engineering proceedings

MDPI

Proceeding Paper

Development and Characterization of Novel Hybrid Materials Formed from Poly(2-aminophenyl disulfide)@Silica Gel for Dye Adsorption Application †

Mounya Zenasni [1], Abdelghani Benyoucef [2,*] and Lilia Sabantina [3,*]

[1] Department of Electrical Engineering, University Djillali Liabès of Sidi Bel Abbès, Sidi bel Abbes 22000, Algeria; zenasni_mounya@yahoo.fr
[2] Water Science and Technology Laboratory, University of Mustapha Stambouli Mascara, Mascara 29000, Algeria
[3] Department of Apparel Engineering and Textile Processing, Berlin University of Applied Sciences-HTW Berlin, 12459 Berlin, Germany
* Correspondence: a.benyoucel@univ-mascara.dz (A.B.); lilia.sabantina@htw-berlin.de (L.S.)
† Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: https://asec2023.sciforum.net/.

Abstract: Poly(2-aminophenyl disulfide)@silica gel (P2APDS@SiO_2), a new hybrid adsorbent, was successfully prepared using the in situ polymerization method and the product was analyzed by XRD, TEM, TGA, FTIR and BET techniques. Furthermore, this investigation also included a comprehensive study of the effect of the silica gel on the electrochemical performance of the hybrid nanomaterial based on P2APDS employing cyclic voltammetry. Moreover, to determine methylene blue (MB) adsorption, the effective parameters of the adsorption process, including the concentration, pH and temperature, were investigated. The results indicated that the maximum amount of MB adsorption on the fabricated hybrid material occurred at pH 6.7 with a capacity of 109.82 mg·g^{-1}. Furthermore, P2APDS@SiO_2 is interesting for the elimination of dyes because of its recyclability and high adsorption capacity.

Keywords: poly(2-aminophenyl disulfide); silica gel; dye; adsorption

Citation: Zenasni, M.; Benyoucef, A.; Sabantina, L. Development and Characterization of Novel Hybrid Materials Formed from Poly(2-aminophenyl disulfide)@Silica Gel for Dye Adsorption Application. *Eng. Proc.* **2023**, *56*, 281. https://doi.org/10.3390/ASEC2023-16604

Academic Editor: Manoj Gupta

Published: 6 December 2023

1. Introduction

Methylene blue (MB) dye is widely used in the textile industry. A large amount of dye wastewater is generated in the dyeing and printing industry processes. The dye wastewater has characteristics such as a high chromaticity, large volume of discharge, poor biodegradability, and high organic matter concentration, and it significantly affects the photosynthesis of microorganisms and the water body health of the water environment [1–4].

The study of adsorbents with a large surface area, good sensitivity, good adsorbent–adsorbate affinity, porosity and low cost has been steadily increasing for the removal of non-specific analytes (organics and inorganics) and has resulted in new research, development and innovation of these adsorbents for use in material preparation techniques by a solid phase for elimination. Moreover, gel materials, especially silica gels, are characterized by outstanding properties such as a high porosity, high specific surface area, low density, low thermal conductivity and low dielectric constant [5–7]. These outstanding properties make silica gels suitable for various applications.

Conducting polymers (CPs) are electrically electroactive materials. They have a conjugated π electron system in their chain structure, making them naturally conductive. The single and double bonds that alternately present in the polymer's backbone provide the delocalized electrons that act as charge carriers. The conductivity of PCs, such as polyacetylene, poly(p-phenylene), polyaniline (PANI), polythiophene, polypyrrole, and

poly(phenylene vinylene) classes, has been the subject of extensive study. The family of conjugated polymers has attracted interest in various fields because they are inexpensive, easy to prepare, have a high electrical conductivity, and are also environmentally stable [8–10].

