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RESEARCH PAPER

Preparation and Characterization of SiO_2/Polyazomethine/Poly(o-Anisidine) Nanocomposite for the Removal of Methylene Blue Dye from Aqueous Solutions

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ABSTRACT

In this work, a novel ternary nanocomposite based on nano-silica, polyazomethine, and poly(o-anisidine) denoted SiO_2/PAM/P-o-Ans was synthesized via combined condensation and oxidative polymerization and evaluated as an adsorbent for methylene blue (MB) from aqueous media. Nano-SiO_2 was extracted from rice husks by alkaline dissolution–acid precipitation. Characterization was performed using FT-IR, XRD, TEM, FESEM, AFM, and TGA. FT-IR confirmed azomethine (C=N) linkages and poly(o-anisidine) incorporation. XRD indicated a predominantly amorphous structure. TEM and FESEM revealed spherical nanoparticles (10–100 nm). AFM gave an average particle diameter of 81.20 nm with Sa = 54.08 nm. TGA showed multi-stage decomposition with 26.2% residual mass. GPC yielded Mw = 38,700 g/mol and dispersity of 1.82. Batch adsorption achieved maximum MB removal of 92.20% at pH 9, with equilibrium at 90 min. Adsorption data fitted the Langmuir model. Thermodynamic analysis revealed negative $\Delta G°$, $\Delta H°$, and $\Delta S°$ values, confirming spontaneous, exothermic adsorption of MB onto the nanocomposite.

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INTRODUCTION

Contamination of water bodies by synthetic dyes remains one of the most pressing environmental challenges of our time. Textile, paper, and pharmaceutical industries routinely discharge dye-laden effluents into surface and groundwater, where their chemical stability and poor biodegradability allow them to persist [1,2]. Methylene blue (MB), a cationic thiazine dye, is of concern due to its carcinogenic potential and adverse effects on aquatic photosynthesis [3]. Among various treatment strategies, adsorption has gained traction owing to its simplicity, cost-effectiveness, and regeneration possibility [4,5].

Over the past decade, polymeric nanocomposites have attracted interest as adsorbents because their high surface area and tuneable functionality suit them for capturing pollutants [1,6]. Polyazomethines bearing imine (C=N) linkages offer coordination and electrostatic interaction sites, while poly(o-anisidine) brings amine and methoxy functional groups for dye binding [7,8]. Reinforcing with SiO_2 nanofillers boosts thermal stability and porosity [5,9].

The present study synthesizes a ternary SiO_2/PAM/P-o-Ans nanocomposite through sequential

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condensation–oxidative polymerization and evaluates its MB removal efficiency. The influence of pH, adsorbent dose, contact time, initial concentration, and temperature was investigated. Adsorption data were analysed using Langmuir and Freundlich models, and thermodynamic parameters were calculated.

MATERIALS AND METHODS

Raw Materials

1,3-Benzenedialdehyde and 1,4-diaminobenzene (Santa Cruz, USA), HCl (BDH), potassium persulfate, NaOH, DMF, o-anisidine, glacial acetic acid (CDH), methylene blue ($C_{16}H_{18}ClN_3S$, MW = 319.85), and deionized water were used as received.

Preparation of SiO_2 Nanoparticles

Nano-silica was synthesized from rice husks by alkaline extraction–acid precipitation [10–12]. Husks were washed, dried at 70 °C, and calcined at 900 °C for 7 h. The ash (5 g) was dissolved in 0.5 M NaOH (500 mL), heated 4 h with stirring. The filtrate was adjusted to pH 7 with HCl, aged 24 h, centrifuged, and dried at 70 °C for 6 h.

Synthesis of Polyazomethine (PAM)

PAM was synthesized by condensation of 1,3-benzenedialdehyde (0.1341 g in 10 mL DMF) with 1,4-diaminobenzene (0.1082 g in 10 mL DMF) at 90 °C with glacial acetic acid catalyst for 12–18 h [13–15]. The product was precipitated, washed, and dried under vacuum.

