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

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Abstract: Poly(2-aminophenyl disulfide)@silica gel (P2APDS@SiO_2) new hybrid adsorbent was successfully prepared by in-situ polymerization method and the product was analyzed by XRD, TEM, TGA, FTIR and BET techniques. Furthermore, this investigation also reports 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 the methylene blue (MB) adsorption, the effectiveparameters on 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

1. Introduction

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

The study for adsorbents with a large surface area, good sensitivity, good adsorbent–adsorbate affinity, porosity and low cost has been increasing more and more towards the removal of non-specific analytes (organics&inorganics) and has created new research, development and innovation of these adsorbents for use in material preparation techniques by a solid phase for elimination. Moreover, the gel materials, especially silica gels, are characterizied 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 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 low cost,

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easy to prepare, have high electrical conductivity, and are also environmentally stable. [8-10].

Interestingly, conducting polymer-SiO_2 composites have been used in adsorption process because of its high efficiency and its low cost, and the process is considered to be environmentally friendly [11-13]. Usually, PANI-SiO_2 composites are prepared by 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 an 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 process [17], combined photo-Fenton and biological oxidation [18, 19], and nanofiltration [20]. Nowadays, adsorption process is widely used for the treatment of water contaminated with insecticides, dyes and phenols [21]. The main advantages of adsorption technique include effectiveness even at low contaminant concentrations, selectivity, regenerability, and cost efficiency.

In this work, in the adsorption process, new adsorbent materials have been studied to help in 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 P2APDS matrix into the SiO_2 resulted in the generation of porosity in the adsorbent material. This 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 the dye removal.

2. Preparation of P2APDS@SiO_2

1.0 mL 2-aminophenyl disulfide (2APDS) was added to 25mL of 1 M hydrochloric acid by magnetic stirring. Then the silica gel (SiO_2) (1.0g) was added and ultrasonicated half an hour to disperse it properly. The temperature of the solution was lowered to 5°C. Separately, 25mL of (1M) HCl solution (S1) was added to dissolve 2.5g of oxidizing agent (APS). This solution (S2) was added dropwise to S1 with stirring for 6 hours to complete the oxidation chemistry process. The product was then filtered, washed with C_2H_6O and water and dried for 6 hours 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 adsorbent with 50 mL of initial concentrations of dye, 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 from its 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 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 $lnq_{eq} = lnK_f + \frac{1}{n} lnC_{eq}$ isotherms were applied to analyze the experimental results.

