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

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1.- Introduction

The search for adsorbent materials with a large surface area, porosity, good adsorbent–adsorbate affinity, good sensitivity and low cost has been increasing more and more towards the adsorption of non-specific analytes (organics and inorganics) and has generated new research, innovation and development of these materials for use in sample preparation techniques using a solid phase for adsorption. Moreover, the gel materials, particularly silica gels, are notable for having outstanding properties such as a high specific surface area, high porosity, low density, low dielectric constant, and low thermal conductivity [1-3]. These outstanding properties make silica gels suitable for various applications.

Conducting polymers (CPs) are electrically active polymers. They have a conjugated π electron system in their structures, which makes them naturally conductors. The single and double bonds that alternately exist in the polymer chain of conjugated conducting polymers provide the delocalized electrons that serve as charge carriers. The conductivity of polyaromatics, like polyaniline (PANI), polyacetylene, polythiophene, polypyrrole, poly(p-phenylene), and poly (phenylene vinylene) classes, has been the subject of in-depth research. The high environmental stability in the presence of oxygen and water, unique conduction mechanism, low cost of monomer, ease of synthesis, and special doping chemistry, make the polyaniline family of conjugated polymers, out of all the foregoing classes, a subject of great interest globally followed by polypyrrole (PPY) and polythiophene (PTH) [4-6].

Interestingly, conducting polymer-SiO2 composites have been used in adsorption process because of high efficiency and its low cost, and the process is considered environment-friendly [7-9]. Usually, PANI-SiO2 composites are prepared by chemical oxidative polymerization of aniline in the presence of SiO2 particles. For example, Belalia et al. [7] and Caldas et al. [8] prepared PANI-SiO2 hybrid materials by an in situ oxidative polymerization of aniline in the presence of SiO2. In general, herbicide can be removed through various methods, such as photocatalytic degradation [10], ultrasound technology [11, 12], electrocoagulation process [13], combined photo-Fenton and biological oxidation [14, 15] and nanofiltration [16]. Nowadays, adsorption process is widely used for the treatment of the waters contaminated by insecticides, dyes and phenols [17]. The most advantages of adsorption technique include effectiveness even at low contaminant concentrations, selectivity, regenerability, and cost efficiency.

2.- Experimental

2.1.- Preparation of P2APDS@SiO2

1.0 mL 2-Aminophenyl disulfide (2APDS) was added to 25 mL 1M HCl by magnetic stirring. Then the Silica gel (SiO2) (1.0 g) was added into it and ultrasonicated 30 min to disperse it properly. The temperature of the dispersion was reduced below 5 °C using an ice bath. Separately, 25 mL of HCl (1M) solution was used to dissolve 2.5 g of APS. This solution was added dropwise in the disperse under constant stirring for 6 h under stirring for the completion of the polymerization reaction. Then, the residue has been filtered and washed with HCl, Ethanol and DIW; and dried at 60 °C in an oven for 6 h. The obtained dry powder (P2APDS@SiO2) was collected and stored in a desiccator.

2.2.- Adsorption studies

- The adsorption isotherms were determined by batch equilibration of 0.5 g adsorbent with 50 mL of aqueous solutions of herbicide of initial concentrations, C0 between 10 and 1200 ppm. The experiments were carried out in a thermostatic shaker bath at 25°C for 4 h.

- The effect of pH on adsorption was determined by adjusting the pH of the dispersions with HCl and NaOH solutions.

- The concentration MB was determined from its UV–Vis absorbance characteristic with the calibration curve method at the wavelength of λmax = 664 nm,

- The amount of adsorbed herbicide was calculated by difference between the initial concentration and that after a time t, according to the following equation : $q_t = \frac{(c_0 - c_t)V}{1,000M}$

- Langmuir ($\frac{c_e}{q_e} = \frac{1}{K_l c_m} + \frac{c_e}{q_m}$) and Freundlich ($\ln q_e = \ln K_f + \frac{1}{n}\ln c_e$) isotherms were used to analyze the experimental results.

- The first-order rate expression is expressed as follows : $\frac{dq_t}{dt} = k_1(q_e - q_t)$

- A pseudo-second-order rate law expression was also used; the kinetic rate equation is expressed as : $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$

3.- Characterization of the adsorbents

Fig. 1. shows the nitrogen adsorption/desorption isotherms at 77 K for natural and acidic activated samples. According to IUPAC classification, the shape of these isotherms is similar to Type II. The three isotherms are reversible at low relative equilibrium pressures, but at higher relative pressures they exhibit a hysteresis loop of the H3 type

Table 1. Textural characterization of: P2APDS@SiO2 and SiO2.

Samples	S_{BET} / $m^2.g^{-1}$	V_{DR} (N_2) / $cm^3.g^{-1}$	V_{meso} / $cm^3.g^{-1}$
P2APDS@SiO2	35.20	0.28	0.02
SiO2	264.82	2.08	0.10