Interestingly, conducting polymer-SiO_2 composites have been used in adsorption processes because of their high efficiency and low cost, and the process is considered to be environmentally friendly [11–13]. Usually, PANI-SiO_2 composites are prepared by the chemical oxidative polymerization of aniline in the presence of SiO_2 particles. For example, Belalia et al. [11] and Caldas et al. [12] prepared PANI-SiO_2 hybrid materials by the in situ oxidative polymerization of aniline in the presence of SiO_2. In general, herbicides can be removed by various methods, such as photocatalytic degradation [14], ultrasound technology [15,16], electrocoagulation processes [17], combined photo-Fenton and biological oxidation [18,19], and nanofiltration [20]. Nowadays, adsorption processes are widely used for the treatment of water contaminated with insecticides, dyes and phenols [21]. The main advantages of the adsorption technique include effectiveness even at low contaminant concentrations, selectivity, regenerability, and cost efficiency.

In this work, throughout the adsorption process, new adsorbent materials have been studied to help with the control of pollutants. From this point of view, in this context, a hybrid adsorbent of SiO_2 gel with poly(2-aminophenyl disulfide) (P2APDS) (P2APDS@SiO_2) was formed by the in situ chemical polymerization to be applied as a low-cost material for the elimination of methylene blue (MB) dye. The penetration of the P2APDS matrix into SiO_2 resulted in the generation of porosity in the adsorbent material. These phenomena lead to good contact between the constituents. Furthermore, the synthetized adsorbent materials were analyzed by XRD, FTIR, TEM, TGA and BET before their application to dye removal.

2. Preparation of P2APDS@SiO_2

First, 1.0 mL 2-aminophenyl disulfide (2APDS) was added to 25 mL of 1 M hydrochloric acid by magnetic stirring. Then, the silica gel (SiO_2) (1.0 g) was added and ultrasonicated for half an hour to properly disperse it. The temperature of the solution was lowered to 5 °C. Separately, 25 mL of (1M) HCl solution (S1) was added to dissolve 2.5 g of oxidizing agent (APS). This solution (S2) was added dropwise to S1 with stirring for 6 h to complete the oxidation chemistry process. The product was then filtered, washed with C_2H_6O and water and dried for 6 h at 60 °C. The obtained powders (P2APDS@SiO_2) were collected and stored in a desiccator.

3. Adsorption Studies

The adsorption isotherms were evaluated by batch equilibration of 0.5 g of the adsorbent with 50 mL of initial concentrations of dye, with a C_0 between 10 and 500 ppm. The experiments were carried out at 25 °C for 4h. The pH was adjusted with NaOH and HCl solutions.

The MB concentration was measured via UV–Vis absorbance analysis at λ_{max} = 664 nm wavelength.

The amount of dye was determined by the difference between the initial concentration and the concentration after time (t), according to the following equation: $q_{eq} = \frac{C_0 - C_{eq}}{w}$.

Langmuir $\frac{C_{eq}}{q_{eq}} = \frac{1}{K_l C_m} + \frac{C_{eq}}{q_m}$ and Freundlich $\ln q_{eq} = \ln K_f + \frac{1}{n}\ln C_{eq}$ isotherms were applied to analyze the experimental results.

The pseudo-1st-order rate expression is expressed as follows: $\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303}t$.

A pseudo-2nd-order rate formula expression was also applied; the kinetic rate equation is expressed as follows: $\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_1}t$.

4. Characterization of the Adsorbents

Subsection

The XRD patterns and FTIR spectrum (Figure 1a,b) results in this study confirm the formation of the P2APDS matrix on the SiO_2 surface. Moreover, Figure 1c presents the N_2 adsorption and desorption isotherms at 77 K for the adsorbents. These isotherms are similar to type II and are reversible at low relative equilibrium pressures, but at high relative pressures (P/P^0), they present a hysteresis loop of the H3 class. The detailed data are given in Table 1. It can be observed from this TEM image (Figure 1d) that there is a homogeneous distribution of the polymer matrix on SiO_2, which is consistent with the FTIR and XRD data in this study. Additionally, Figure 1d shows that three distinct weight loss processes led to the degradation of P2APDS@SiO_2. On the other hand, an increase in thermal stability was observed in the SiO_2 sample.

