

# Synthesis of Doped Sol-Gel Glasses as Adsorbents for Water Treatment<sup>†</sup>

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**Abstract:** Doped sol-gel glasses of thiourea (THU), urea (U), n-propylamine (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 sizes 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 which 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 the C=O, N-H, and Si-OH groups, among others, could be involved in adsorption.

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



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## 1. Introduction

Water pollution is a growing global challenge 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<sub>2</sub>O<sub>4</sub> 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 the removal of MB due to their low cost and high removal efficiency. Examples of these include 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) were prepared. The sol-gel synthesis was carried out by preparation of a sol, gelation of the sol, and, finally, removal of the solvent. Removal of the solvent was conducted by either 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 of the following chemicals were purchased from Sigma Aldrich (Schnell-dorf, 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 HNO<sub>3</sub> and 0.55 mol redistilled water was added, and then the pH was adjusted to 2.5. The produced reaction mixture was continuously stirred for 30 min at room temperature (25 ± 2 °C). To conduct thermal treatment, the mixture was heated in an oven adjusted at 60 °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 a 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). The doped sol-gel glasses were prepared using the same method as described above; however, 0.039 mol of the organic dopant (urea, thiourea, n-propylamine, iso-propylamine, or 2-methoxyaniline) was added to the reaction mixture to form U, THU, PA, IPA, or AN, respectively.

### 2.3. Characterization of the Prepared Sol-Gel Glasses

FTIR measurements (Nicolet 380 FT-IR Spectrometer, Thermo Scientific, Madison, WI, USA) for all sol-gels were performed to determine the existing functional groups. Sol-gel glasses (0.01 g) were ground in a blender at 20 rps for 2 min. The particle sizes were measured using sieves (Retsch test sieve, Retsch GmbH 88 Co.KG, Duesseldorf, Germany) 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 each 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 °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, Tokyo, Japan). 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:  $q = \frac{(C_i - C_e)}{m} \times V$ .

The removal percentage was also calculated using the following equation:

$$\% \text{ Removal} = \frac{(C_i - C_e)}{C_i} \times 100$$

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

### 3. Results and Discussion

#### 3.1. Physical Characteristics of the Prepared Nanocomposites

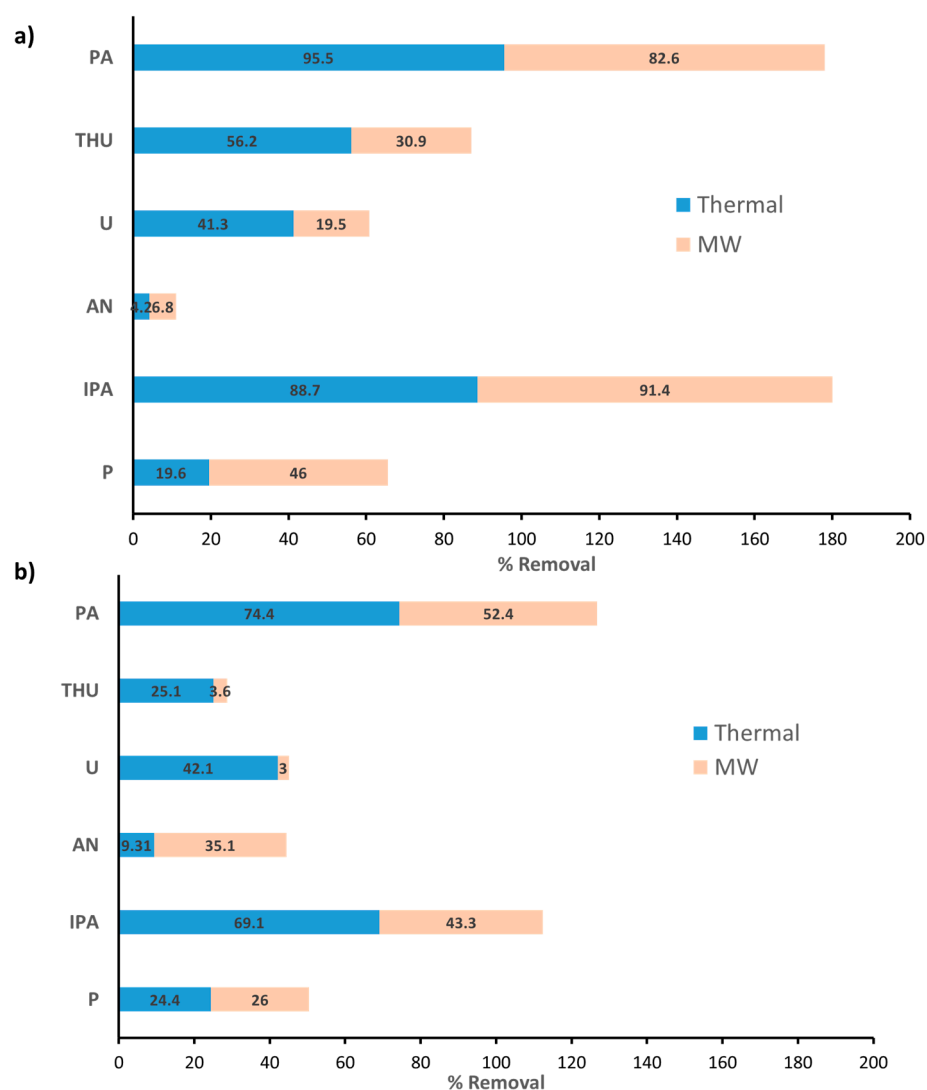
The synthesized sol-gel glasses varied in their color and transparency, as well as in their particle size, which ranged from <250  $\mu\text{m}$  to 2 mm, as shown in Table 1.

