



Composite fabrication and characterization of crosslinked polyaniline/*Pterocladia capillacea*-activated carbon for adsorption of direct blue-86 dye from water

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Abstract

The fabrication of crosslinked polyaniline/*Pterocladia capillacea*-activated carbon composite (CrossPANI/P-AC) at different ratios (1:0, 1:0.2, 1:0.6, and 1:1) was studied. CrossPANI/P-AC composites were fabricated by the in situ polymerization of aniline using hydrogen chloride as an acidic dopant, and ammonium persulfate as initiator, while *Pterocladia capillacea*-activated carbon was synthesized by the chemical activation method and incorporated into the polymer matrix. The samples were characterized by the terms such as Fourier transform infrared (FTIR) spectroscopy, Brunauer–Emmett–Teller, X-ray diffraction (XRD), thermogravimetric analysis, scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDX). FTIR spectroscopy showed the main characteristic peak positions of CrossPANI/P-AC; XRD showed low crystallinity of CrossPANI/P-AC. A high specific surface area for CrossPANI/P-AC was achieved at a ratio of 1:0.2 where Brunauer–Emmett–Teller surface area, total pore volume, and mean pore diameter values were 166.10 m²/g, 0.0141 cm³/g, and 3.40 nm, respectively. The capability of CrossPANI/P-AC (1:0.2) composite as adsorbent for Direct blue-86 (DB-86) dye from aqueous

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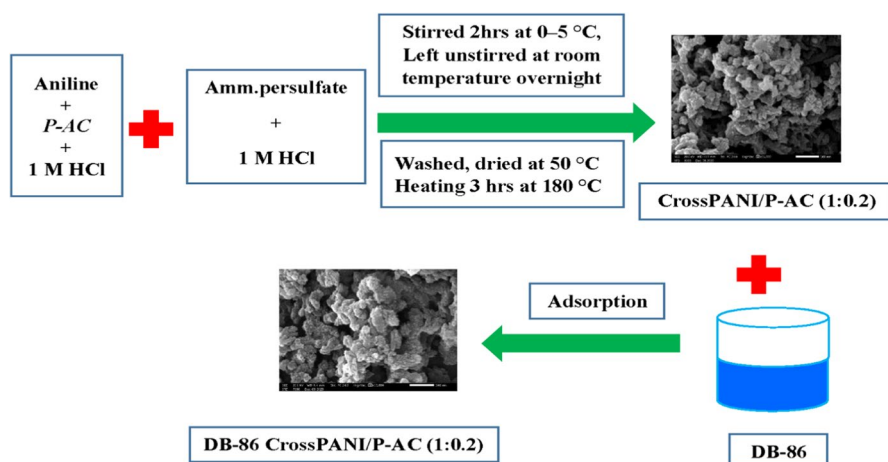
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solution was investigated. The impact of initial dye concentration, temperature, pH, and contact time on the DB-86 dye adsorption from its water solution was examined. The equilibrium adsorption data were well represented by the Langmuir isotherm achieving maximum monolayer capacity (Q_m) of 163.93 mg/g at a dose of 0.5 g/L. In contrast, the kinetic adsorption data were well fit by the pseudo-second-order model. Thermodynamic analysis demonstrated that DB-86 dye adsorption occurs spontaneously, endothermically, and physically in nature. The results demonstrated that these composites effectively removed DB-86 dye from aqueous solutions and could be recycled.

Graphical abstract



Keywords Polyaniline · Activated carbon · *Pterocladia capillacea* · Direct blue-86 dye · Adsorption · Isotherm models · Kinetic models · Thermodynamic model

Introduction

Water is the most valuable human resource on the planet [1], and it necessitates continuous examination and adjustment of water resource policy at all levels. Water pollution has been identified as the most prominent global cause of mortality and disease [2–4], with water contamination responsible for the deaths of 1.8 million people in 2015 [5]. The introduction of numerous colored chemicals into diverse water bodies due to increasing industrialization and urbanization has recently caused a major imbalance in aquatic systems [6]. According to the number of workers, export prices, and local production costs, Egypt's textile industry is one of the country's most important [7]. The textile industry sector, in particular, produces a lot of dye-bearing effluents [8]. Anionic dyes, cationic dyes, and non-ionic dyes are the three types of dyes, and the majority of them are harmful, and some are cancerous [8, 9]. Direct Blue 86 dye (Color Index No. 74180, CAS

No. 1330–38-7), also called Direct Fast Blue GL or Direct Fast Turquoise Blue GL, having chemical formula $C_{32}H_{14}CuN_8Na_2O_6S_2$, is a gray-blue to blue powder, well soluble in water; the solution is lake blue [10]. It is an anionic dye used in the dyeing of cellulosic fabrics such as cotton, flax, viscose rayon, acetate, and jute. It can also be used to color leather and paper [11].

A number of physical or chemical processes were applied for dye treatment [12]. Chemical coagulation [13], chemical oxidation [14], ozonation [7, 15–20], irradiation [21–26], electrochemical oxidation [27], biological process [28], precipitation [29], and adsorption [30–34] are some of these methods. Because of its accuracy, ease of operation, lack of sensitivity to harmful compounds, and capacity to treat concentrated colored solutions, adsorption is a practical and cost-effective approach for removing colors [35]. Many adsorbing materials are used for the adsorption process, including activated alumina, silica gel, activated carbon [30–36], molecular sieve carbon, molecular sieve zeolites, polymeric [37], and polymer composite [38–40].

Recently, carbon-based/polymer composites have been investigated for water treatment, where it easily obtained and characterized. Polymer/activated carbon composite is considered a low-cost adsorbent for removing different pollutants from aquatic environments [39, 40]. The research focused on producing effective activated carbons alternatives to commercial activated carbon by employing biomaterials to make cheap and effective activated carbon [30–36]. There are several suitable biomaterials used to prepare activated carbon, including *Ulva lactuca* [34], orange peel [36], *Pisum sativum* peels [30], Pea peels [31], *Pterocladia capillacea* [41]. Marine biomaterial *Pterocladia capillacea* is available in the Mediterranean, and its chemically activated carbon by zinc chloride achieved a highly specific surface area under the optimized conditions at activation temperature 600 °C, holding time 30 min, and 1 M HCl soaked was 1202.70 m²/g [41].

Polyaniline (PANI), a conducting polymer with unusual characteristics, is one of the oldest researched polymers [42, 43]. Because of its low cost, ease of synthesis, good thermal and electrical properties, and environmental stability, PANI is a very promising polymer [44, 45]. As a result, it is widely employed in various disciplines, including rechargeable batteries, sensors, electrode materials, electrocatalysis, and anticorrosion [45]. The imine-to-amine nitrogen ratio in polyaniline can exist in three different oxidant states [46, 47]. Specifically, emeraldine base (EB) is a half-reduced form, leucoemeraldine (LB) is a fully reduced form, and pernigrani is a fully oxidized form [48]. PANI was synthesized by two kinds of polymerization: one is the chemical oxidation and the other is the electrochemical method [45]. Recently, polyaniline (PANI), CrossPolyaniline (CrossPANI) and their composites have recently demonstrated very high removal capacity for heavy metals such as Cr(VI) [49–56], Cr(III) [57], Zn(II) [58], Cd(II) [59], Pb(II) [60], Cu(II) [61], Hg(II) [61], dyes such as Direct Green 6 [62], Reactive Orange 16 [62], methyl orange [63], methylene blue [63], Reactive red 198 [64], Brilliant Green [65].

Therefore, the aim of this work was to fabricate crosslinked polyaniline/*Pterocladia capillacea*-activated carbon composites (CrossPANI/P-AC) as adsorbents and study their characterization using X-ray diffraction (XRD),

scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and Brunner–Emmett–Teller (BET) surface area analysis. Furthermore, we estimate the adsorption behavior of CrossPANI/P-AC for removing of the Direct Blue 86 dye (an anionic dye) from the aquatic environment.

Materials and methods

Chemicals

Aniline ($C_6H_5NH_2$, M.W=93.13 g, Assy=99.5%) was purchased from Loba Chemie PVT. LTD, India. Ammonium persulfate $[(NH_4)_2S_2O_8]$, M.W=228.19 g, Assy=98%] was purchased from Oxford Lab Chem (Navghar Road, India). Hydrochloric acid (HCl, M.W=36.46 g, Assy=30–34%) was obtained from SD Fine-Chem Limited, Mumbai, India. Sodium hydroxide (NaOH, M.W=40 g, Min. Assy 96%) and ethanol (C_2H_6O , M.W=46.07 g, Assy=99.5%) were purchased from ADWIC, El Nasr pharmaceutical chemical company, Egypt. Sulfuric acid (H_2SO_4 , M.W=98.07 g, Assy=98.0%) purchased from SD Fine-Chem Limited, Mumbai, India. Direct Blue–86, Chemical formula $C_{32}H_{14}O_6N_8S_2CuNa_2$ (M.W=780.2 g) obtained from Sigma-Aldrich, USA (Fig. 1). All of the substances used in this experiment were analytical-grade reagents. All of the solutions and reagents were made with distilled water.

Synthesis of *Pterocladia capillacea*-activated carbon (PC-AC) nanoparticles

Pterocladia capillacea-activated carbon (PC-AC) nanoparticles were prepared by the chemical activation method [41]. In briefly, *Pterocladia capillacea* was collected from the Mediterranean, washed with distilled water, dried in an oven then milled, crushed and stored until used. The dried *Pterocladia capillacea* (10 g) was soaked

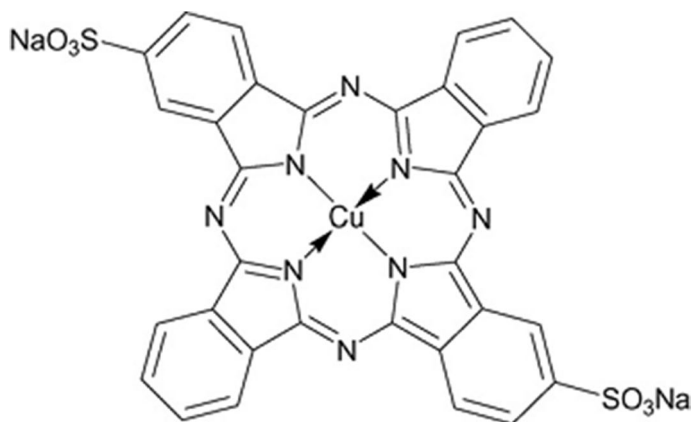


Fig. 1 Structure of DB-86 dye (Direct Fast Turquoise Blue GL), MW = 778.96

with solution of ZnCl_2 (5 g) for 24 h. After that the mixtures were dehydrated in 24 h at 110 °C and then pyrolysis in a quartz tube under N_2 atmosphere at carbonized temperature 600 °C, holding time 30 min. The activated carbon was chilled at ambient temperature before being washed with boiling water and dried in a 70 °C oven. The samples were then refluxed in a Soxhlet extractor for 2 h with 1 M HCl, then filtered and washed with distilled water until pH was neutral. The activated carbon was then dried at 70 °C, crushed, sieved smaller than 100 μm , and stored in a glass bottle until needed.