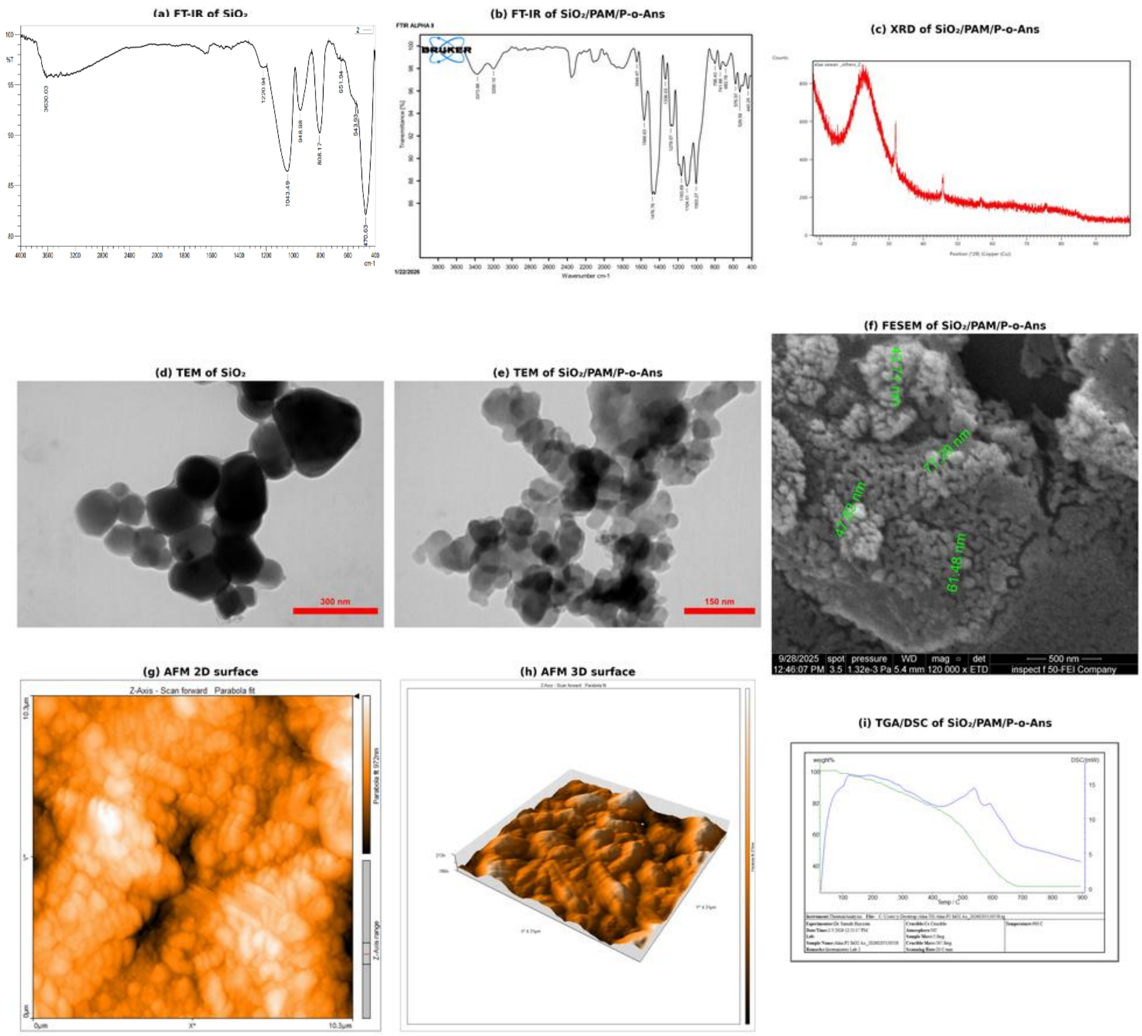

Fig. 1. Characterization: (a) FT-IR of SiO_2; (b) FT-IR of nanocomposite; (c) XRD; (d) TEM of SiO_2; (e) TEM of nanocomposite; (f) FESEM; (g) AFM 2D; (h) AFM 3D; (i) TGA/DSC.

Synthesis of Poly(o-anisidine)

Poly(o-anisidine) was prepared by oxidative polymerization: o-anisidine (3 mL) in 1 M HCl (10 mL) was polymerized with $K_2S_2O_8$ (4 g in 10 mL HCl) in an ice bath for 2 h, then left 12 h [16].

Preparation of SiO_2/PAM and SiO_2/PAM/P-o-Ans

For the binary composite, 0.5 g nano-SiO_2 was sonicated in DMF (30 min) and used in the PAM condensation as described above [17,18]. For the ternary composite, SiO_2/PAM (0.5 g) was dispersed in water by ultrasonication, then o-anisidine was polymerized onto it using $K_2S_2O_8$ in ice-bath conditions (2 h stirring, 12 h aging) [19,20].

Characterization

Materials were characterized by FT-IR (Bruker ALPHA II; Shimadzu IRSpirit, 400–4000 cm^{-1}), XRD (PANalytical, Cu Kα), TEM, FESEM (FEI Inspect F50, 120,000×), AFM (MountainsSPIP Academic), TGA/DSC/DTG (20 °C/min to 900 °C), and GPC.