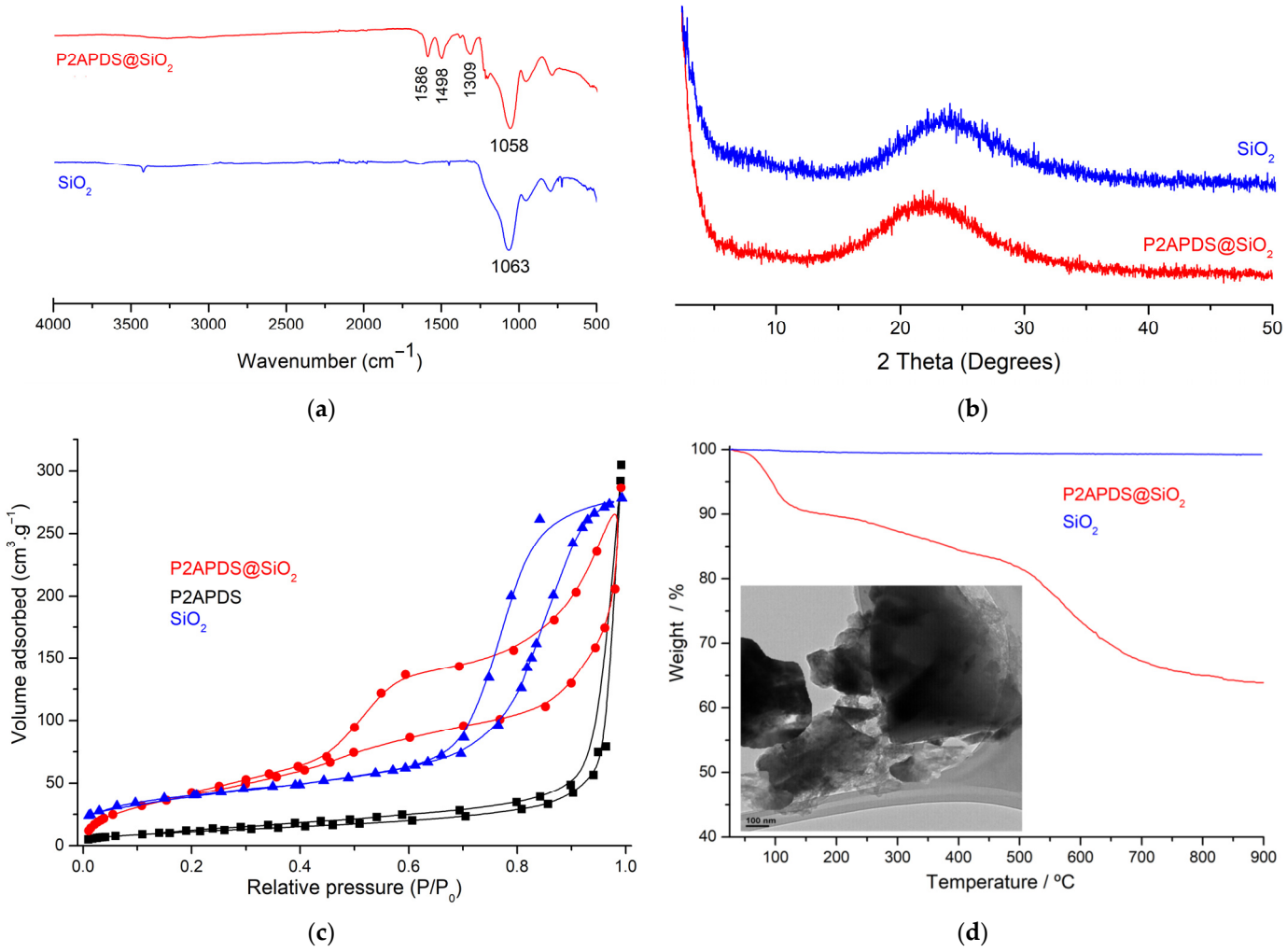

Figure 1. (**a**): FTIR analysis; (**b**): XRD patterns; (**c**): nitrogen adsorption isotherms of the samples; and (**d**): TGA curves of materials and the inset figure is the TEM image of P2APDS@SiO_2.