Synthesis crosslinked Polyaniline/*Pterocladia capillacea*-activated carbon composite (CrossPANI/P-AC)

Polyaniline (PANI) was synthesized on the surface of the P-AC with ratio (1:0, 1:0.2, 1:0.6, 1:1) as follows: aniline and *Pterocladia capillacea*-activated carbon were premixed in HCl (1 M) for 2 h under cooling the mixture below 5 °C using ice bath. A pre-cooled $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.3 M) in HCl solution (1 M) was slowly added under stirring to the monomer (aniline) solution for 30 min. The reaction vessel was placed in an ice bath cooling system during oxidation cooling since the reaction is highly exothermic ($\Delta H = 372 \text{ kJ mol}^{-1}$). After complete oxidation, the reaction mixture was stirred for two hours at low temperature (0–5 °C) and then left unstirred overnight at room temperature. The precipitated polymer (dark blue powder) was filtered, washed with copious amounts of distilled water, and then diluted with HCl solution until the washing liquid was colorless. Then, we washed with ethanol to remove oligomers and non-polymeric impurities and dried under vacuum at 50 °C to produce the aimed material. Heating PANI/P-AC produced CrossPANI/P-AC at 180 °C for 3 h [61].

Characterization

X-ray diffraction (XRD) patterns were obtained using Bruker's X-ray diffractometer (model: 2D Phaser, Germany), in the range 2θ : 10°–80°, with $\text{CuK}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). FTIR was studied using Bruker VERTEX70 Spectrometer connected with platinum ATR (model V-100, Germany) over the range of (400–4000 cm^{-1}) to determine the chemical bonds and functional groups. Thermal stabilities studies were operated by Simultaneous Thermal Analyzer (model: SDT650, USA) instrument in the temperature range of room temperature to 900 °C, with a ramping temperature of 5 °C per minute under an atmosphere of nitrogen gas (100 mL/min). The Brunner–Emmett–Teller (BET) surface areas were determined by N_2 adsorption–desorption isotherm using (BELSORP – model: Mini II, BEL Japan). The morphological structure was performed using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) using (JEOL-JSM-5300 LV, Tokyo, Japan). The point of zero charges (pH_{pzc}) was determined as described in [66] using pH meter JENCO (model 6173, USA). UV–visible spectra

of direct blue 86 dye before and after adsorption were recorded on PG instrument (model T80, UK) spectrophotometer.

Removal of Direct Blue 86 dye by batch method

Direct Blue 86 dye stock solution (1000 mg/L) was prepared by dissolving 1.0 g of DB-86 dye in 1000 ml distilled water. All working solutions with various concentrations were obtained by successive dilution with distilled water. Measurement of DB-86 dye concentration was carried out by spectrophotometer at ($\lambda_{\text{max}} = 615 \text{ nm}$) using a standard curve. The removal of DB-86 dye was performed via batch equilibrium method. The removal % of DB-86 dye using CrossPANI/P-AC composites with different ratios was determined. The influence of pH, contact time, CrossPANI/P-AC dosage, initial DB-86 dye concentration and adsorption temperature were investigated.

The removal % of DB-86 dye on CrossPANI/P-AC with different ratios (1:0, 1:0.2, 1:0.6, 1:1) was tested by adding 50 mg of each composite to 100 mL of 50 mg/L DB-86 dye solution at pH 2.2, and shaking at 200 rpm for 180 min contact time. The adsorption capacity of CrossPANI/P-AC for DB-86 dye is calculated from equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the adsorption capacity of DB-86 dye-loaded adsorbent (mg/g), C_0 and C_e represent the initial and equilibrium concentrations of DB-86 dye (mg/L), m is the amount of CrossPANI/P-AC (mg), and V is the volume (L) of DB-86 dye solution.

The effect of solution pH on the adsorption was conducted by adding 0.05 g of CrossPANI/P-AC (1:0.2) composite to 100 mL of 50 mg/L DB-86 dye solution at pH range from 2.2 to 8.5 adjusted using JENCO pH meter and shaken in a shaker operated at 200 rpm at 27 ± 1 °C. After three hours, an appropriate amount of the reaction solution was taken out and then centrifuged, and the remained concentration were measured.

The effect of adsorbent mass on DB-86 dye adsorption was investigated by adding different amounts of CrossPANI/P-AC (1:0.2) (0.05, 0.075, 0.1, 0.125, and 0.150 g) into a number of flasks containing 100 mL known DB-86 dye solutions concentration and shaking at 200 rpm at 27 ± 1 °C to the equilibrium uptake (180 min) by determining the amount of DB-86 dye adsorption was.

At pH 2.2, shaking speed 200 rpm, and temperature 27 ± 1 °C, the effect of time and kinetics experiments was carried out in a series of flasks containing 0.05 g of adsorbent and 100 mL of DB-86 dye of various concentrations (50–150 mg/L) at time intervals of 5–180 min. At predetermined intervals, an appropriate amount of the solution was taken out and then centrifuged, and concentration was determined. The linear kinetic models such as pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion, and film diffusion were used to generate the theoretical kinetics graphic (Table 1) [67–71].

Table 1 The linear kinetic models of pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion and film diffusion

Models	Linear equation	Parameters	References
Pseudo-first-order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$ (2)	q_e (mg/g): adsorption capacity at equilibrium, q_t (mg/g): adsorption capacity at time t , K_1 (L/mg): rate constant of pseudo-first-order adsorption	[67]
Pseudo-second-order	$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (3)	K_2 (g/mg min): second-order constants h (mg/g min): initial sorption rate, $h = k_2 q_e^2$	[68]
Intraparticle diffusion	$q_t = K_{diff} t^{1/2} + C$ (4)	C (mg/g): the intercept related to the thickness of the boundary layer, K_{diff} (mg/g min ^{1/2}): intraparticle diffusion rate constant	[69, 70]
Liquid film diffusion	$\ln(1 - F) = -K_{FD} t$ (5)	F : the fractional attainment of equilibrium ($F = q_t/q_e$), K_{FD} : the film diffusion rate constant	[71]

The effect of initial concentrations was investigated at temperature 25 ± 1 °C and pH 2.2 by shaking (0.05, 0.075, 0.1, 0.125, 0.15) g of adsorbent CrossPANI/P-AC(5:1) with 100 mL of DB- 86 solution of various concentrations from (50, 75, 100, 125, 150 mg/L) and shaken in a shaker operated at 200 rpm. The adsorbent was removed by centrifugation after equilibrium, the supernatant was collected, and the concentration of DB-86 dye that remained was measured. Table 2 summarizes the adsorption isotherms for removing DB-86 dye using the Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich isotherm equations. Coefficient of determination (R^2) and average percentage errors (APE%) function determined using Eq. (6) were used to determine the validity of the isotherm models fitted by the nonlinear regression method [68].

$$APE(\%) = \frac{100}{N} \times \sum_{i=1}^N \left| \frac{q_{e, isotherm} - q_{e, calc}}{q_{e, isotherm}} \right|_i \quad (6)$$

The temperature effect on the adsorption process of DB-86 dye was investigated by adding 0.05 g of CrossPANI/P-AC (1:0.2) into flasks containing 100 mL solutions of 50 mg/L dye concentration at temperatures 35, 40, 45, and 50 ± 1 °C. The parameters of thermodynamic study such as Gibbs free energy (ΔG , J/mol), entropy change (ΔS , J/K mol) and enthalpy change (ΔH , J/mol) use van't Hoff Eqs. (11, 12, 13) [78]:

$$\Delta G = -RT \ln K_d \quad (11)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

where K_d is distribution coefficient ($K_d = q_e/C_e$, L/g), R (8.314 J/mol K), T (K) are the universal gas constant and the absolute temperature, respectively. The values of ΔH and ΔS were determined from the plot of $\ln K_d$ versus $1/T$.

Desorption experiments were studied through the following two steps. First, the samples utilized in the adsorption experiments performed with 50 mg/L initial concentration of DB-86 dye solution and 50 mg CrossPANI/P-AC(1:0.2) dose at pH 2.2 conditions and shaking at speed 200 rpm for three hours were collected and then dried at 70 °C. Secondly, 50 mg of DB-86 dye-loaded composites was immersed in 100 mL elution media NaOH (0.1 M) under shaking at a speed of 200 rpm at a temperature 27 ± 1 °C for 2 h, and then, the sample was rinsed with distilled water several times until neutral pH and dried. The eluted DB-86 dye per gram of adsorbent (q_{des}) from the concentration of DB-86 dye desorbed (C_{des}) in the solution is calculated by Eq. (14).

$$q_{des} = C_{des} \frac{V}{m} \quad (14)$$

Table 2 Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich isotherm parameters

Models	Linear equation	Parameters	Refer- ences
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} \times C_e$ (7)	q_e (mg/g): amount of adsorbate adsorbed per unit weight of adsorbent, Q_m (mg/g): maximum adsorption capacity, K_a (L/mg): adsorption equilibrium constant that is related to the apparent energy of sorption, C_e (mg/L): equilibrium adsorbate aqueous phase concentration	[72]
Freundlich	$\log q_e = \log K_f + \frac{1}{n} \log C_e$ (8)	K_f ((mg/g): Freundlich constant n : heterogeneity factor	[73]
Tempkin	$q_e = B \ln A + B \ln C_e$ (9)	$B = (RT/b)$: Tempkin constant; b : heat of adsorption (J/mole); R : universal gas constant (8.314 J/K mol); T : absolute temperature (K); A : related to the heat of sorption binding constant (L/min)	[74]
Dubinin–Radushkevich	$\ln q_e = \ln q_m - K \varepsilon^2$ (10)	q_m : monolayer adsorption capacity (mg/g); K : constant related to the adsorption energy [mol ² /kJ ²]; $E = 1/\sqrt{(2K)}$: mean free energy of sorption (kJ/mol); $\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$ Polanyi potential	[75–77]

where V is the volume of the eluent used in liters and m is the weight of the adsorbent in grams. Desorption % was calculated by comparing DB-86 dye desorbed (q_{des}) to the DB-86 dye adsorbed (q) using Eq. (15).

$$Desorption\% = \frac{q_{des}}{q} \times 100 \quad (15)$$

Three adsorption–desorption cycles were performed on the samples to ensure that the composites could function as practical DB-86 dye adsorbents.