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

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

4. Characterization of the adsorbents

3.1. Subsection

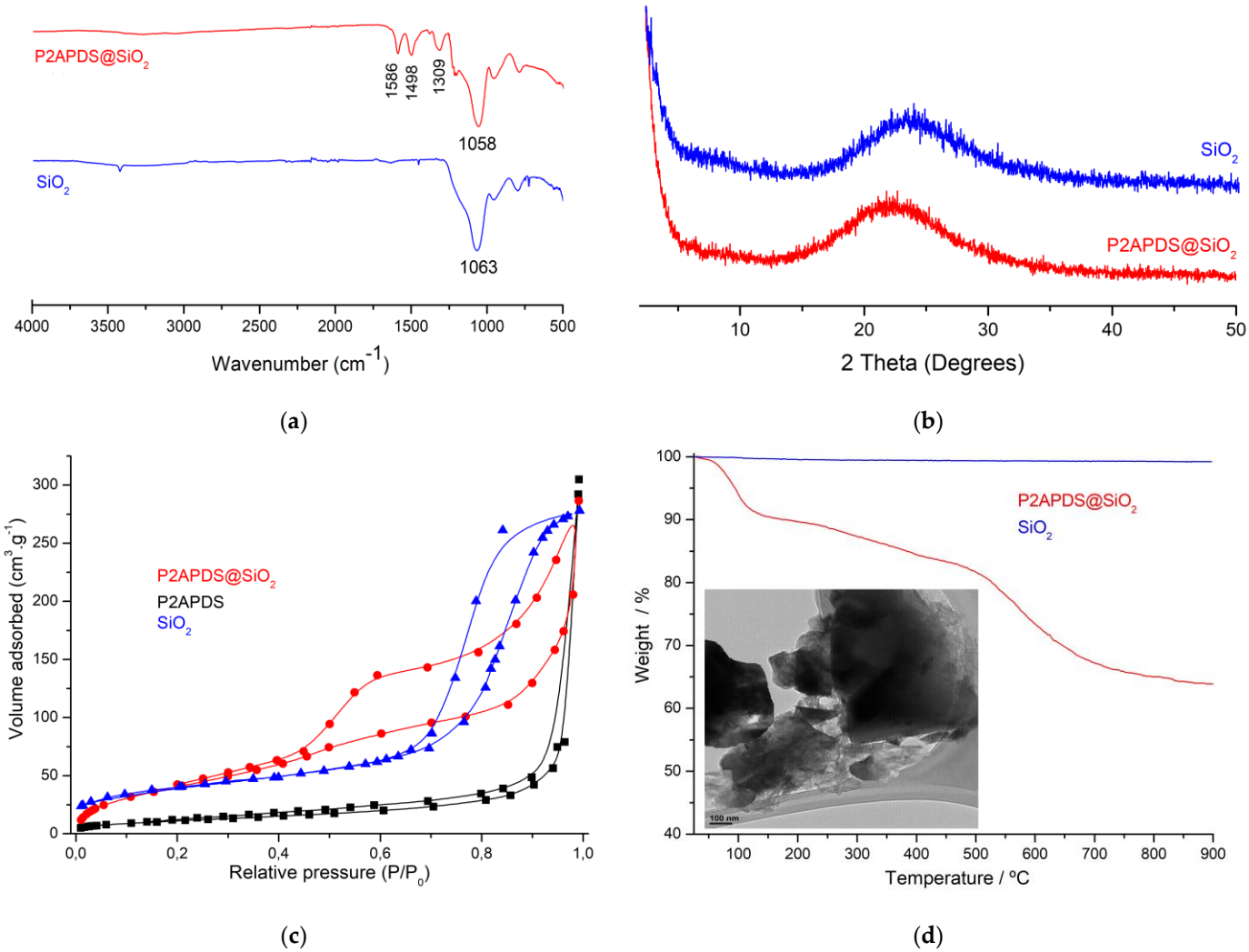


Figure 1. (a): FTIR analysis; (b): XRD patterns; (c): Nitrogen adsorption isotherms of the samples; and (d): TGA curves of materials and the inset figure is the TEM image of P2APDS@SiO_2.

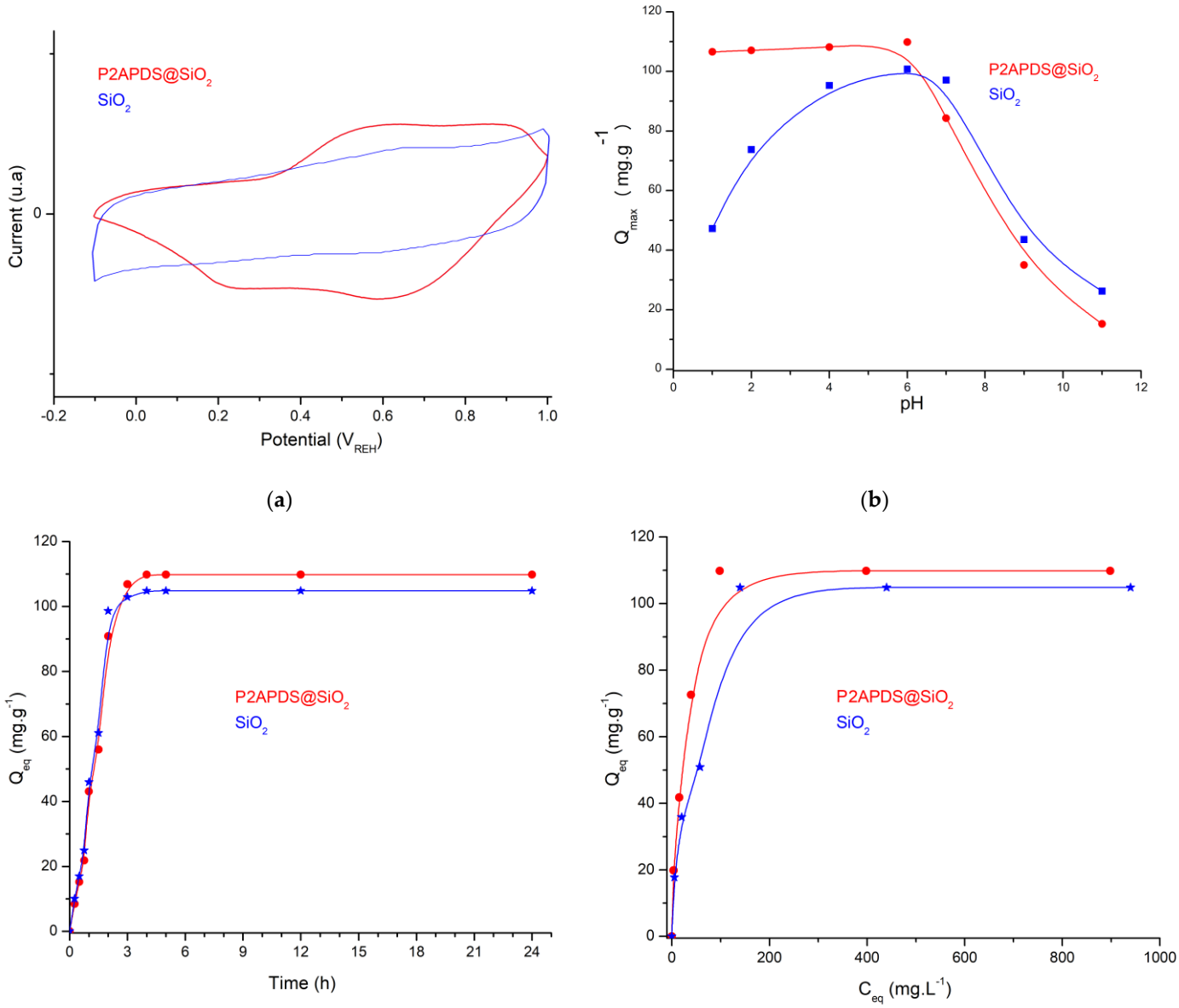
The XRD patterns and FTIR spectrum (Figure 1-a and 1-b) results in this study confirm the formation of P2APDS matrix on SiO_2 surface. Moreover, the Figure 1c. presents the N_2 adsorption&desorption isotherms at 77K for adsorbents. These isotherms are similar to type II and its are reversible at low 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 remarked from this TEM (Figure 1-d) that there is a homogeneos distribution of the polymer matrix on SiO_2, which is consistent with the FTIR and XRD data in this study. Additionally, the Figure 1-d, shown three distinct weight loss process led to the degradation of P2APDS@SiO_2. Otherwise, an increase in thermal stability was observed in SiO_2 sample.