Table 1. Textural characterization of PANI, SiO_2 and PANI/SiO_2.

Adsorbents	S_{BET} ($m^2 \cdot g^{-1}$)	V_{DR} (N_2) ($cm^3 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)
P2APDS@SiO_2	35.20	0.28	0.02
SiO_2	264.82	2.08	0.10

The electrochemical study of samples was carried out in HCl (1 M). The electrodes were prepared as reported by Toumi et al. [3]. Figure 2a shows the cyclic voltammetry of the electrode modified by the samples. The voltametric behavior of P2APDS@SiO_2 exhibits an electroactive character, whereas SiO_2 presents a nearly ideal rectangular shape.

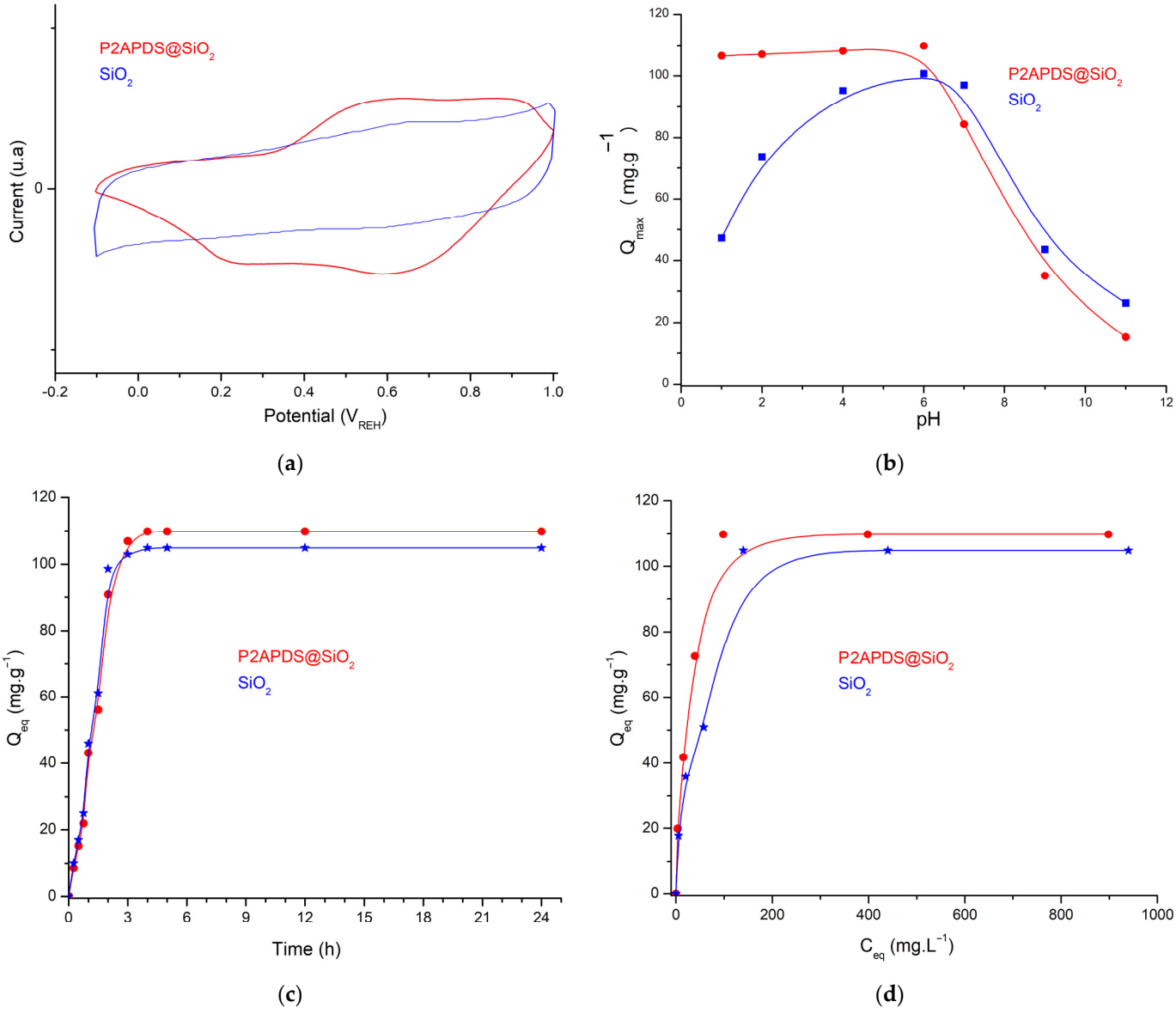

Figure 2. (**a**): Cyclic voltammetry curves of materials dropped on a glassy carbon electrode in 1M HCl at a scan rate of 50 $mV{\cdot}s^{-1}$; (**b**): the effect of pH on the removal process; (**c**): the contact time; (**d**): adsorption isotherms (adsorbent doses: 0.5 g; C_0:50 $mg{\cdot}L^{-1}$; pH: 6.7; T: 298 K).

The highest removal capacity produced at pH 6.7 was 109.82 $mg{\cdot}g^{-1}$ (Figure 2b); however, by increasing the pH, it decreased to 15.20 $mg{\cdot}g^{-1}$ at pH 12.0. These results suggest that an acidic condition is more suitable for MB elimination by P2APDS@SiO_2.

The analysis indicated that the adsorption of MB dye using the adsorbents was rapid in the first 0.5 h (Figure 2c) and then slowed down with time, reaching equilibrium in 90 min for P2APDS@SiO_2 and 1.0 h for SiO_2. With 3.0 h of shaking, the highest removal capacities