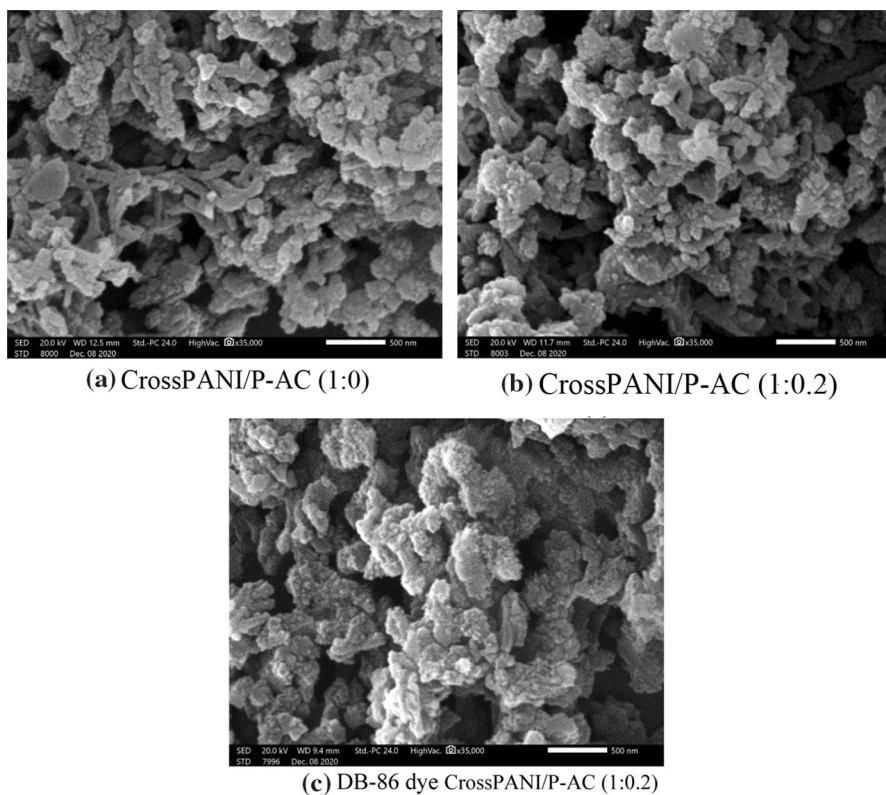


Fig. 2 SEM image of (a) CrossPANI/P-AC (1:0), b Cross PANI/P-AC (1:0.2), and (c) DB-86 dye Cross PANI/P-AC (1:0.2)

Results and discussion

Characterization

SEM and EDX analysis

The surface morphology of CrossPANI/P-AC (1:0), Cross PANI/P-AC(1:0.2), and DB-86 dye adsorbed onto CrossPANI/P-AC (1:0.2) was obtained by SEM and is presented in Fig. 2a, b, c, respectively. CrossPANI/P-AC (1:0) shows its relatively amorphous structure, and CrossPANI/P-AC (1:0.2) indicates that the polymerization has occurred on the surface of P-AC. After adsorption of DB-86 dye, the surface became more a denser structure, indicating that adsorption occurred on the surface of the CrossPANI/P-AC (1:0.2).

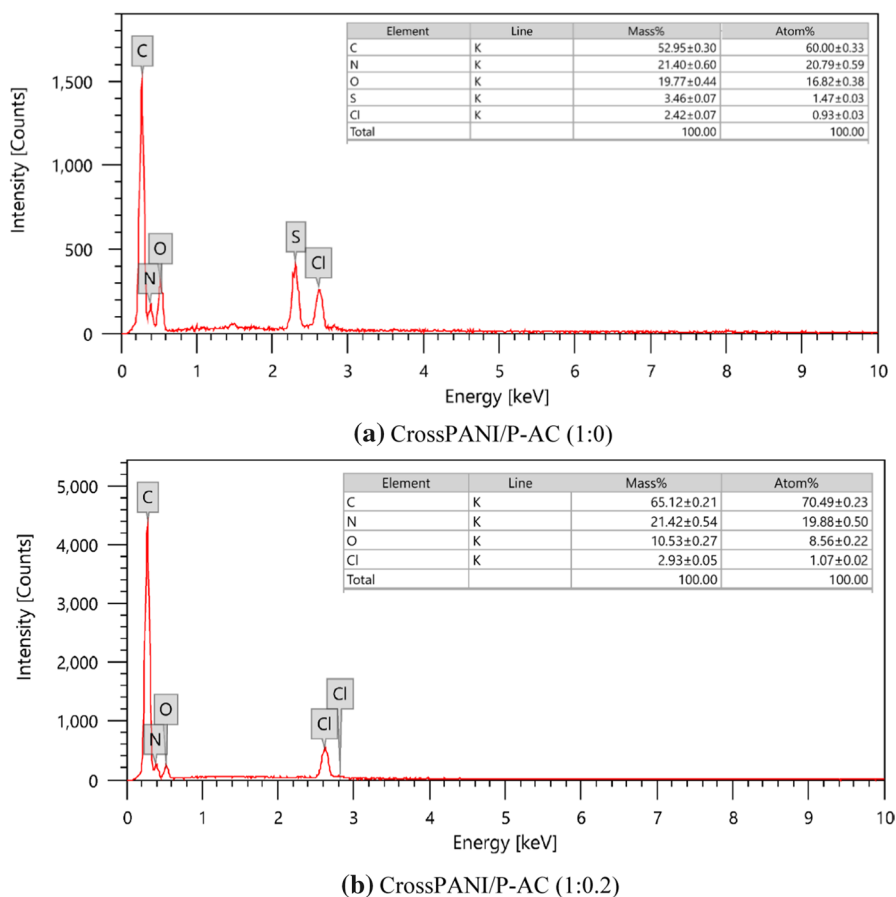


Fig. 3 EDX image of (a) Cross PANI/P-AC (1:0) and (b) Cross PANI/P-AC (1:0.2)

EDX data of CrossPANI/P-AC (1:0) and CrossPANI/P-AC (1:0.2) showed that the overall amount of the carbon (C), nitrogen (N), and oxygen (O) elements present in the fabricated composite were estimated using EDX analysis that confirmed the presence of PANI[(C₆H₅NH-) _n] (Fig. 3). Besides, sulfur and chloride were also presented in the EDX analysis, presumably due to ammonium persulfate (APS) and the reaction medium, respectively. The mass % of carbon on CrossPANI/P-AC (1:0.2) is higher than in CrossPANI/P-AC (1:0) due to addition of P-AC.

FTIR analysis

Figure 4 shows FTIR spectra of P-AC, CrossPANI/P-AC (1:0), CrossPANI/P-AC (1:0.2), and DB-86-CrossPANI/P-AC (1:0.2). Figure 4a shows FTIR of P-AC, the

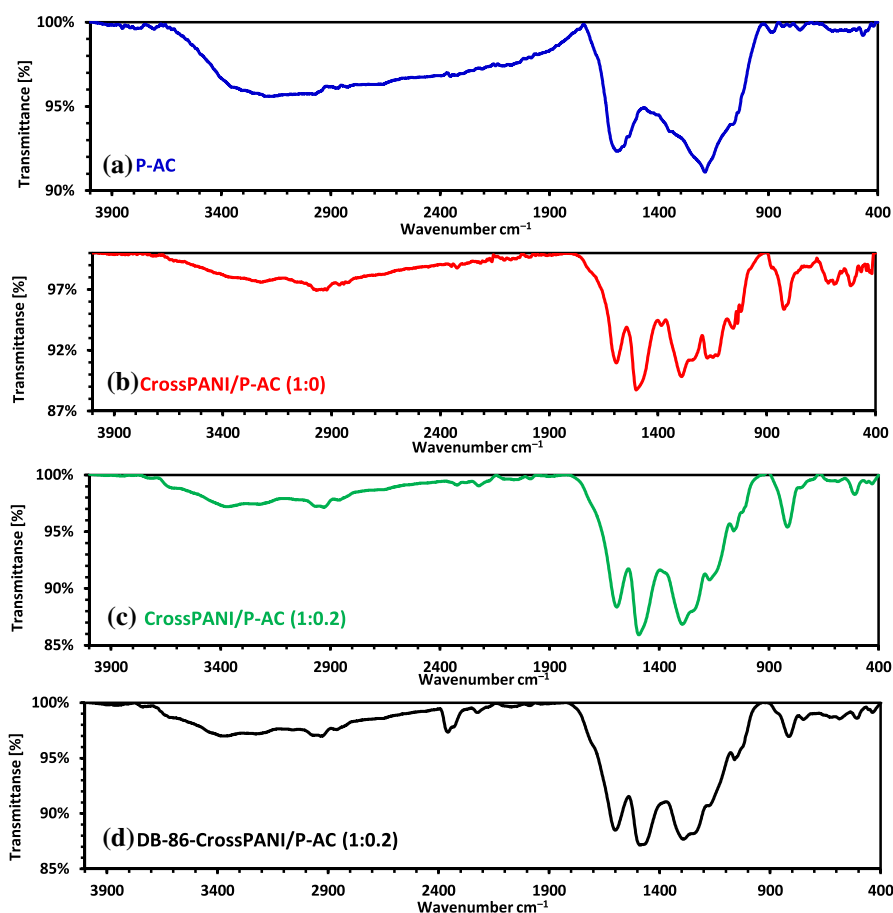


Fig. 4 FT-IR spectra of (a) P-AC, b CrossPANI/P-AC (1:0), c CrossPANI/P-AC (1:0.2), and (d) DB-86 dye CrossPANI/P-AC (1:0.2)

peaks at 3852–3707 and 3195 cm^{-1} representing bonded and non-bonding $-\text{OH}$ groups, respectively, on their surface [79]. The band of $\text{C}=\text{O}$ at 1590 cm^{-1} is characteristic of aldehydes, ketones, quinone and carboxylated groups [80, 81]. Also, the band at 1190 cm^{-1} represented the $\text{C}-\text{O}$ stretching vibrations, and the band at 886–756 cm^{-1} indicated $\text{H}_2\text{PO}_4^{4-}$ and PO_4^{2-} disulfide or aromatic structures [82]. Meanwhile, the band at 467 cm^{-1} indicates metal oxide or aromatic structures [65, 83]. CrossPANI/P-AC (1:0.2) shows similar transmittance bands to CrossPANI/P-AC (1:0). Figure 4b, c of CrossPANI/P-AC (1:0) and CrossPANI/P-AC (1:0.2) shows the main characteristic peak positions of PANI; the broadband at ~ 3223.52 and 3372.92 cm^{-1} , respectively, is attributed to the $\text{N}-\text{H}$ stretching vibration due to the protonation of nitrogen [84, 85]; and the characteristic band at ~ 2966.29 and 2930.89 cm^{-1} , respectively, can be assigned to the stretching vibration of the methyl group ($-\text{CH}_3$). The stretching vibrations of the quinoid and benzenoid rings are represented by the two bands at 1591.06, 1593.86 cm^{-1} and 1499.75–1492.75 cm^{-1} , respectively. The $\text{C}-\text{N}=\text{stretching}$ vibration between benzenoid and quinoid units in CrossPANI/P-AC(1:0) is responsible for the peak at 1384.22 cm^{-1} [84, 86]. The band at ~ 1291.33 , 1294.13 cm^{-1} and ~ 820.81 , 814.95 cm^{-1} , respectively, can be assigned for the stretching of $\text{C}-\text{N}$ and bending of $\text{C}-\text{H}$ (out of plane) in the benzene ring [87]. The peaks at ~ 1054.59 and 1060.50 cm^{-1} are related to the $\text{S}=\text{O}$ and $\text{S}-\text{O}$ stretching vibrations of the sulfonate groups linked to the aromatic rings, indicating that the produced PANI nanostructures were doped [84]. FTIR spectra of CrossPANI/P-AC (1:0.2) (Fig. 4d) after adsorption of DB-86 dye showed the same characteristic peak of CrossPANI/P-AC (1:0.2) with a small shift in peaks, and its intensity due to adsorption of DB-86 dye, indicating that the adsorption process occurred.