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

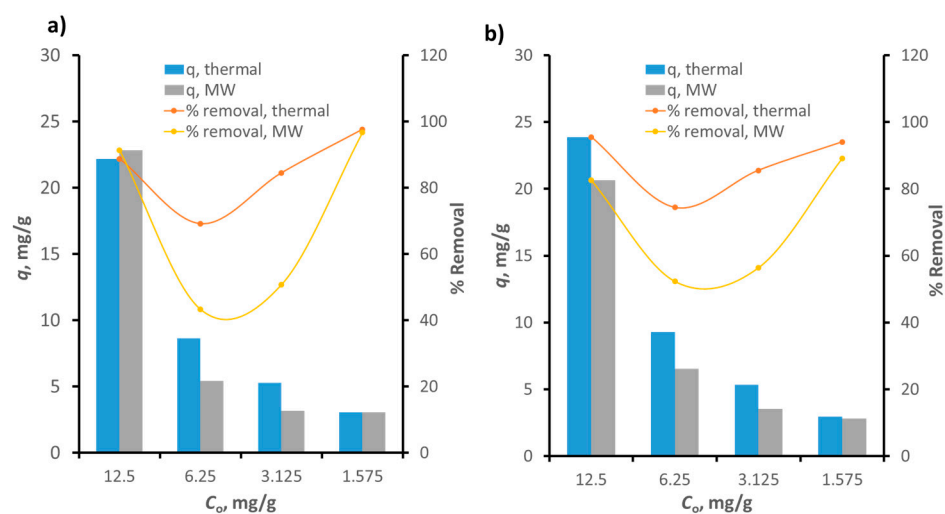
| Sol-Gel Glass | Conventional Thermal Treatment |              |                         | Microwave Irradiation |              |                       |
|---------------|--------------------------------|--------------|-------------------------|-----------------------|--------------|-----------------------|
|               | Color                          | Transparency | Particle Size           | Color                 | Transparency | Particle Size         |
| P             | Colorless                      | Transparent  | 500–630 $\mu\text{m}$   | Colorless             | Transparent  | 300–500 $\mu\text{m}$ |
| U             | Orange                         | Transparent  | 500–630 $\mu\text{m}$   | White                 | Opaque       | 250–500 $\mu\text{m}$ |
| THU           | Yellow                         | Opaque       | <250 $\mu\text{m}$      | White                 | Opaque       | <250 $\mu\text{m}$    |
| PA            | Orange                         | Opaque       | 250 $\mu\text{m}$ –2 mm | Orange                | Opaque       | 250–630 $\mu\text{m}$ |
| IPA           | Orange                         | Opaque       | 500 $\mu\text{m}$ –2 mm | Orange                | Opaque       | 250–630 $\mu\text{m}$ |
| AN            | Black                          | Opaque       | 500–630 $\mu\text{m}$   | Black                 | Opaque       | 250–630 $\mu\text{m}$ |