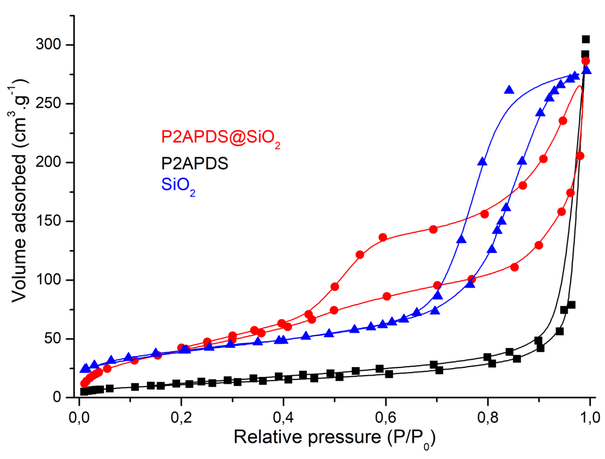

Fig. 1.N2 Adsorption Isotherms at 77 K of P2APDS@SiO2 and SiO2

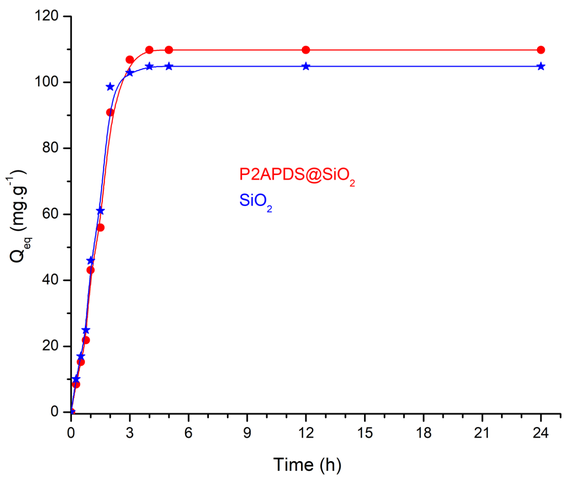

Fig. 2. Contact Time (C0 (MB): 50 mg.L-1; pH: 6.7; T: 298K; adsorbents dose: 10 mg)

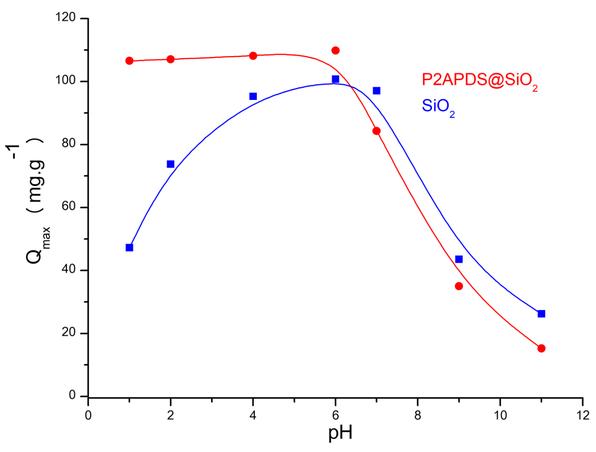

Fig. 3. Effect of pH on MB Adsorption by adsorbents. Initial Concentration of MB = 50 mg.L-1, Adsorption time = 3 h

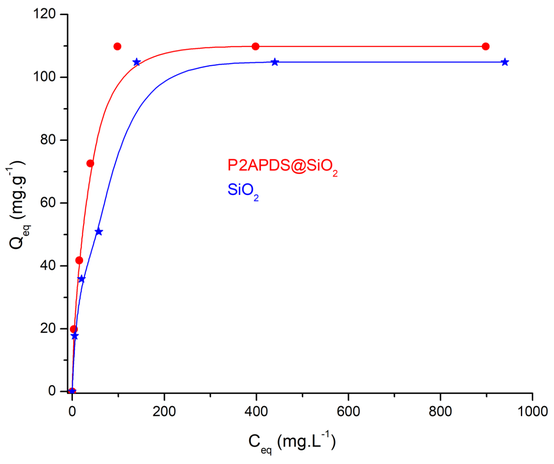

Fig. 4. Adsorption isotherms of MB by adsorbents (adsorbent dose: 10 mg; C0 (MB): 25 mL; T: 298 K; pH: 6.7).

Table 2. Langmuir and Freundlich coefficients obtained from the adsorption isotherms of MB onto: P2APDS@SiO2 and SiO2 at 298 K and pH = 6.7,

Adsorbents	Langmuir parameters				Freundlich parameters		
	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@SiO2	104.18	0.05	0.02	0.998	2.11	1.04	0.804
SiO2	87.82	0.02	0.08	0.989	1.93	2.31	0.715

Table 3. Comparison of the first- and second-order adsorption rate constants, for calculated (qe,cal) and experimental (qe,exp) values at 298 K, pH = 6,7 and MB concentration is 50 mg.L-1.

Adsorbents	$q_{e.Exp}$ (mg.g^{-1})	First-order kinetic model			Second-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@SiO2	109.82	0.0135	87.47	0.77	0.0012	105.79	0.99
SiO2	95.81	0.0071	55.85	0.89	0.0006	88.55	0.98

4.- Conclusions

The adsorption behavior of MB on P2APDS@SiO2 and SiO2 was studied as a function of the concentration of the adsorbate, contact time and nature of adsorbent. Analysis of the results shows that the MB adsorption process on adsorbents was increased as the initial concentration of MB increased. Furthermore the effect of contact time was conducted and the balance time was achieved at 3 hours. But adsorption capacity of MB decreases with increases the amount of adsorbent dose. From this study, the adsorption isotherm studies were performed and from this the Langmuir separation factor is between 0 and 1 and hence the process of MB adsorption on three adsorbents is well fitted with the Langmuir adsorption isotherm. However the Freundlich adsorption intensity 1/n is greater than one and the Freundlich constant is less than one, which indicates unfavorable adsorption.

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6.- References

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