of 109.82 $mg{\cdot}g^{-1}$ and 95.81 $mg{\cdot}g^{-1}$ were obtained for P2APDS@SiO_2 and SiO_2, respectively. As a result, the optimum contact time for maximum MB adsorption was 3 h for the adsorbent materials. Furthermore, for the P2APDS@SiO_2 adsorbent, there was an increase in the amount of MB adsorbed (Figure 2d), and the amount adsorbed

(Q_{eq}) increased from 95.81 mg·g^{-1} for SiO_2 to 109.82 mg·g^{-1} for the hybrid adsorbent. It can be said that the P2APDS matrix formed on the SiO_2 surface has an effect on the MB removal process.

The Freundlich isotherm model has the highest correlation coefficients (R^2), indicating its best suitability to explain the adsorption of MB on homogeneous and heterogeneous surfaces (Table 2). The adsorption of MB dye was shown by kinetic analysis to conform to a second-order kinetic model (Table 3). Therefore, it was found that the adsorption capacity of P2APDS@SiO_2 decreased by 7.51% after three cycles of using the adsorbents, which is considered as an insignificant loss of activity.

Table 2. Langmuir and Freundlich parameters obtained from MB on SiO_2 and PANI-SiO_2 at 298 K and pH = 6.7.

Adsorbents	Langmuir				Freundlich		
	q_m mg·g^{-1}	K_L L·mg^{-1}	R_L	R^2	K_f mg$^{1-1/n}$L$^{1/n}$g^{-1}	n	R^2
P2APDS@SiO_2	104.18	0.05	0.02	0.998	2.11	1.04	0.804
SiO_2	87.82	0.02	0.08	0.989	1.93	2.31	0.715

Table 3. Pseudo-1st-order and 2nd-order kinetic models for the MB adsorption of adsorbents at 298 K, pH 6.7 and C_0 50 mg.L^{-1}.

