas O, Rahmah SA, Fadhila AN, Aryana N, Kurniawan HH, Andreas A, RestuWK, Aulia F, Sudiro T, Nanto D. Amorphous silica microsphere from openly burned rice husk ash as an efficient adsorbent for ultrasound-assisted methylene blue removal. *Rasayan Journal of Chemistry*. 2024;17(1):95-104. DOI: 10.31788/RJC.2024.1718726.
3. Sharma A, Kumar D, Kumar V, Singh SP, Sharma AR, Sharma SK. Electronic structure and chemical states of green synthesized silica nanoparticles from biomasses. *Hybrid Advances*. 2024;5:100133. DOI: 10.1016/j.hybadv.2023.100133.
4. Terhürne T, Amochkina T, Bruns S, Farr P, Melzig T, Trubetskov MK, Vergöhl M. Optical dispersion and band gap of Silicon-SiO<sub>2</sub> quantizing nanolaminates. *Applied Optics*. 2026;65(5):A113-A121. DOI: 10.1364/AO.575179.
5. Flores-Contreras EA, Gonzalez-Gonzalez RB, Pizana-Aranda JJP, Parra-Arroyo L, Rodriguez-Aguayo AA, Iniguez-Moreno M, Gonzalez-Meza GM, Araujo RG, Ramirez-Gamboa D, Parra-Saldivar R, Melchor-Martinez EM. Agricultural waste as a

- sustainable source for nanoparticle synthesis and their antimicrobial properties for food preservation. *Frontiers in Nanotechnology*. 2024;6:1346069. DOI: 10.3389/fnano.2024.1346069.
6. Yaqueen MN, Kuity A, Ahmed MA. Sustainable Nano Silica Production from Agricultural Residues: A Review of Green Synthesis Techniques and Performance in Asphalt Applications. *International Journal of Pavement Research and Technology*. 2025;19(8):2056-2073. DOI: 10.1007/s42947-025-00585-6.
7. Nazir I, Haq ZU, Bashir A, Qureashi A, Ganaie FA, Fatima K, Irfan S, Dar GN, Pandith AH. Electrochemical detection and catalytic reduction of nitrobenzene using a bimetallic NiS<sub>2</sub>/Fe<sub>3</sub>S<sub>4</sub> magnetic heterostructure: an innovative approach for environmental remediation. *New Journal of Chemistry*. 2024;48:4909-4921. DOI: 10.1039/D3NJ05947B.
8. Sonawane LD, Mandawade AS, Gite AB, Shinde SD, Patil GE, Nikam LK, Goswami VH, Bhise RB, Sarawade PB, Shinde MS. Sol-gel synthesis of silicon oxide (SiO<sub>2</sub>) nanoparticles: exploring gas sensing and photocatalytic applications. *Journal of Materials Science: Materials in Engineering*. 2025;20:8. DOI: 10.1186/s40712-025-00209-8.
9. Peralta YM, Molina R, Moreno S. Chemical and structural properties of silica obtained from rice husk and its potential as a catalytic support. *Journal of Environmental Chemical Engineering*. 2024;12(2):112370. DOI: 10.1016/j.jece.2024.112370.
10. Meftah A, Hani A, Merdas A. Extraction and Physicochemical Characterization of Highly-pure Amorphous Silica Nanoparticles from Locally Available Dunes Sand. *Chemistry Africa*. 2023;6:3039-3048. DOI: 10.1007/s42250-023-00688-2.
11. Rezaei F, Ahmed ZZ, Zohuri GH. Eco-Friendly Synthesis of Flower-Wrinkle Silica Nanoparticles From Rice Husk. *Advances in Polymer Technology*. 2025;2025:8896690. DOI: 10.1155/adv/8896690.
12. Ellerbrock RH, Stein M, Schaller J. Comparing silicon mineral species of different crystallinity using Fourier transform infrared spectroscopy. *Frontiers in Environmental Chemistry*. 2024;5:1462678. DOI: 10.3389/fenvc.2024.1462678.
13. International Centre for Diffraction Data (ICDD). Powder Diffraction File (PDF-2), Card No. 46-1045,  $\alpha$ -Quartz (SiO<sub>2</sub>). 2004.
14. Gražulis S, Chateigner D, Downs RT, Yokochi AFT, Quirós M, Lutterotti L, Manakova E, Butkus J, Moeck P, Le Bail A. Crystallography Open Database – an open-access collection of crystal structures. *Journal of Applied Crystallography*. 2009;42:726-729. DOI: 10.1107/S0021889809016690.
15. Aphane ME, Maggott ED, Doucet FJ, Mapolie SF, Landman M, van der Merwe EM. Synthesis and Evaluation of Mesoporous Silica Nanoparticle Catalyst Supports Prepared from South African Coal Fly Ash. *Waste and Biomass Valorization*. 2024;15:5053-5068. DOI: 10.1007/s12649-024-02496-2.
16. Bressi V, Chiarotto I, Ferlazzo A, Celesti C, Michenzi C, Len T, Iannazzo D, Neri G, Espro C. Voltammetric Sensor Based on Waste-Derived Carbon Nanodots for Enhanced Detection of Nitrobenzene. *ChemElectroChem*. 2023;10:e202300004. DOI: 10.1002/celec.202300004.
17. Pandiyarajan C, Perumal R, Murugesan S, Selvaraj M. Silver nanoparticles-supported graphitic-like carbon nitride for the electrochemical sensing of nitrobenzene and its derivatives. *Journal of Materials Science: Materials in Electronics*. 2021;32:19912-19924. DOI: 10.1007/s10854-021-06515-z.
18. Qi B, Lin F, Bai J, Liu L, Guo L. An ordered mesoporous carbon/didodecyltrimethylammonium bromide composite and its application in the electro-catalytic reduction of nitrobenzene. *Materials Letters*. 2008;62:3670-3672. DOI: 10.1016/j.matlet.2008.04.027.
19. Liang F, Liu B, Deng Y, Yang S, Sun C. Preparation and characterization of attapulgite-silver nanocomposites, and their application to the electrochemical determination of nitrobenzene. *MicrochimicaActa*. 2011;174:407-412. DOI: 10.1007/s00604-011-0647-7.
20. Yadav DK, Ganesan V, Sonkar PK, Gupta R, Rastogi PK. Electrochemical investigation of gold nanoparticles incorporated zinc based metal-organic framework for selective recognition of nitrite and nitrobenzene. *ElectrochimicaActa*. 2016;200:276-282. DOI: 10.1016/j.electacta.2016.03.092.
21. Yanilkin VV, Nastapova NV, Nasretdinova GR, Osin YN. Fullerene mediated electrosynthesis of Au/C<sub>60</sub> nanocomposite. *ECS Journal of Solid State Science and Technology*. 2017;6(4):M19-M23. DOI: 10.1149/2.0011704jss.