#### 3.2. Adsorption Study on MB

The as-synthesized adsorbents were examined for their capacity to remove MB from aqueous solutions, and two concentrations of MB, 6.5 and 12.5 mg/L, were tested as shown in Figure 1a,b, respectively. Clearly, the highest removal efficiencies were exhibited by PA, IPA, and THU prepared by either the thermal or MW method. Among all the tested adsorbents, the thermally-prepared PA yielded the highest removal, reaching 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,b, respectively. It can be observed that both adsorbents behaved similarly with regard to both adsorption capacity and percent removal. The capacity increased as the concentration was increased due to the higher concentration gradient, which improved the mass transfer of MB from the bulk solution to the adsorbent surface [8,9]. On the other hand, the removal, which was dependent on the ratio of concentration gradient to initial concentration, decreased with the increasing concentration due to saturation of active sites [8,10]. However, it increased again at the highest concentration of 12.5 mg/L due to the effect of the concentration gradient [9,11] which counteracted the effect of site saturation. Thus, the removal showed a minimum value at 6.25 mg/L. The highest removal efficiencies for both adsorbents, prepared thermally or by MW, were achieved at the lowest and highest concentrations of 1.6 and 12.5 mg/L. The MW-treated PA, however, showed a slightly lower removal and adsorption capacity than the other sol-gels at these two concentrations. In light 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 dye concentrations.

### 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 shared O-H,  $\text{sp}^3$  C-H,  $\text{CH}_3$ , 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 ( $\text{cm}^{-1}$ ) | Functional Group          | Thermally-Treated |         | MW-Treated      |         |
|---------------------------------|---------------------------|-------------------|---------|-----------------|---------|
|                                 |                           | PA                | IPA     | PA              | IPA     |
| 3500–3400                       | O-H stretch               | ✓                 | ✓       | ✓ broad         | ✓ broad |
| 2800–3000                       | $\text{sp}^3$ C-H stretch | ✓                 | ✓       | ✓               | ✓       |
| 2350                            | Si-H                      | ✓                 | ---     | ✓ small doublet | ---     |
| 1500–1550                       | N-H bending               | ✓                 | ✓       | ✓               | ✓       |
| 1600                            | C=O                       | ✓                 | ✓       | ✓               | ---     |
| 1380                            | $\text{CH}_3$ bending     | ✓                 | ✓ sharp | ✓ sharp         | ✓       |
| 1075–1100                       | Si-O-Si                   | ✓                 | ✓ sharp | ✓ sharp         | ✓ sharp |
| 942–972                         | Si-OH stretch             | ✓                 | ✓       | ✓ small         | ✓       |

After the adsorption of MB onto the thermally treated PA sol-gel glass, no change in the FTIR bands was observed except in the  $2357.7 \text{ cm}^{-1}$  bands pertaining to Si-H, the  $3039.9\text{--}2975.2 \text{ cm}^{-1}$  bands assigned for C-H and the band at  $952.1 \text{ cm}^{-1}$  for Si-OH, since they all disappeared after adsorption. For the MW-treated PA sol-gel glasses, the Si-H band at  $2359.4 \text{ cm}^{-1}$  and the bands of C-H at  $3073.7 \text{ cm}^{-1}$  and  $2976.4 \text{ cm}^{-1}$  disappeared, while the bands of  $1^\circ$  amine and C=O at  $1631.3 \text{ cm}^{-1}$  and  $1512.4 \text{ cm}^{-1}$  shifted to  $1642.8 \text{ cm}^{-1}$  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  $2854.2 \text{ cm}^{-1}$ , the band of  $\text{CH}_3$  at  $1384.1 \text{ cm}^{-1}$ , the band of Si-OH at  $959.7 \text{ cm}^{-1}$ , and the symmetric vibrational band of Si-O-Si at  $797.5 \text{ cm}^{-1}$ . In contrast, the MW-treated sol-gel glasses showed no change after MB adsorption except for the bands of C-H at  $3061.5 \text{ cm}^{-1}$  and  $2985.6 \text{ cm}^{-1}$ , which disappeared after adsorption. This suggests that Si-H, Si-OH, Si-O-Si, C=O, N-H, C-H, and  $\text{CH}_3$  could be involved in adsorption.

### 3.4. Mechanism of Adsorption

PA and IPA had the highest reactivity among the synthesized sol-gel doped glasses towards removal of MB, while AN had the lowest reactivity. This could be attributed to the higher basicity of the aliphatic amines of PA ( $K_b = 4.7 \times 10^{-4}$ ) and IPA ( $K_b = 4.0 \times 10^{-4}$ ) relative to the aromatic amine AN ( $K_b = 3.00 \times 10^{-10}$ ), which resulted in increased interaction between the lone pair of electrons on the amino nitrogen and MB. With respect to urea, although it had lower basicity than the aromatic amine AN ( $K_b = 1.5 \times 10^{-14}$ ), it showed a higher adsorption capacity and better removal efficiency than AN. In some 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 solutions; hence, urea can destabilize MB aggregates [12]. Furthermore, electrostatic interactions or redox reactions 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 interact similarly with thiourea, but to a lesser extent than urea, owing to the acidic properties of the electron-deficient sulfur on thiourea.

### 3.5. Conclusions

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

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

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