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Synthesis of doped sol-gel glasses as adsorbents for water treatment†

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Abstract: Doped sol-gel glasses of thiourea (THU), urea (U), n-propoylamine (PA), iso-propylamine (IPA), and 2-methoxyaniline (AN) were prepared and treated by two methods, thermal and microwave (MW) irradiation. The optical properties and particle size of the as-synthesized doped sol-gels and plain sol-gel (P) were measured. The sol-gels were then tested for their capacity to adsorb methylene blue dye (MB) and remove it from aqueous solutions. The highest removal efficiencies were exhibited by PA, IPA and THU that were prepared by either the thermal or MW method. Amongst all the tested adsorbents, the thermally-prepared PA yielded the highest removal of over 95% for 12.5 mg/L of MB, and about 75% for 6.5 mg/L of MB. The MW-prepared PA showed the second highest removal efficiencies, while IPA, prepared thermally or by MW, showed comparable results to its PA counterpart. This behavior could be attributed to the higher basicity of aliphatic amines relative to aromatic amines, which resulted in increased interaction between the lone pair of electrons on amino nitrogen and MB. On the other hand, the interaction between U or THU, and MB is suggested to have possibly occurred via electrostatic attraction or redox reaction between them. The characteristic Fourier Infrared (FTIR) spectra of PA and IPA before and after adsorption suggest that C=O, N-H and Si-OH groups, among other groups, could be involved in adsorption.

Keywords: synthesis; sol-gel glasses; doping; water treatment

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1. Introduction

Water pollution is one of the growing global challenges due to increased industrialization and consequent escalation in the number of wastewater treatment plants [1]. Wastewater effluents from textile industries contain a variety of hazardous dyes such as methylene blue (MB) which is a cationic photosensitizer that tends to aggregate and can undergo electron transfer reactions [2]. The sol-gel method is considered a promising technology for synthesizing adsorbents that remove heavy metals and dyes. Amine-functionalized $MgFe_2O_4$ nanoparticles prepared by the sol-gel route were successful in removing heavy metals via chemisorption that involved formation of coordinative bonds between the amine groups and metal ions [3]. Amine functionalization of silica aerogels improved their removal efficiency for lead and Rubi Levafix CA dye to above 90%, by changing their microstructure, hydrophilicity and surface charge [4]. Silica and silica-based adsorbents proved efficient in removal of MB due to their low cost and high removal efficiency, examples of which are amine and sulfonic acid functionalized mesoporous silica nanoparticles [5], amine functionalized mesoporous silica nanospheres [6], and non-functionalized silica nanoparticles synthesized from naturally occurring diatomite [7]. In this

study, sol-gel glasses doped with n-propyl amine (PA), iso-propyl amine (IPA), urea (U), thiourea (THU), and methoxyaniline (AN) have been prepared. The sol-gel synthesis has been carried out by preparation of a sol, gelation of the sol, and finally removal of the solvent. Removal of solvent has been conducted by conventional thermal heating or microwave (MW) irradiation. The sol-gels were then examined as adsorbents for MB.

2. Materials and methods

2.1. Materials and reagents

Tetramethoxysilane (TMOS) was purchased from Fluka (98%, MW 152.22, and density 1.027 mg/mL). All the following chemicals were purchased from Sigma Aldrich (Germany), n-propyl amine (98%, FW 59.1, and density 0.719 mg/mL), isopropyl amine (99%, FW 59.1, and density 0.694 mg/mL), 2-methoxyaniline (99%, MW 123.25), urea (98%, MW 60.06), and thiourea (99%, MW 76.12).

2.2. Preparation of plain and doped sol-gel glasses

To prepare the plain sol-gel glass (P), a mixture was prepared by mixing 0.05 mol of the TMOS precursor to 0.35 mol of methanol. To the reaction vessel, a mixture of 0.039 mol HNO3 and 0.55 mol redistilled water was added, then the pH was adjusted to 2.5. The produced reaction mixture was continuously stirred for 30 min at room temperature (25±2 ^{o}C). To conduct thermal treatment, the mixture was heated in an oven adjusted at 60^{o}C for 7 days. For microwave treatment, the mixture was left in air for 1, 2 or 3 h, then 10 mL of the solution was placed in 10 mL plastic microwavable container and exposed to microwave irradiation (Olympic electric Microwave oven, KOG-134K) at 100 KW power for 30 s (10 rounds per second). Doped sol-gel glasses were prepared by the same method mentioned above, however 0.039 mol of the organic dopant (urea, thiourea, n-propylamine, iso-propylamine and 2-methoxyaniline) was added to the reaction mixture to form U, THU, PA, IPA and AN, respectively.