Batch Adsorption

Adsorption was studied in batch mode (10 mL dye solution + adsorbent, agitated). Residual MB was measured spectrophotometrically (calibration: Ce = (A − 0.0001)/0.0314). R(%) = (C_0 − Ce)/C_0 × 100 and qe = (C_0 − Ce) × V/m. Effects of pH (3–11), mass (0.01–0.05 g), time (15–150 min), concentration, and temperature (25–80 °C) were studied at C_0 = 100 ppm, V = 10 mL.

RESULTS AND DISCUSSION

Characterization

The FT-IR spectrum of nano-SiO_2 (Fig. 1a) showed bands at 3630 cm^{-1} (O–H of Si–OH), 1221

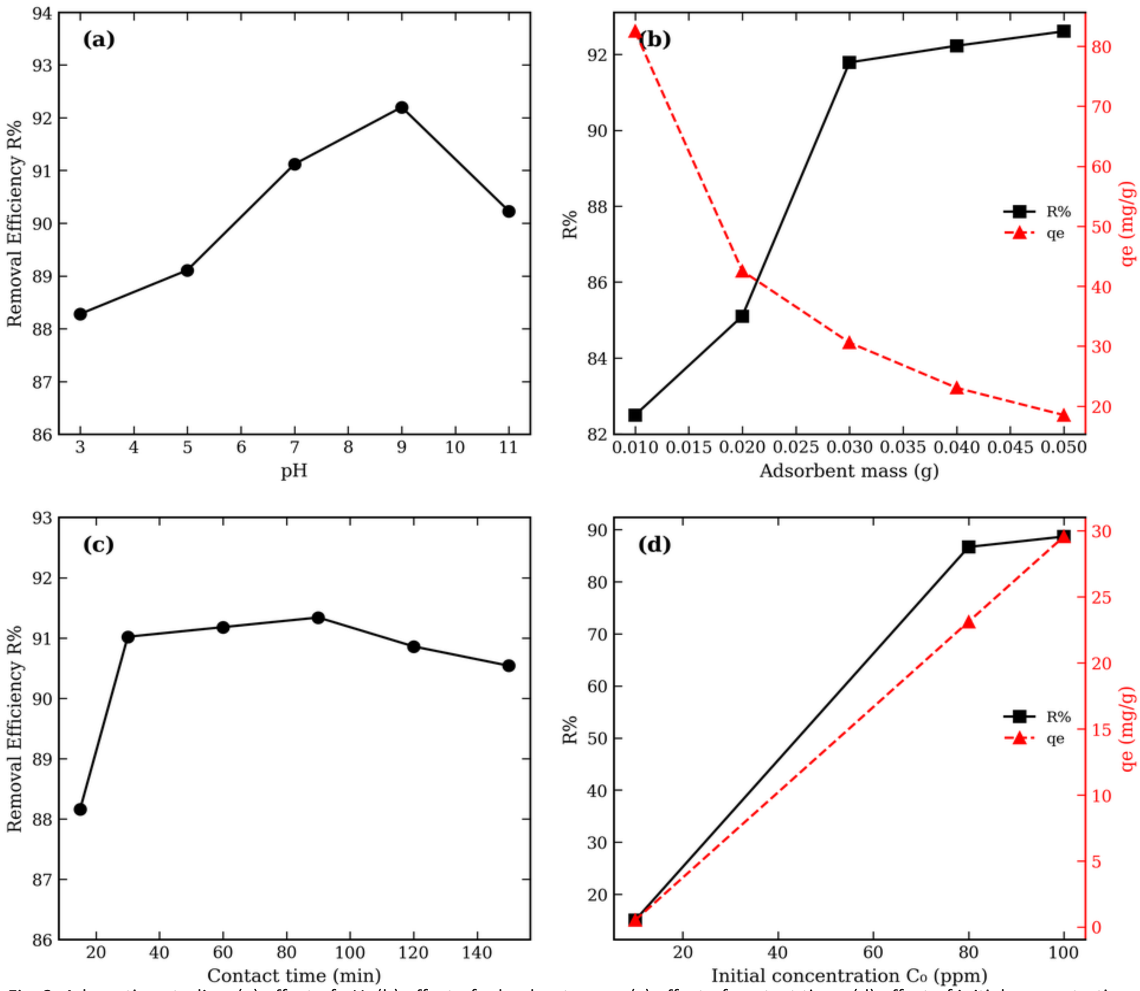

Fig. 2. Adsorption studies: (a) effect of pH; (b) effect of adsorbent mass; (c) effect of contact time; (d) effect of initial concentration.