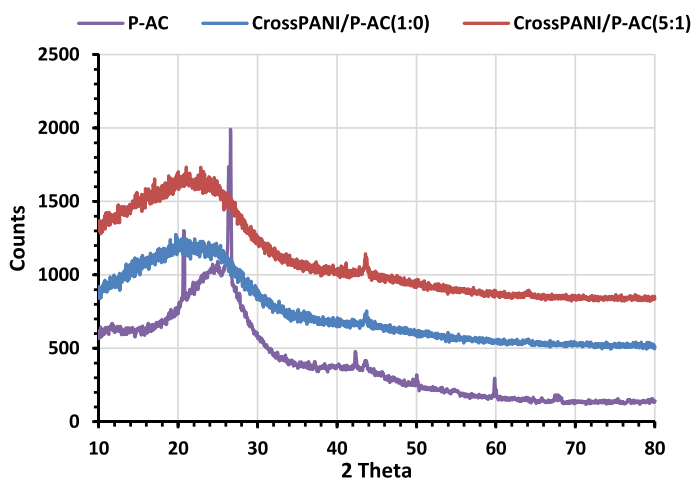


Fig. 5 XRD of P-AC, CrossPANI/P-AC(1:0), and CrossPANI/P-AC(1:0.2)

XRD analysis

Figure 5 shows the X-ray diffraction of P-AC, CrossPANI/P-AC(1:0), and CrossPANI/P-AC(1:0.2). The XRD pattern of P-AC showed characteristic diffraction peaks of crystalline structures of the graphitic-activated carbon. The presence of a sharp peak around $2\theta=21.14^\circ$, 26° , and 42° was due to the formation of a disordered graphitic phase [88–90]. The diffraction patterns of CrossPANI/P-AC(1:0) consisted of broad crystalline peaks; the prominent diffracted peaks at an angle of $2\theta=17.114^\circ$, 20.740° , 24.715° , respectively, due to the repeating of benzenoid and quinoid rings in PANI chains, poor crystallinity for conductive polymers are ascribed to the polymer chain, showing low crystallinity for conductive polymers [46, 51, 91, 92]. According to Ali et al. [93], new PANI peaks occurred at $2\theta=43.822^\circ$, 49.958° , and 63.974° due to new arrangements or cross-linking in the

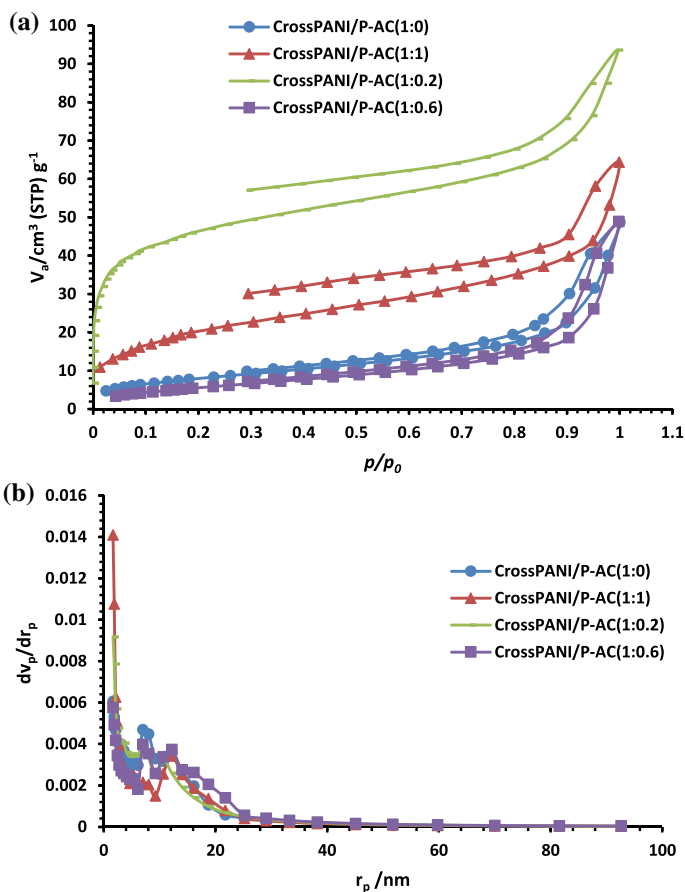


Fig. 6 **a** N_2 gas adsorption–desorption isotherms; **b** BJH desorption pore size distributions of CrossPANI/P-AC(1:0), CrossPANI/P-AC(1:1), CrossPANI/P-AC(1:0.2), and CrossPANI/P-AC(1:0.6)

PANI structure. The CrossPANI/P-AC(1:0.2) peaks were found to slightly shift than CrossPANI/P-AC(1:0) peaks to 16.208, 20.88, 25.064, 43.682, 50.307, 63.974. The gross intensity of the peaks was raised following the addition of P-AC nanoparticles to the PANI matrix due to an interaction between P-AC nanoparticles and PANI caused by the creation of hydrogen bonding between H–N and oxygen of P-AC.

Pore structure analysis

Figure 6A shows the adsorption–desorption isotherms of nitrogen at 77 K on CrossPANI/P-AC(1:0), CrossPANI/P-AC(1:1), CrossPANI/P-AC(1:0.2), and CrossPANI/P-AC(1:0.6). CrossPANI/P-AC(1:0) and CrossPANI/P-AC(1:0.6) exhibit type-V isotherm with H3 hysteresis loop; this implies containing slit-like pores. The composites CrossPANI/P-AC(1:1) and CrossPANI/P-AC(1:0.2) show changes in N₂ adsorption–desorption isotherm to type-IV with remarkable hysteresis loops according to the IUPAC classification [94]. This implies that the pores are mostly mesoporous and macroporous.

Furthermore, Fig. 6b shows BJH desorption pore size distributions of CrossPANI/P-AC(1:0), CrossPANI/P-AC(1:1), CrossPANI/P-AC(1:0.2), and CrossPANI/P-AC(1:0.6). It can be noted that the pores between 2 and 30 nm were dominant for all; that is, both mesopores and macropores are present. The porous structure parameters of CrossPANI/P-AC(1:0), CrossPANI/P-AC(1:1), CrossPANI/P-AC(1:0.2), and CrossPANI/P-AC(1:0.6) from the basis of the nitrogen adsorption data are summarized in Table 3. BET surface area and monolayer volume of CrossPANI/P-AC(1:0) reach 29.38 m²/g and 6.7503 cm³/g, respectively, which increased after the addition of P-AC to 166.10 m²/g and 38.163 cm³/g in CrossPANI/P-AC(1:0.2) and then decreased to 21.59 m²/g and 4.9593 cm³/g in CrossPANI/P-AC(1:0.6). The mean pore diameter of samples ranges 2–50 nm, meaning that samples' pore size is in mesopore.

Thermal analysis

The TGA/DTA thermograms of CrossPANI/P-AC(1:0) and CrossPANI/P-AC(1:0.2) were examined in the temperature range of 30 to 900 °C at a heating rate of 10 °C min^{−1} under a nitrogen atmosphere. Figure 7a,b indicates TGA/DTA plots of the decomposition of CrossPANI/P-AC(1:0) and CrossPANI/P-AC(1:0.2).

Table 3 The porous structure parameters of CrossPANI/P-AC(1:0), CrossPANI/P-AC(1:1), CrossPANI/P-AC(1:0.2), and CrossPANI/P-AC(1:0.6)

	$a_{s,BET}$ (m ² /g)	V_m (Cm ³ /g)	Mean pore diameter (nm)	Total pore volume
PANI/P-AC(1:0)	29.38	6.7503	9.43	6.93E-02
PANI/P-AC(1:1)	75.74	17.402	4.81	9.12E-02
PANI/P-AC(1:0.2)	166.10	38.163	3.40	1.41E-01
PANI/P-AC(1:0.6)	21.59	4.9593	12.64	6.82E-02