2.3. Characterization of the prepared sol-gel glasses

FTIR measurements (Thermo Scientific Nicolet 380 FT-IR Spectrometer) for all sol-gels were performed to determine the existing functional groups. Sol-gel glasses (0.01g) were ground in a blender at 20 rps for 2 minutes. The particle size was measured using sieves (Retsch test sieve, Retsch GmbH 88 Co.KG) with different pore sizes (250 µm-2 mm).

2.4. Adsorption experiments

To conduct the batch adsorption experiments for MB, 0.01 g of the powdered sol-gel glass was added to 10 mL of the MB solutions (1.575, 3.125, 6.25, and 12.5 mg/L) prepared by serial dilutions. The solutions were heated on a thermostatic shaking water bath adjusted at 27±1 ^{o}C for 4 h, then centrifuged for 5 min at 300 rpm. The supernatants were collected and their absorbance was measured using UV-vis spectroscopy (Cary 500 Scan, Varian). The concentrations were determined using a calibration curve, while the amount of adsorbed MB at equilibrium (q) was calculated using the following mass balance equation $\boldsymbol{q = \frac{(C_i - C_e)}{m} \times V}$

The removal percentage was also calculated using the following equation: $\% \boldsymbol{Removal = \frac{(C_i - C_e)}{C_i} X100}$

where $\boldsymbol{C_i}$ is the initial concentration of MB in solution and $\boldsymbol{C_e}$ is the equilibrium concentration of MB in solution, $\boldsymbol{V}$ is the volume of solution, and $\boldsymbol{m}$ is the mass of adsorbent.

3. Results and discussion

3.1. Physical characteristics of the prepared nanocomposites

The synthesized sol-gel glasses vary in their color and transparency, as well as in their particle size which range from < 250 μm up to 2 mm as shown in Table 1.

Table 1. Physical appearance and particle size range of sol-gel glasses synthesized by different techniques of heating.

Sol-gel glass	**Conventional thermal treatment**			**Microwave irradiation**		
	color	**transparency**	**particle size**	**color**	**transparency**	**particle size**
P	Colorless	Transparent	500-630 μm	Colorless	Transparent	300-500 μm
U	Orange	Transparent	500-630 μm	White	Opaque	250-500 μm
THU	Yellow	Opaque	< 250 μm	White	Opaque	< 250 μm
PA	Orange	Opaque	250 μ-2 mm	Orange	Opaque	250-630 μm
IPA	Orange	Opaque	500 μ-2 mm	Orange	Opaque	250-630 μm
AN	Black	Opaque	500 -630 μm	Black	Opaque	250-630 μm

3.2. Adsorption study on MB

The as-synthesized adsorbents were examined for their capacity to remove MB from aqueous solutions. Two concentrations of MB, 6.5 and 12.5 mg/L were tested as shown in Figure 1a and b, respectively. Clearly, the highest removal efficiencies were exhibited by PA, IPA and THU that were prepared by either the thermal or MW method. Amongst all the tested adsorbents, the thermally-prepared PA yielded the highest removal of over 95% for 12.5 mg/L of MB, and about 75% for 6.5 mg/L of MB. The MW-prepared PA, on the other hand, removed about 83% and 52% of 12.5 and 6.5 mg/L of MB, respectively. IPA, prepared thermally or by MW, showed comparable results to its PA counterpart. To further investigate this, the adsorption capacity and percent removal of the thermally-prepared and MW-prepared PA and IPA were obtained at different initial concentrations as depicted in Figure 2a and b, respectively. It can be observed that both adsorbents behave similarly with regard to both the adsorption capacity and percent removal. The capacity increases with increasing the concentration due to the increased concentration gradient which improves the mass transfer of MB from the bulk solution to the adsorbent surface [8,9]. On the other hand, the removal which is dependent on the ratio of concentration gradient to initial concentration decreases with increasing concentration due to saturation of active sites [8,10]; but increases again at the highest concentration of 12.5 mg/L due to the effect of concentration gradient [9, 11] which counteracted the effect of site saturation. Thus, the removal shows a minimum value at 6.25 mg/L. The highest removal efficiencies for both adsorbents, prepared thermally or by MW, are achieved at the lowest and highest concentrations of 12.5 and 1.6 mg/L. The MW-treated PA, however, shows slightly lower removal and adsorption capacity than the other sol-gels at these two concentrations. In view of the above results, PA and IPA were chosen for further FTIR characterization.