Adsorbents	1st-Order Kinetic Model				2nd-Order Kinetic Model		
	$q_{e.Exp}$ mg·g^{-1}	k_1 in^{-1}	$q_{e.Cal}$ mg·g^{-1}	R^2	$k_{2.ads}$ g·mg^{-1}·min^{-1}	$q_{e.Cal}$ mg·g^{-1}	R^2
P2APDS@SiO_2	109.82	0.0135	87.47	0.77	0.0012	105.79	0.99
SiO_2	95.81	0.0071	55.85	0.89	0.0006	88.55	0.98

On the other hand, the reusability tests of the adsorbents were examined using 0.1 M NaOH and 0.1 M HCl solutions. After five repetitions, the P2APDS@SiO_2 displayed an excellent reusability of 97.82% in the MB elimination test.

5. Conclusions

The adsorption behavior of MB on P2APDS@SiO_2 and SiO_2 was investigated as a function of the adsorbent type, adsorbate concentration and contact time. The analysis of the results demonstrated that the removal process by the adsorbents increased with increasing initial concentrations of MB. Furthermore, the influence of contact time was tested and the equilibrium time was reached at 3 h. However, the removal capacity of MB decreased with the increase in the amount of the adsorbent dose. In this work, adsorption isotherm models were used and from this, it was found that the process of MB adsorption on three adsorbents followed the Langmuir model. Moreover, the reusability test proved that P2APDS@SiO2 has the potential to be a reusable adsorbent for MB adsorption.

Author Contributions: Conceptualization: M.Z. and L.S.; methodology: M.Z., L.S. and A.B.; software: M.Z.; validation: all authors.; visualization: all authors.; formal analysis: M.Z. and L.S.; investigation: M.Z., A.B. and L.S.; data curation: M.Z. and A.B.; writing—original draft preparation: all authors; visualization: A.B. and L.S.; supervision, A.B. writing—review and editing: all authors. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be made available upon reasonable request.