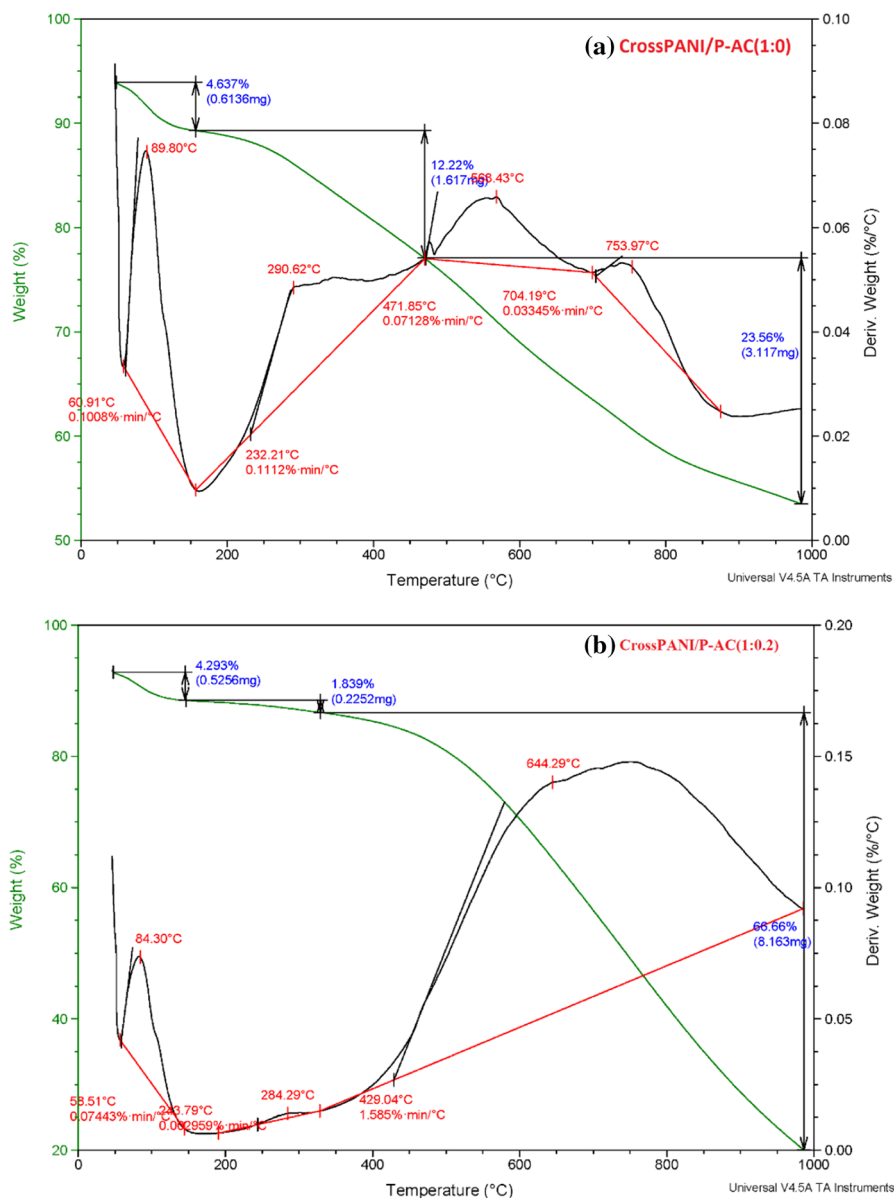


Fig. 7 TGA, DTA of (a) CrossPANI/P-AC(1:0), and (b) CrossPANI/P-AC(1:0.2)

The first stage involves water evaporation with approximately weight loss of 4.637, 4.293%, and an exothermic peak of 81.19, 84.30 °C is found in the DTA curve, respectively [93]. The second weight-loss stage had an exothermic peak at 290.62 and 284.29 °C, respectively, and a weight loss of 12.22 and 1.84 percent. This is due to the loss of amine groups as low molecular weight polymers

degrade (NH_2) [61]. In the third weight-loss stage for CrossPANI/P-AC(1:0), the weight loss was 23.56 with two exothermic peaks at 568.43 and 753.97 °C; for CrossPANI/P-AC(5:1) the weight loss was 66.66% with an exothermic peak at 644.29 °C due to thermal degradation of low molecular weight of PANI chains, loss of amine groups (NH_2) and the elimination of P-AC [51]. The CrossPANI/P-AC(1:0.2) also shows the same stages of weight loss of CrossPANI/P-AC(1:0), with higher weight loss in the third stage as compared to CrossPANI/P-AC(1:0) due to the incorporation of P-AC in PANI matrix and a weight loss of 66.66% was observed. On examining TGA curves, it is observed that CrossPANI/P-AC(1:0) has higher thermal stabilities than CrossPANI/P-AC(1:0.2), as indicated by the decreased weight loss.

Points of zero charge PZCs

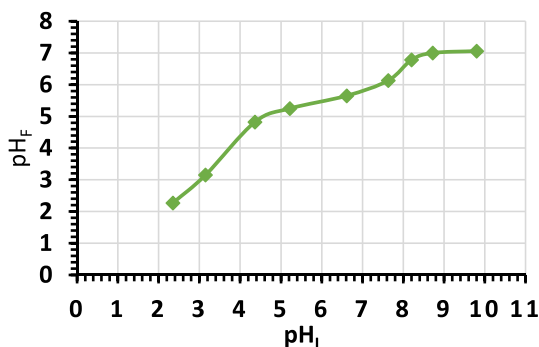
The point of zero charges is the pH required to affect a net zero charge on a solid surface without particular sorption (pH_{PZC}). The adsorbent CrossPANI/P-AC(1:0.2) surface may exhibit positive and negative surface charges at $\text{pH} < 3.15$ and $\text{pH} > 3.15$, respectively, as presented in Fig. 8. From these values, it can be assumed that when immersed in a solution with a pH below 3.15, the composite surface will be positively charged, thus favoring the adsorption of anionic specimens. When the pH is greater than 3.15, the surface becomes negatively charged, facilitating the adsorption of cationic materials.

Adsorption behavior toward DB-86 dye

The removal % of DB-86 dye on CrossPANI/P-AC(1:0.2) with different ratios

The removal % of DB-86 dye on CrossPANI/P-AC with different ratios (1:0, 1:0.2, 1:0.6, 1:1) was tested at DB-86 dye of 50 mg/L, $\text{pH} = 2.2$, dose of 50 mg, contact time of 180 min, and shaking speed 200 rpm. Figure 9 shows that CrossPANI/P-AC with different ratios (1:0, 1:0.2, 1:0.6, 1:1) affects B-86 dye adsorption capacity as calculated using Eq. 1. The maximum DB-86 dye adsorption capacity obtained by CrossPANI/P-AC(1:0.2) reached 83.69 mg/g and was selected to perform the batch

Fig. 8 pH_{PZC} of CrossPANI/P-AC(1:0.2)



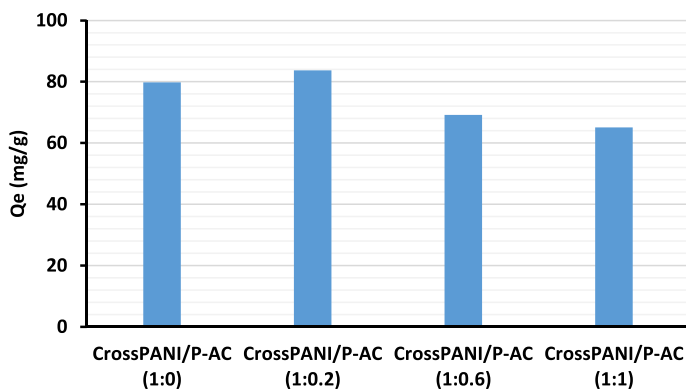


Fig. 9 Adsorbed amount of DB-86 dye on the composites of CrossPANI/P-AC at different ratios at (adsorbent dosage: 50 mg, DB-86 dye concentration: 50 mg/L, pH: 2.2, solution volume: 100 mL, contact time: 180 min, shaking speed = 200 rpm, and temperature: 27 ± 1 °C)

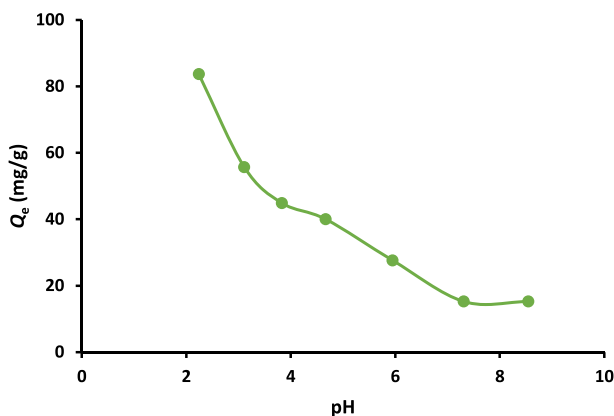


Fig. 10 Effect of pH on adsorption capacity of DB-86 dye (50 mg/L) onto CrossPANI/P-AC(1:0.2) (0.05 g/100 mL) at $t = 180$ min, shaking speed = 200 rpm, and $T = 27 \pm 2$ °C

experimental. It can be noticed that the addition of P-AC to PANI increased DB-86 dye removal% at 0.2 dose and then decreased removal % with an increase dose than 0.2 dose. This can be explained by increased P-AC, blocking the adsorption sites on the PANI surface.

Influence of pH

The adsorption of DB-86 dye on CrossPANI/P-AC(1:0.2) as a function of pH at [DB-86 dye = 50 mg/L, dose = 50 mg, temperature = 25 ± 2 °C, shaking speed = 200 rpm, contact time = 180 min] decreases with the increase in pH

where the maximum capacity reaches 83.69 mg/g at pH 2.2 and the minimum adsorption capacity reaches 15.48 mg/g at both pH 7.3 and 8.5 (Fig. 10). That may be attributed to the point of zero charge (pH_{PZC}) of CrossPANI/P-AC(1:0.2) surface, which is equal to 3.15. This leads to assuming that when CrossPANI/P-AC(1:0.2) is immersed in a DB-86 dye solution with pH below 3.15, the composite surface will be positively charged, thus favoring the adsorption of anionic specimens of DB-86 dye. Because the surface of CrossPANI/P-AC(1:0.2) is negatively charged, adsorption decreases as pH rises, creating conflict between anionic DB-86 dye and excess OH ions in the solution. The adsorption of DB-86 dye on activated carbon produced from orange peel [95], shrimp chitosan [96], and alginate-encapsulated activated carbon (PnsAC-alginate) [97] followed a similar trend of pH impact.

Influence of initial concentration

The adsorption experiments at initial DB-86 dye concentrations from 50 to 150 mg/L were performed with CrossPANI/P-AC(1:0.2) doses (0.5, 0.75, 1.0, 1.25 and 1.5 g/L), and the results are represented in Fig. 11. The results indicated that the percentage removal of DB-86 dye adsorbed on CrossPANI/P-AC(1:0.2) was inversely proportional to DB-86 dye concentration. The percentage of DB-86 dye removed was higher at lower initial DB-86 dye concentrations and smaller at higher initial concentrations, indicating that DB-86 dye adsorption from its aqueous solution was dependent on its initial concentration and that increasing DB-86 dye concentration reduced active surface size [80]. The percentage removal of DB-86 dye at dose 0.5 g/L, 1.5 g/L decreased from 83.69 to 56.83 and 97.14 to 91.11% when the initial DB-86 dye concentration increased from 50 to 150 mg/L, respectively. On the other hand, the maximum adsorption capacity at doses of 0.5 g/L and 1.5 g/L increased from 38.69 to 170.48 mg/g and 32.38

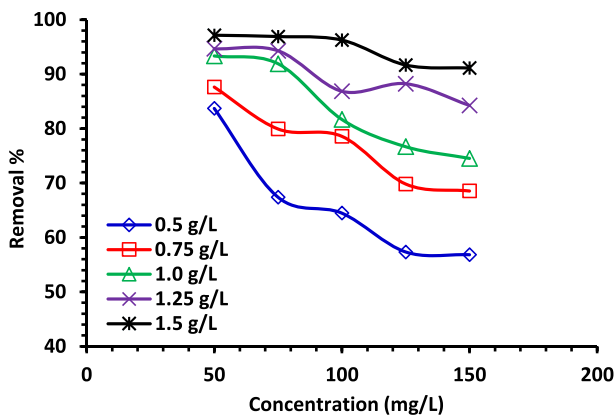


Fig. 11 Using different doses of CrossPANI/P-AC(1:0.2), the percent of DB-86 dye adsorbed at equilibrium and its starting concentration were compared

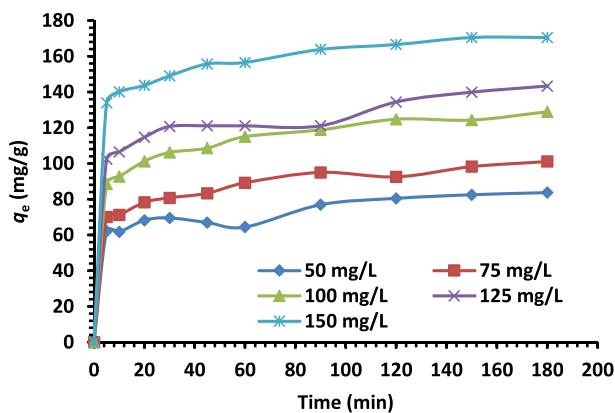


Fig. 12 Using CrossPANI/P-AC(1:0.2) (0.05 g/100 mL) at pH 2.2 and temperature 27 ± 2 °C, the effect of contact duration on the elimination of varied initial concentrations of DB-86 dye

to 91.11 mg/g, respectively, when the initial DB-86 dye concentration increased from 50 to 150 mg/L.