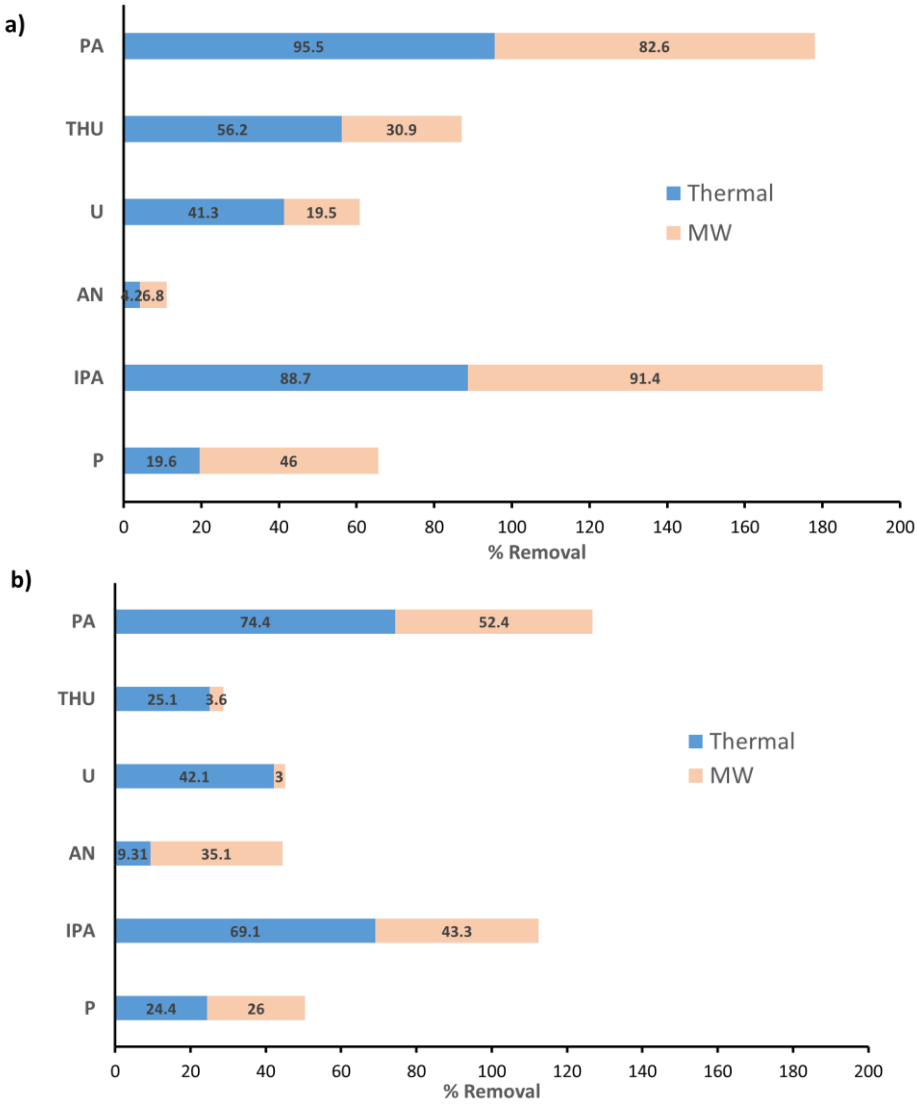

Figure 1. Percent removal of a) 12.5 mg/L and b) 6.5 mg/L of MB onto the different prepared sol-gel glasses.

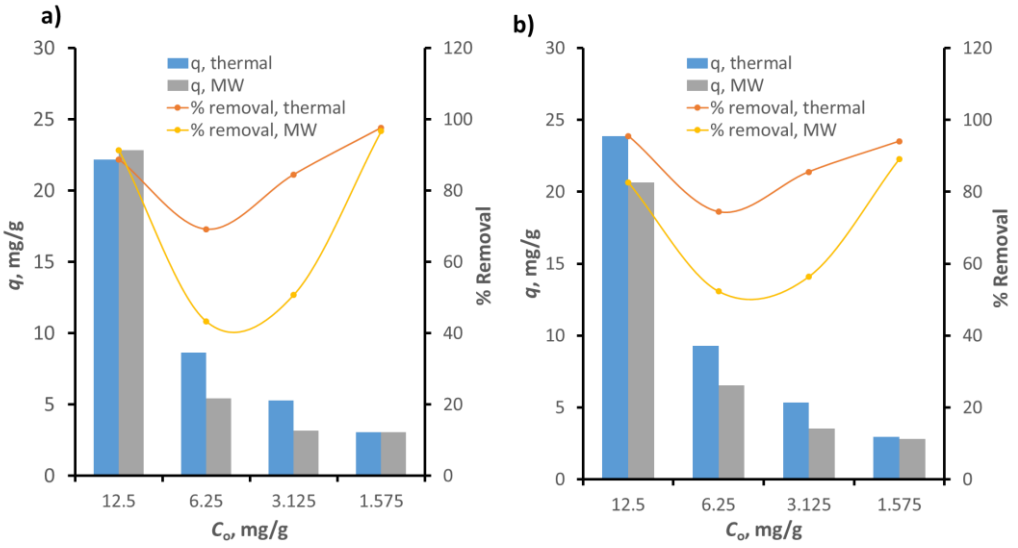

Figure 2. Adsorption capacity and % removal of MB onto IPA (a) and PA (b) at different initial concentrations of the dye.