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

Adsorbent	S_{BET} ($m^2.g^{-1}$)	V_{DR} (N_2) ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)
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 (1M). The electrodes were prepared as reported by Toumi et al. [3]. Figure 2-a. showed the cyclic voltammetry of electrode modified by samples. The voltammetric behaviour of P2APDS@SiO_2 exhibits a charecter electroactive, whereas SiO_2 presents nearly ideal rectangular shape.

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



(**a**) (**b**)

(**c**) (**d**)

Figure 2. (a): Cyclic voltammetry curves of materials dropped on a glassy carbon electrode in 1M HCl scan rate 50mV·s^{-1}; (b): The effect of pHs on the removal ; (c): The contact time; (d): Adsorption isotherms (adsorbents dose: 0.5 g; C_0:50 mg.L^{-1}; pH: 6.7; T:298K).

The analysis indicated that the adsorption of MB dye using the adsorbents was rapid in the first 0.5 hours (Figure 2-c), then slowed down with time, reaching equilibrium in 90 minutes for P2APDS@SiO_2 and 1.0 hour for SiO_2. With 3.0 hours of shaking, the highest removal capacities of 109.82 mg.g^{-1} and 95.81 mg.g^{-1} were obtained for P2APDS@SiO_2 and SiO_2, respectively. As a result, the optimum contact time for maximum MB adsorption was measured to be 3 h for adsorbent materials. Furthermore, for P2APDS@SiO_2 adsorbent, there was an increase in the amount of MB adsorbed (Figure 2-d), and the amount adsorbed (Q_{eq}) increased from 95.81 mg.g^{-1} for SiO_2 to 109.82 mg.g^{-1} for hybrid adsorbent. It can be said that there is an effect of P2APDS matrix formed on SiO_2 surface in the MB removal process.

The Freundlich isotherm model has the highest correlation coefficients (R2), 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 haswas 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.

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.

Table 2. Langmuir&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 on adsorbents at 298 K, pH 6.7 and C_0 50 mg.L-1.

Adsorbents	$q_{e.Exp}$ mg.g^{-1}	1st-order kinetic model			2nd-order kinetic model		
		k_1 min^{-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

4. Conclusion

The adsorption behaviour of MB on P2APDS@SiO_2 and SiO_2 was investigated as a function of adsorbent type, adsorbate concentration and contact time. Analysis of the results exhibits that the removal process by adsorbents was increased with increasing initial concentrations of MB. Furthermore, the influence of contact time was tested and the equilibrium time was reached at 3 hours. However, the removal capacity of MB decreased with the increase in the amount of adsorbent dose. From this work, the adsorption isotherm models were performed and from this the process of MB adsorption on three adsorbents is well fitted with the Langmuir model. Moreover, the reusability test proved that P2APDS@SiO2 has the potential to be a reusable adsorbent for MB adsorption.

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