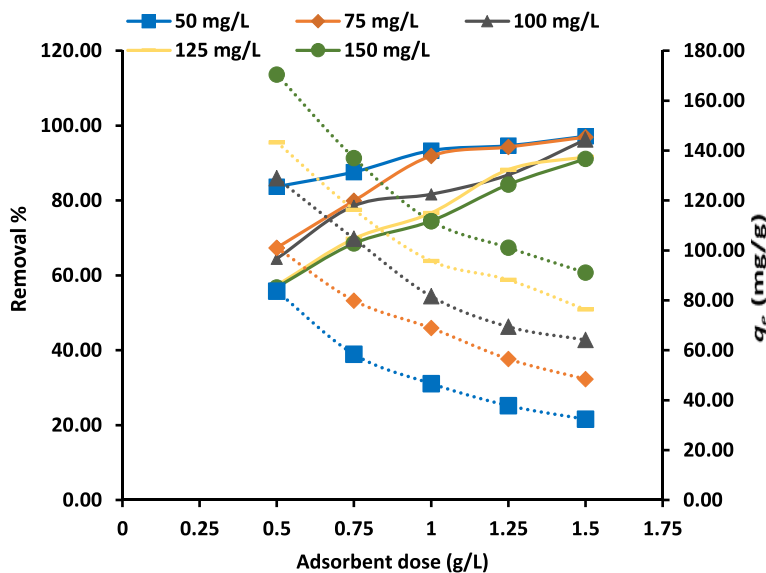


Fig. 13 Effect of mass (g) of CrossPANI/P-AC(1:0.2) concentration on q_e of DB-86 dye (C_0 : 50–150 mg/L, pH 2.2, shaking speed: 200 rpm and temperature: 27 ± 2 °C)

Effect of contact time

Figure 12 shows the effect of contact time on the adsorption capacity of DB-86 dye by CrossPANI/P-AC(1:0.2) at different shaking times at concentrations 50, 75, 100, 125 and 150 mg/L. The adsorption capacity of DB-86 dye increases with the increase of the adsorption time and initial concentration, where the adsorption equilibrium was basically achieved within 90 min for an initial concentration of 50–150 mg/L for DB-86 dye.

Effect of CrossPANI/P-AC(1:0.2) dose

The effect of the adsorbent CrossPANI/P-AC(1:0.2) dose on DB-86 dye adsorption was performed by varying the dose from 0.5 to 1.5 g/L and different concentrations of DB-86 dye varying from 50–150 mg/L at pH 2.2 (Fig. 13). It is observed that the increase of the amount of the CrossPANI/P-AC(1:0.2) resulted in an increase of DB-86 dye removal with a maximum of 97.14% at 50 mg/L DB-86 dye, and so decreased the equilibrium adsorption capacity (q_e) of DB-86 dye. These results are because greater sorbent dosages offer more sorbent functional groups, surface area, and pores volume accessible for DB-86 dye adsorption on the CrossPANI/P-AC(1:0.2) surface.

Adsorption kinetics

The kinetic adsorption data of DB-86 dye onto CrossPANI/P-AC(1:0.2) were processed to understand and predict the nature of the adsorption process. Table 1 summarizes the five linear equations of kinetic models employed to understand the reaction mechanism. Figure 14 and Table 4 display the pseudo-first-order and pseudo-second-order kinetics model of DB-86 adsorption onto CrossPANI/P-AC(1:0.2) parameters values. Data showed that in the pseudo-first-order kinetic model, the $q_{e(\text{exp})}$ values are not in agreement with the predicted $q_{e(\text{th})}$ values but they are in agreement with predicted $q_{e(\text{th})}$ values of pseudo-second-order with R^2 values greater than 0.993. The rate constant of pseudo-second-order adsorption increased with increase DB-86 dye concentration and CrossPANI/P-AC(1:0.2) doses. Therefore, the pseudo-second-order kinetic model is more adequate to describe the adsorption process of DB-86 dye onto CrossPANI/P-AC(1:0.2). Meanwhile, Fig. 14 and Table 5 display parameter values of Elovich, intraparticle diffusion, and liquid film diffusion model of DB-86 dye adsorption onto CrossPANI/P-AC(1:0.2). Results showed that the R^2 values were ranged from (0.959–0.999), (0.909–0.991), and (0.912–0.998), respectively, for Elovich, intraparticle diffusion and liquid film diffusion model. In Elovich model, the initial sorption rate α has a wavy and identified role with DB-86 dye concentration and adsorbent dose. The desorption constant, β , decreases with increasing the initial concentration of DB-86 dye while increasing with increasing adsorbent dose. The results do not accord with the initial sorption rate, h , calculated using the pseudo-second-order model, indicating that this model is unsuitable for the experimental data obtained for the adsorption of DB-86 dye on CrossPANI/P-AC (1:0.2). The intraparticle diffusion plots did not

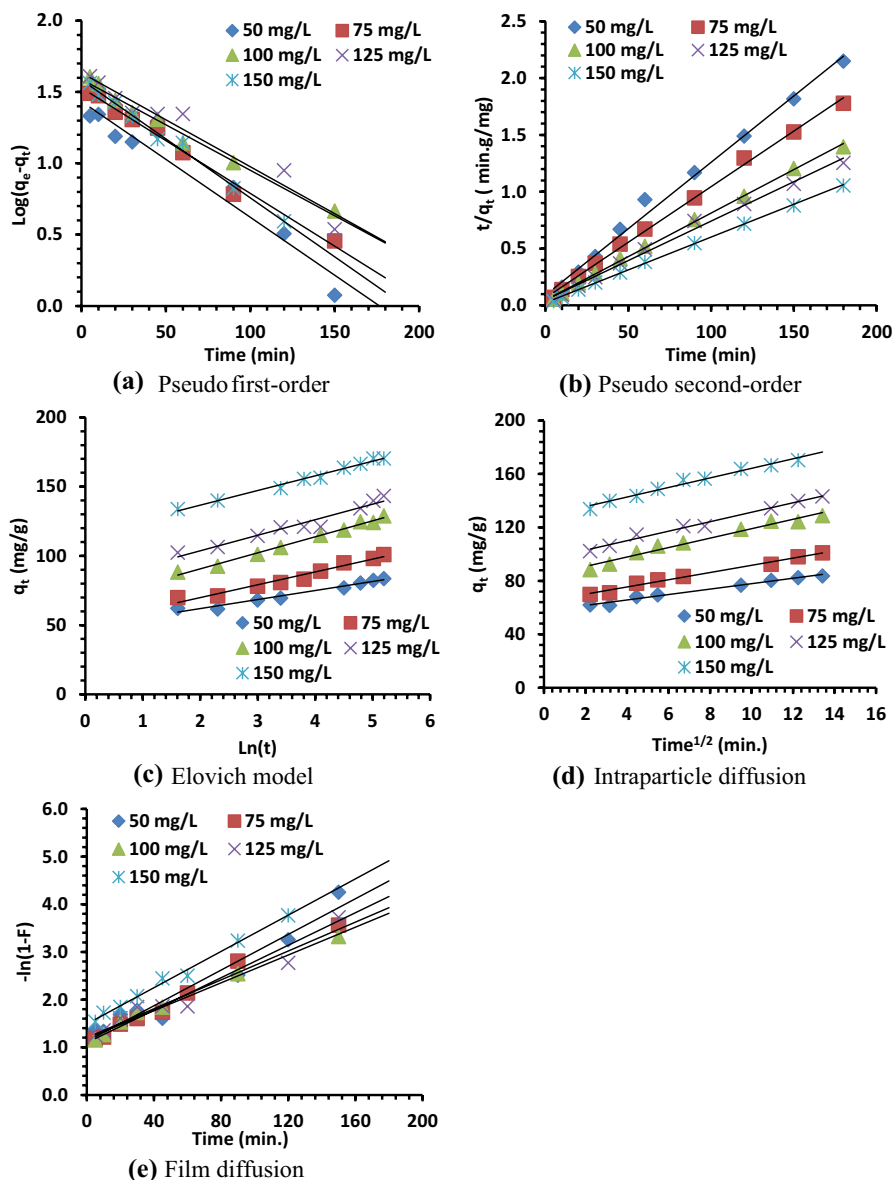


Fig. 14 **a** Pseudo-first-order, **b** pseudo-second-order, **c** Elovich, **d** intraparticle diffusion, and **(e)** film diffusion of DB-86 dye (50–150 mg/L) adsorbed over CrossPANi/P-AC(1:0.2) (0.5 g/L) at pH 2.2 and temperature $(27 \pm 1^\circ \text{C})$

pass through the origin, indicating that intraparticle diffusion was not the only rate-controlling step, although it was involved in the process. The K_{dif} and C values are directly proportional with DB-86 dye concentration and inversely proportional with

Table 4 Comparison of kinetics parameters of pseudo-first-order and pseudo-second-order kinetic model values for different initial DB-86 dye and CrossPANI/P-AC(1:0.2) concentrations