cm^{-1} (symmetric Si–O–Si), 1043 cm^{-1} (asymmetric Si–O–Si), 949 cm^{-1} (Si–OH), 808 cm^{-1} (Si–O–Si bending), and 471 cm^{-1} (Si–O rocking) [21,22]. The nanocomposite spectrum (Fig. 1b) confirmed azomethine formation at 1567 cm^{-1} (C=N), with bands at 3374 cm^{-1} (N–H), 1477 cm^{-1} (C=C aromatic), 1279 cm^{-1} (C–N), 1003 cm^{-1} (C–O–C methoxy), and 742 cm^{-1} (C–H aromatic) [23–25]. The XRD pattern (Fig. 1c) showed a broad hump at 2θ ≈ 22°, confirming amorphous structure [21]. TEM of SiO_2 (Fig. 1d) revealed spherical particles (20–100 nm) with agglomeration, while the nanocomposite TEM (Fig. 1e) showed particles embedded in a polymeric matrix [26,27]. FESEM (Fig. 1f) showed granular surface with particles of 44–77 nm within the polymer matrix [28]. AFM analysis (Fig. 1g,h) gave Sa = 54.08 nm, Sq = 67.98 nm, Sdr = 10.36%, mean diameter = 81.20 nm, and 369 detected features [29]. TGA (Fig. 1i) showed multi-stage decomposition with 26.2% residual mass at 897 °C, corresponding to the SiO_2 fraction [30,31]. GPC yielded Mn = 21,200, Mw = 38,700, Mz = 66,300 g/mol, and Đ = 1.82 [32,33].

Adsorption Studies

The effect of pH (Fig. 2a) showed R% increasing from 88.28% (pH 3) to 92.20% (pH 9) then declining to 90.23% (pH 11). At low pH, protonated surface amines repel cationic MB; deprotonation at higher pH creates negative surface charge enhancing attraction [34,35]. The effect of adsorbent mass (Fig. 2b) showed R% rising from 82.49% (0.01 g) to 92.61% (0.05 g), while qe decreased from 82.49 to 18.52 mg/g due to unsaturated sites at higher doses [36]. An optimum of 0.03 g was selected (R% = 91.79%, qe = 30.60 mg/g). Contact time (Fig. 2c) showed rapid uptake to 91.02% at 30 min, with equilibrium at 90 min (91.34%) [37,38]. The concentration study (Fig. 2d) showed R% increasing from 15.00% at 10 ppm to 88.67% at 100 ppm, with qe rising from 0.50 to 29.56 mg/g [39].

Adsorption Isotherms

The Langmuir model (Ce/qe = 1/(Qm·b) + Ce/Qm) and Freundlich model (log qe = log Kf + (1/n) log Ce) were applied to the equilibrium data (Fig.

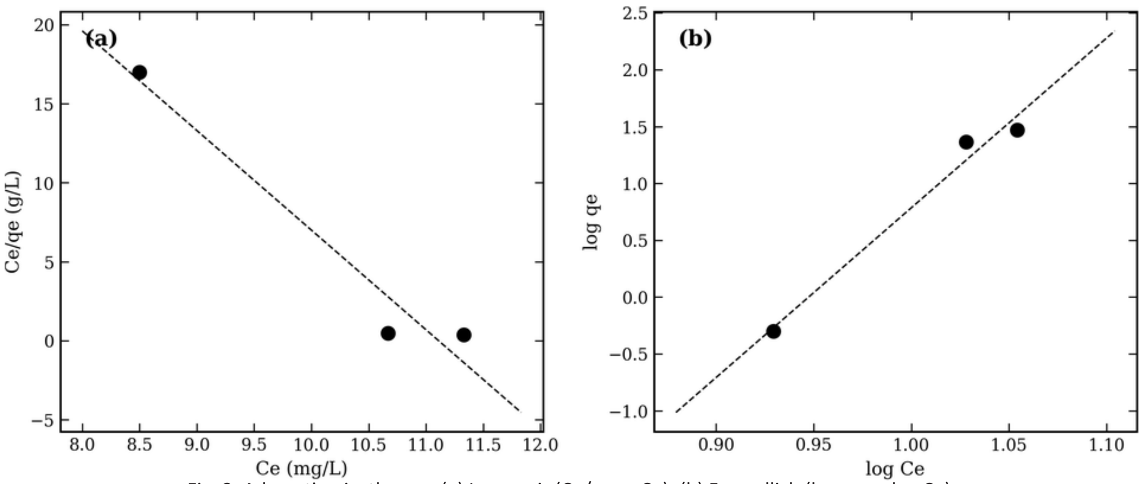

Fig. 3. Adsorption isotherms: (a) Langmuir (Ce/qe vs Ce); (b) Freundlich (log qe vs log Ce).