Acknowledgments: The authors wish to thank their parental universities for providing the necessary facilities to accomplish the present work.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Kuang, Y.; Zhang, X.; Zhou, S. Adsorption of Methylene Blue in Water onto Activated Carbon by Surfactant Modification. *Water* **2020**, *12*, 587. [CrossRef]
2. Wong, Y.C.; Szeto, Y.S.; Cheung, W.H.; McKay, G. Adsorption of acid dyes on chitosan—Equilibrium isotherm analyses. *Process. Biochem.* **2004**, *39*, 695–704. [CrossRef]
3. Toumi, I.; Djelad, H.; Chouli, F.; Benyoucef, A. Synthesis of PANI@ZnO Hybrid Material and Evaluations in Adsorption of Congo Red and Methylene Blue Dyes: Structural Characterization and Adsorption Performance. *J. Inorg. Organomet. Polym. Mater.* **2022**, *32*, 112–121. [CrossRef]
4. Mennas, N.; Lahreche, S.; Chouli, F.; Sabantina, L.; Benyoucef, A. Adsorption of Methylene Blue Dye by Cetyltrimethylammonium Bromide Intercalated Polyaniline-Functionalized Montmorillonite Clay Nanocomposite: Kinetics, Isotherms, and Mechanism Study. *Polymers* **2023**, *15*, 3518. [CrossRef]
5. Parale, V.G.; Choi, H.; Kim, T.; Phadtare, V.D.; Dhavale, R.P.; Lee, K.Y.; Panda, A.; Park, H.H. One pot synthesis of hybrid silica aerogels with improved mechanical properties and heavy metal adsorption: Synergistic effect of in situ epoxy-thiol polymerization and sol-gel process. *Sep. Purif. Technol.* **2023**, *308*, 122934. [CrossRef]
6. Lee, K.Y.; Mahadik, D.B.; Parale, V.G.; Park, H.H. Composites of silica aerogels with organics: A review of synthesis and mechanical properties. *J. Korean Ceram. Soc.* **2020**, *57*, 1–23. [CrossRef]
7. Parale, V.G.; Lee, K.Y.; Jung, H.N.R.; Nah, H.Y.; Choi, H.; Kim, T.H. Facile synthesis of hydrophobic, thermally stable, and insulative organically modified silica aerogels using co-precursor method. *Ceram. Int.* **2018**, *44*, 3966–3972. [CrossRef]
8. Abhishek, N.; Verma, A.; Singh, A.; Vandana; Kumar, T. Metal-conducting polymer hybrid composites: A promising platform for electrochemical sensing. *Inorg. Chem. Commun.* **2023**, *157*, 111334. [CrossRef]
9. Kumar, D.; Sharma, R. Advances in conductive polymers. *Eur. Polym. J.* **1998**, *34*, 1053–1060. [CrossRef]
10. Hangarter, C.M.; Chartuprayoon, N.; Hernández, S.C.; Choa, Y.; Myung, N.V. Hybridized conducting polymer chemiresistive nano-sensors. *Nano Today* **2013**, *8*, 39–55. [CrossRef]
11. Belalia, A.; Zehhaf, A.; Benyoucef, A. Preparation of Hybrid Material Based of PANI with SiO_2 and Its Adsorption of Phenol from Aqueous Solution. *Polym. Sci. Ser. B* **2018**, *60*, 816–824. [CrossRef]
12. Caldas, C.M.; Calheiros, L.F.; Soares, B.G. Silica–polyaniline hybrid materials prepared by inverse emulsion polymerization for epoxy-based anticorrosive coating. *J. Appl. Polym. Sci.* **2017**, *134*, 45505–45514. [CrossRef]
13. Sambyal, P.; Ruhi, G.; Dhawan, R.; Dhawan, S.K. Designing of smart coatings of conducting polymer poly(aniline-co-phenetidine)/SiO_2 composites for corrosion protection in marine environment. *Surf. Coat. Technol.* **2016**, *303*, 362–371. [CrossRef]
14. Ispas, C.R.; Crivat, G.; Andreescu, S. Review: Recent developments in enzyme-based biosensors for biomedical analysis. *Anal. Lett.* **2012**, *45*, 168–186. [CrossRef]
15. Borole, D.D.; Kapadi, U.R.; Mahulikar, P.P.; Hundiwale, D.G. Influence of TiO_2 and SiO_2 on electrochemical, optical and electrical conductivity of polyaniline, poly(o-toluidine) and their co-polymer. *Des. Monomers Polym.* **2009**, *12*, 523–532. [CrossRef]
16. Borole, D.D.; Kapadi, U.R.; Mahulikar, P.P.; Hundiwale, D.G. Studies on electrochemical, optical and electrical conductivity of conducting composite of o-anisidine, o-toluidine and their co-polymer. *Des. Monomers Polym.* **2009**, *12*, 129–138. [CrossRef]
17. Waware, U.S.; Umare, S.S. Chemical synthesis, spectral characterization and electrical properties of poly(aniline-co-m-chloroaniline. *React. Funct. Polym.* **2005**, *65*, 343–350. [CrossRef]
18. Frank, S.; Poncharal, P.; Wang, Z.L.; Heer, W.A. Carbon Nanotube Quantum Resistors. *Science* **1998**, *290*, 1744–1746. [CrossRef]
19. Kubies, D.; Pantoustier, N.; Dubois, P.; Rulmont, A.; Jerome, R. Controlled ring-opening polymerization of epsilon-caprolactone in the presence of layered silicates and formation of nanocomposites. *Macromolecules* **2002**, *35*, 3318–3320. [CrossRef]
20. Sestrem, R.H.; Ferreira, D.C.; Landers, R.; Temperini, M.L.A.; do Nascimento, G.M.D. Structure of chemically prepared poly-(para-phenylenediamine) investigated by spectroscopic techniques. *Polymer* **2009**, *50*, 6043–6046. [CrossRef]
21. Overney, G.; Zhong, W.; Tomanek, D.Z. Structural rigidity and low frequency vibrational modes of long carbon tubules. *Z. Für Phys. D-At. Mol. Clust.* **1993**, *27*, 93–96. [CrossRef]