CrossPANI/P-AC(1:0.2) dose	DB-86 (mg/L)	First-order kinetic model				Second-order kinetic model			
		q_e (exp.)	q_e (calc.)	$k_1 \times 10^3$	R^2	q_e (calc.)	$k_2 \times 10^3$	h	R^2
0.5 g/L	50	83.69	27.16	18.65	0.949	85.47	1.51	11.06	0.993
	75	101.07	33.81	17.04	0.988	102.04	1.47	15.34	0.997
	100	128.93	38.72	14.74	0.984	129.87	1.26	21.32	0.998
	125	143.33	43.00	15.20	0.951	144.93	1.02	21.37	0.994
	150	170.48	38.43	19.11	0.992	172.41	1.46	43.48	0.999
0.75 g/L	50	58.41	20.36	19.11	0.990	59.52	2.58	9.14	0.998
	75	79.92	30.17	16.81	0.998	81.30	1.58	10.43	0.998
	100	104.76	36.38	15.66	0.993	106.38	1.32	14.99	0.998
	125	116.35	38.06	14.97	0.997	117.65	1.15	15.97	0.996
	150	137.06	42.07	17.96	0.996	138.89	1.19	23.04	0.998
1.0 g/L	50	46.67	16.92	26.95	0.988	47.85	4.04	9.25	1.000
	75	68.93	24.81	19.11	0.991	70.42	2.13	10.55	0.999
	100	81.67	29.92	16.58	0.991	83.33	1.63	11.29	0.998
	125	95.833	33.16	16.12	0.998	97.09	1.41	13.32	0.997
	150	111.79	33.78	14.51	0.992	112.36	1.38	17.36	0.998
1.25 g/L	50	37.86	7.40	19.81	0.992	38.31	7.52	11.04	1.000
	75	56.57	17.68	19.81	0.995	57.47	3.21	10.59	0.993
	100	69.48	23.52	22.11	0.989	71.43	2.49	12.72	0.999
	125	88.24	26.03	16.12	0.972	88.50	2.06	16.16	0.998
	150	101.10	26.72	9.90	0.912	100.00	1.90	19.01	0.997
1.5 g/L	50	32.38	3.59	18.19	0.912	32.68	18.47	19.72	1.000
	75	48.45	13.09	25.79	0.987	49.50	4.39	10.76	0.999
	100	64.17	14.11	26.25	0.973	64.94	5.44	22.94	1.000
	125	76.39	21.34	14.28	0.963	76.92	2.42	14.31	0.999
	150	91.11	25.66	17.04	0.971	92.59	2.09	17.89	0.998

CrossPANI/P-AC(1:0.2) doses. The film diffusion plots are linear, but they do not pass through the origin, explaining how the film diffusion mechanism affects the adsorption rate. With DB-86 dye concentration and CrossPANI/P-AC(1:0.2) dosages, the values of K_{FD} and C play a wavy and indefinite role.

Adsorption isotherm

To describe the experimental result of DB-86 dye removal isotherm on CrossPANI/P-AC(1:0.2) composite, four isotherm models, which are Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) isotherms, have been investigated. The equations representing these models are compiled in Table 2. Fig. 15 and Table 6 illustrate each linearized isotherm model's plots and related parameters. However, the arrangement of adsorptive removal of DB-86 dye by

Table 5 For various starting DB-86 dye and CrossPANI/P-AC(1:0.2) doses, Elovich kinetics parameters, intraparticle diffusion, and film diffusion kinetics model values were calculated

CrossPANI/P-AC (1:0.2) dose	DB- 86 (mg/L)	Elovich		Intraparticle diffusion			Film diffusion		
		β	A	R^2	K_{dif}	C	R^2	K_{FD}	C
0.5 g/L	50	0.15	1.18E+04	0.966	2.026	57.57	0.982	0.0187	1.125
	75	0.11	2.42E+03	0.962	2.715	64.50	0.988	0.0170	1.095
	100	0.09	3.98E+03	0.991	3.529	83.70	0.972	0.0146	1.187
	125	0.09	1.59E+04	0.952	3.550	95.86	0.989	0.0151	1.204
	150	0.09	5.74E+05	0.987	3.578	128.48	0.980	0.0190	1.490
0.75 g/L	50	0.17	6.25E+02	0.992	1.675	37.27	0.981	0.0190	1.054
	75	0.12	6.37E+02	0.983	2.656	46.90	0.984	0.0168	0.974
	100	0.10	1.32E+03	0.990	2.904	66.65	0.981	0.0141	1.139
	125	0.09	1.48E+03	0.969	3.065	74.77	0.991	0.0149	1.117
	150	0.08	2.90E+03	0.976	3.643	91.42	0.960	0.0180	1.146
1.0 g/L	50	0.23	1.54E+03	0.983	1.448	31.38	0.956	0.0283	0.986
	75	0.14	7.25E+02	0.999	1.944	44.29	0.976	0.0190	1.022
	100	0.12	5.82E+02	0.999	2.184	53.10	0.983	0.0162	1.052
	125	0.10	6.67E+02	0.993	2.830	59.19	0.980	0.0160	1.061
	150	0.10	3.07E+03	0.991	2.966	72.73	0.985	0.0146	1.139
1.25 g/L	50	0.43	1.47E+05	0.993	0.529	31.09	0.978	0.0198	1.633
	75	0.19	1.53E+03	0.997	1.577	37.00	0.955	0.0197	1.163
	100	0.14	9.30E+02	0.993	2.015	46.25	0.927	0.0222	1.083
	125	0.14	6.39E+03	0.983	2.287	58.19	0.980	0.0160	1.221
	150	0.13	1.09E+04	0.976	2.618	66.55	0.942	0.0101	1.294

Table 5 (continued)

CrossPANI/P-AC (1:0.2) dose	DB- 86 (mg/L)	Elovich		Intraparticle diffusion			Film diffusion		
		β	A	R^2	K_{dif}	C	R^2	K_{FD}	C
1.5 g/L	50	0.85	7.36E+09	0.987	0.374	27.88	0.958	0.0181	2.201
	75	0.23	2.20E+12	0.988	1.299	32.79	0.930	0.0258	1.186
	100	0.21	3.48E+04	0.987	1.436	48.16	0.909	0.0224	1.610
	125	0.15	2.52E+03	0.995	2.083	49.73	0.950	0.0144	1.275
	150	0.12	3.38E+03	0.989	2.127	64.14	0.952	0.0168	1.262

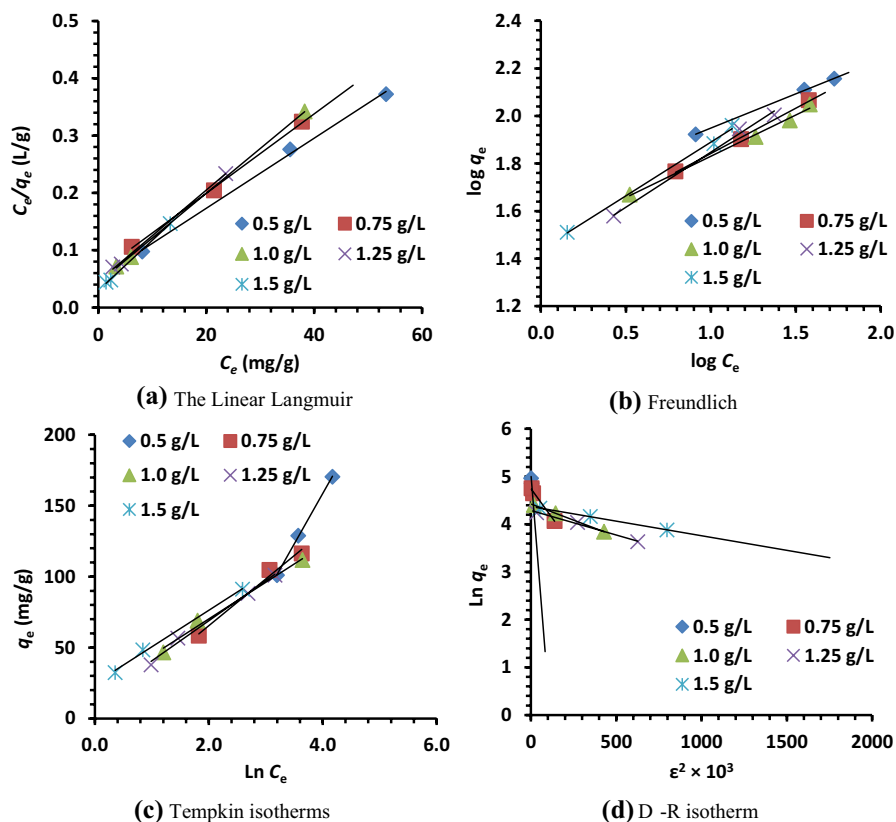


Fig. 15 Isotherm models: **(a)** the linear Langmuir, **(b)** Freundlich, **(c)** Tempkin isotherms, and **(d)** D-R isotherm of DB-86 dye (50–150 mg/L) adsorbed onto CrossPANI/P-AC(1:0.2) (0.5–1.5 g/L)

CrossPANI/P-AC(1:0.2) isotherm as Langmuir < Dubinin-Radushkevich < Tempkin < Freundlich based on the coefficient of determination values (R^2) and the low value of APE% error model.

According to the Langmuir model, DB-86 dye adsorption occurs on a homogeneous surface via monolayer adsorption, without interaction between adsorbed species [98–100]. The maximum monolayer capacity (Q_m) was 163.93 mg/g at dose 0.5 g/L. The separation factor R_L is calculated using the following equation: $R_L = 1/(1 + K_a C_o)$ [33, 83]. It was found that the adsorption process of DB-86 dye onto CrossPANI/P-AC(1:0.2) is a favorable process. Meanwhile, Freundlich isotherm suggested the adsorption process of DB-86 dye based on adsorption heterogeneous surface. The degree of nonlinearity between solution concentration and adsorption is indicated by the n value [68]. Results showed that the adsorption process is a favorable physical process where the value of $n < 1$. According to the Tempkin isotherm model, the heat of adsorption of all molecules in the layer declines linearly with coverage due to adsorbate–adsorbate interactions, and adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy. Table 6 shows the values of the Tempkin isotherm parameters. D–R isotherm was

Table 6 The coefficient isotherm models for DB-86 dye adsorption onto CrossPANI/P-AC(1:0.2) were compared

Isotherm models	Parameters	CrossPANI/P-AC(5:1) concentrations				
		0.5 g/L	0.75 g/L	1.0 g/L	1.25 g/L	1.5 g/L
Langmuir	Q_m (mg/g)	163.93	144.93	128.21	126.58	114.94
	K_a (L/g)	0.12	0.11	0.18	0.17	0.29
	R_L	0.052–0.1423	0.0554–0.1496	0.0995–0.0355	0.1039–0.0372	0.0639–0.0223
	R^2	0.9977	0.9987	0.9998	0.9982	0.9988
	APE%	0.0034				
Freundlich	$1/n$	0.29	0.38	0.35	0.46	0.45
	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	45.75	28.90	30.44	24.23	2.83
	R^2	0.9996	0.9982	0.9943	0.9935	0.9965
	APE%	1.0277				
Tempkin	A_T	0.17	0.99	2.03	1.55	2.61
	B_T	71.10	32.91	25.90	28.23	24.74
	b_T	35.08	75.78	96.32	88.36	100.81
	R^2	0.9996	0.9855	0.9890	0.9938	0.9964
	APE%	0.0321				
Dubinin–Radushkevich	Q_m (mg g ⁻¹)	158.634	115.261	83.781	73.069	79.052
	$K \times 10^6$ (mol kJ ⁻¹) ²	44.900	4.900	1.400	1.000	0.600
	E (kJ mol ⁻¹)	0.1055	0.3194	0.5976	0.7071	0.9129
	R^2	0.9986	0.9929	1.0000	0.9943	0.9998
	APE%	0.0042				