3.3. Chemical characteristics of the prepared sol-gel glasses

FTIR spectral analysis of the thermally-treated and MW-treated PA and IPA sol-gels (Table 2) revealed that they all share O-H, sp^3 C-H, CH_3, N-H, Si-O-Si, and Si-OH functional groups.

Table 2. Main functional groups in thermally-treated and MW-treated PA and IPA sol-gels and their characteristic FTIR bands.

Wavenumber (cm^{-1})	Functional Group	Thermally-treated		MW-treated	
		PA	***IPA***	***PA***	***IPA***
3500-3400	O-H stretch	✓	✓	✓broad	✓ broad
2800-3000	sp^3 C-H stretch	✓	✓	✓	✓
2350	Si-H	✓	---	✓ small doublet	---
1500-1550	N-H bending	✓	✓	✓	✓
1600	C=O	✓	✓	✓	---
1380	CH_3 bending	✓	✓ sharp	✓ sharp	✓
1075-1100	Si-O-Si	✓	✓ sharp	✓ sharp	✓ sharp
942- 972	Si-OH stretch	✓	✓	✓ small	✓

After adsorption of MB onto the thermally treated PA sol-gel glass, no change in the FTIR bands was observed except in the 2357.7 cm^{-1} bands pertaining to Si-H, the 3039.9-2975.2 cm^{-1} bands assigned for C-H and the band at 952.1 cm^{-1} for Si-OH since they all disappeared after adsorption. For the MW-treated PA sol-gel glasses, the Si-H band at 2359.4 cm^{-1} and the bands of C-H at 3073.7 cm^{-1} and 2976.4 cm^{-1} disappeared, while the bands of 1° amine and C=O at 1631.3 cm^{-1} and 1512.4 cm^{-1} shifted to 1642.8 cm^{-1} after MB adsorption. For thermally-treated IPA sol-gel glasses, MB adsorption resulted in the disappearance of the broad bands of C-H at 2984.0, 2925.4, and 2854.2 cm^{-1}, the band of CH_3 at 1384.1 cm^{-1}, the band of Si-OH at 959.7 cm^{-1}, and the symmetric vibrational band of Si-O-Si at 797.5 cm^{-1}. In contrast, the MW-treated sol-gel glasses showed no change after MB adsorption except for the bands of C-H at 3061.5 cm^{-1} and 2985.6 cm^{-1} which disappeared after adsorption. This suggests that Si-H, Si-OH, Si-O-Si, C=O, N-H, C-H, and CH_3 could be involved in adsorption.

3.4. Mechanism of adsorption

PA and IPA have the highest reactivity among the synthesized sol-gel doped glasses towards removal of MB, while AN has the lowest reactivity. This could be attributed to the higher basicity of the aliphatic amines of PA ($K_b = 4.7x10^{-4}$) and IPA ($K_b = 4.0x10^{-4}$) relative to the aromatic amine AN ($K_b = 3.00x10^{-10}$), which resulted in increased interaction between the lone pair of electrons on the amino nitrogen and MB. With respect to urea, although it has lower basicity than the aromatic amine AN ($K_b = 1.5x10^{-14}$), yet it shows higher adsorption capacity and removal efficiency than AN. In previous literature, molecular dynamics simulations that computed the free energy of dimer association confirmed that MB monomers are more stable in urea solutions than in aqueous solution; and hence urea can destabilize MB aggregates [12]. Furthermore, electrostatic interaction or redox reaction are likely to occur between the positively charged nitrogen or sulfur in MB and the lone pair electrons on the carbonyl carbon in urea. MB can similarly interact with thiourea, but to a lesser extent than urea owing to the acidic properties of the electron deficient sulfur on thiourea.

3.5. Conclusion

Amine-doped and urea-doped sol-gel glasses successfully adsorbed MB from aqueous solutions with removal percentages that reached above 95%. Mechanisms involved in

adsorption include electrostatic physical attraction and redox reaction involving electron transfer.

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