Table 1. Langmuir and Freundlich isotherm parameters.

Model	Parameter	Value
Langmuir	Qm (mg/g)	27.50
	b (L/mg)	1.24
	R^2	0.9999
Freundlich	Kf	37.60
	1/n	0.099

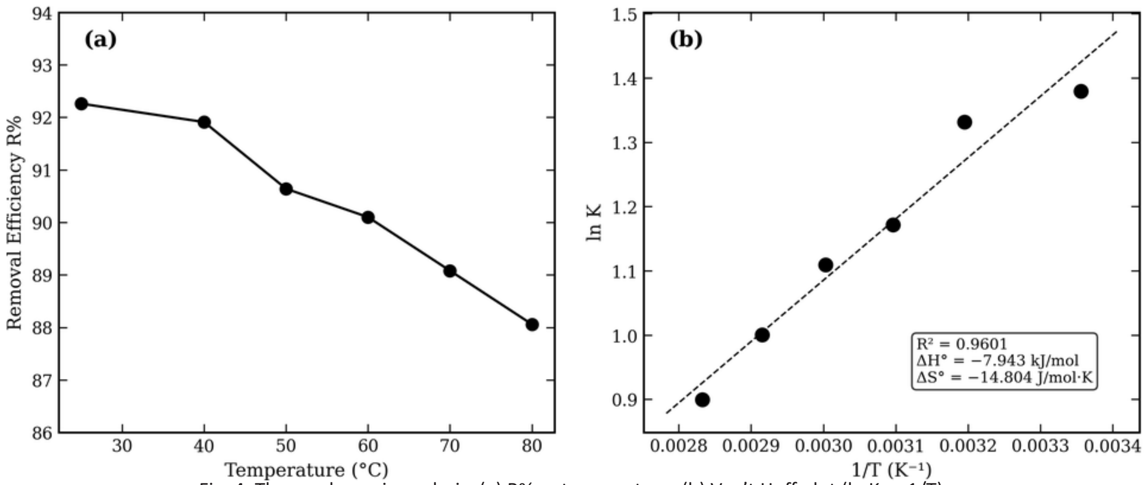

Fig. 4. Thermodynamic analysis: (a) R% vs temperature; (b) Van't Hoff plot (ln K vs 1/T).

Table 2. Van't Hoff parameters.

ΔH° (kJ/mol)	ΔS° (J/mol·K)	R^2
−7.943	−14.804	0.9603

3). The isotherm parameters derived from the linear plots are summarised in Table 1.

Temperature and Thermodynamics

R% decreased from 92.26% at 25 °C to 88.06% at 80 °C (Fig. 4a), confirming exothermic character. Thermodynamic parameters (Table 2) were obtained via $\Delta G° = -RT \ln K$ and the Van't Hoff equation: $\ln K = -\Delta H°/RT + \Delta S°/R$ (Fig. 4b, $R^2 = 0.9603$) [40,41]. All ΔG° values are negative (−3.47 to −2.64 kJ/mol), confirming spontaneous adsorption. The magnitudes (< 20 kJ/mol) indicate physisorption [38]. Negative ΔH° (−7.943 kJ/mol) confirms exothermic process. Negative ΔS° (−14.804 J/mol·K) indicates ordered MB arrangement on the surface [42,43].

CONCLUSION

A ternary SiO_2/PAM/P-o-Ans nanocomposite was successfully prepared via sequential condensation and oxidative polymerization. FT-IR confirmed azomethine (C=N) linkage formation at 1567 cm^{-1} alongside poly(o-anisidine) incorporation. XRD revealed a predominantly amorphous structure ($2\theta \approx 22°$). TEM and FESEM showed spherical nanoparticles (44–77 nm), while AFM gave a mean particle diameter of 81.20 nm (Sa = 54.08 nm). TGA indicated 26.2% residual mass at 897 °C, and GPC yielded Mw = 38,700 g/mol with Đ = 1.82. Batch adsorption experiments demonstrated a maximum methylene blue removal of 92.20% at pH 9, adsorbent dose 0.03 g, contact time 90 min, and 25 °C. Removal decreased with rising temperature (88.06% at 80 °C), confirming an exothermic process. Thermodynamic analysis yielded ΔG° = −3.42 to −2.64 kJ/mol, ΔH° = −7.943 kJ/mol, and ΔS° = −14.804 J/mol·K, indicating spontaneous physisorption. These results highlight SiO_2/PAM/P-o-Ans as a promising adsorbent for cationic dye remediation.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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