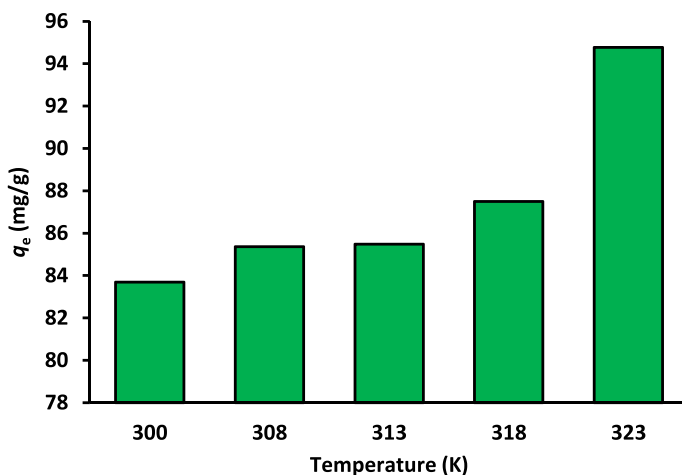


Fig. 16 Impact of temperature on the capacity of adsorption using CrossPANI/P-AC(1:0.2) (0.05 g/100 mL) at pH 2.2, DB-86 dye = 50 mg/L after 180 min

also applied to estimate the porosity of apparent free energy and the characteristics of adsorption. It may be used to explain adsorption on both homogenous and heterogeneous surfaces [68, 101]. The maximum capacity Q_m obtained for DB-86 adsorption is 158.63 mg/g, less than the Q_m obtained using the Langmuir isotherm model. The computed E values range from 0.1055 to 0.9129 kJ/mol, with values less than 8 kJ/mol, showing that the physical-sorption process is important in the adsorption of DB-86 dye onto CrossPANI/P-AC(1:0.2).

Thermodynamic study

The removal of DB-86 dye onto CrossPANI/P-AC(1:0.2) as a function of reaction temperature was estimated in the temperature range 25–50 °C and is represented in Fig. 16. The capacity of DB-86 dye onto CrossPANI/P-AC(1:0.2) was directly proportional to temperature. The adsorptive removal processes of DB-86 dye are proceeding in endothermic reactions. The maximum DB-86 adsorption capacity was 94.76 mg/g using the initial concentration of solution 50 mg/L at about 50 °C, pH 2.2 and 0.5 g/L adsorbent dosage.

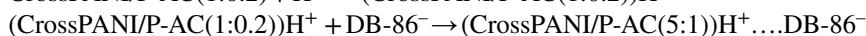
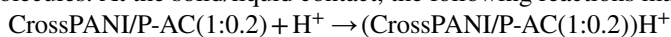
Table 7 Thermodynamic parameters for the adsorption of DB-86 dye onto CrossPANI/P-AC(1:0.2)

T(K)	ΔS (J/K mol)	ΔH (K J/mol)	ΔG (K J/mol)
300	65.05	13.720	−5.794
308			−6.314
313			−6.640
318			−6.965
323			−7.290

According to Table 7, all ΔG° values were negative and increased with increasing temperature, indicating that the DB-86 dye adsorption process on CrossPANI/P-AC(1:0.2) was spontaneous suggesting stronger adsorptive forces between adsorbent and adsorbate. The positive ΔH° value (13.720 kJ/mol) of DB-86 dye adsorption on CrossPANI/P-AC(1:0.2) confirmed the involvement of an endothermic process. The enthalpy changes ΔH° were less than 84 kJ/mol, indicating that the physisorption adsorption process was taking place [102, 103]. The entropy (ΔS°) value was also positive (65.05 J/K mol), which explains the enhanced randomness at the solid/solution interface during the adsorption of DB-86 dye onto CrossPANI/P-AC(1:0.2).

Mechanism of adsorption

The chemical structure of the adsorbents influences the adsorption phenomena. The following steps in order could be used to describe the adsorption mechanism of DB-86 dye onto CrossPANI/P-AC(1:0.2): (i) through a boundary layer, DB-86 dye is transported from a bulk solution to the external surface of CrossPANI/P-AC(1:0.2) (liquid film diffusion); (ii) as illustrated in Fig. 17, dye adsorption on the adsorbent surface may be owing to the establishment of weak hydrogen bonds between the positively charged CrossPANI/P-AC(1:0.2) and the oxygen atoms of DB-86 dye molecules. At the solid/liquid contact, the following reactions may have occurred:



(Electrostatic interaction causes the formation of a weak hydrogen bond)

(iii) DB-86 dye transport from the exterior to the pores of CrossPANI/P-AC (1:0.2) (intraparticle diffusion); then, (iv) DB-86 dye adsorption on the active site in the inner and outer surface of the CrossPANI/P-AC (1:0.2).

Desorption and regeneration studies

Desorption experiments of DB-86 dye from the loaded CrossPANI/P-AC(1:0.2) were performed using 0.1 N NaOH as an eluted medium to investigate the economic

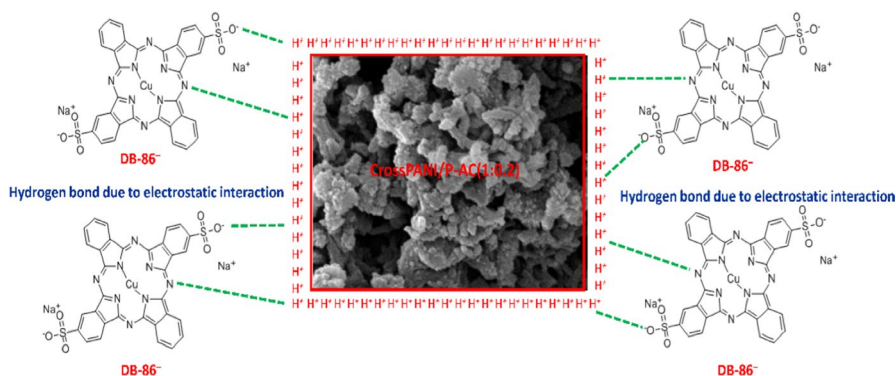


Fig. 17 Probable sorption mechanism of DB-86 dye on CrossPANI/P-AC(1:0.2)

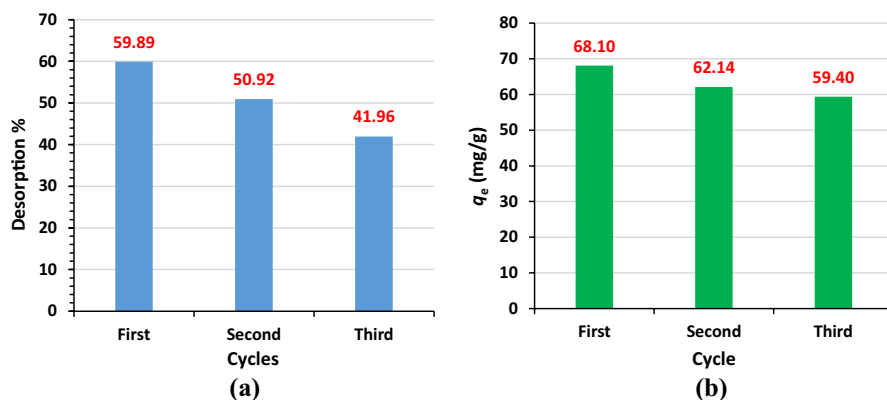


Fig. 18 **a** Desorption % of DB-86 dye from CrossPANI/P-AC(1:0.2). **b** Regeneration of CrossPANI/P-AC(1:0.2)

feasibility and reusability CrossPANI/P-AC(1:0.2) adsorbents. In this condition, the desorption % decreased with increased regeneration cycles, as shown in Fig. 18a. The regenerated CrossPANI/P-AC(1:0.2) composite was applied in three consecutive cycles of adsorption/desorption. The adsorption amount presented was consistent through the cycles and experienced the adsorption capacity decreased by 24.29 mg/g after third generation, which suggests it may be used as a sustainable DB-86 dye removal (Fig. 18b).

Comparative adsorption capacities of different adsorbents for DB-86 dye

The adsorption capacity of CrossPANI/P-AC(1:0.2) composite was compared with some previously reported adsorbents (Table 8).

Table 8 Comparative adsorption capacities of different adsorbents for DB-86 at different experimental conditions

Adsorbent	pH	Q_m (mg/g)	Isotherm	Kinetics	ΔH	References
Alginate-encapsulated peanut shell-activated carbon (PnsAC-alginate)	3.5	21.60	Langmuir	Pseudo-second-order	Endothermic	[97]
Shrimp chitosan	2	60	Langmuir	—	—	[96]
Carbon-alumina composite pellet		500.16	Langmuir	—	—	[11]
Orange peel-activated carbon	2	33.78	Langmuir	Pseudo-second-order	—	[95]
PANI/P-AC(5:1)	2.2	163.93	Langmuir	Pseudo-second-order	Endothermic	This study

Conclusion

The in situ polymerization method was used to synthesize crosslinked polyaniline /*Pterocladia capillacea*—activated carbon composites (CrossPANI/P-AC) at different ratios (1:0, 1:0.2, 1:0.6, and 1:1). The samples were characterized by FTIR, BET, XRD, TGA, SEM, and EDX. Analysis showed that the main characteristic peak positions of CrossPANI/P-AC by FTIR, low crystallinity nature by XRD, 166.10 m²/g a high specific surface area for CrossPANI/P-AC(1:0.2) were achieved by BET, amorphous nature and polymerization occurred at the surface of activated carbon by SEM. The performance of CrossPANI/P-AC (1:0.2) composite on the DB-86 dye removal from aqueous solution was reviewed in detail. The pH of the reaction was discovered to play a significant influence in the DB-86 dye removal process, with pH 2.2 being the ideal pH for DB-86 dye removal. The maximum monolayer capacity (Q_m) was 163.93 mg/g at dose 0.5 g/L. The results for DB-86 dye sorption fit the Langmuir isotherm model better than the Freundlich model. The values (ΔG° , ΔH° , and ΔS°) of thermodynamic parameters support that the DB-86 dye adsorption by CrossPANI/P-AC(1:0.2) composite was physical adsorption, endothermic, and spontaneous in nature. The kinetic data were then fitted into a pseudo-second-order model. Based on these findings, the CrossPANI/P-AC(1:0.2) composite can be considered a promising adsorbent for effectively removing DB-86 dye ions from industrial effluent while also being recyclable.

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Declarations

Conflict of interest The authors have no conflict of interest.

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