



# Starch-grafted-poly(acrylic acid)/*Pterocladia capillacea*–derived activated carbon composite for removal of methylene blue dye from water

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## Abstract

Starch-g-poly(acrylic acid)/*Pterocladia capillacea*–derived activated carbon (St-g-P(AA)/P-AC) composites were prepared via aqueous solution graft copolymerization using starch, acrylic acid, and activated carbon of red alga *Pterocladia capillacea* (0–10%) with *N,N'*-methylenebisacrylamide crosslinker and ammonium persulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> initiator. Fourier-transform infrared (FTIR) spectroscopy, Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) were used to characterize St-g-P(AA)/P-AC composites. Additionally, St-g-P(AA)/P-AC composites were investigated for methylene blue (MB) dye removal from water. The impact of the beginning concentration of MB dye, temperature, pH, and adsorption time on MB dye removal was examined. The maximum adsorption capacity obtained at pH 8 was 496.29 mg/g at 0.02 mg/L composites dose and 100 mg/L MB dye. The properties of adsorption were studied by the adsorption isotherm, kinetic, and thermodynamic models. The pseudo-first-order and Freundlich isotherm models demonstrated the kinetics and equilibrium adsorptions data, respectively. The maximum monolayer capacity ( $q_m$ ) was 1428.57 mg/g from Langmuir isotherm. Thermodynamic parameters indicated that the MB dye adsorption is exothermic physisorption and spontaneous. The results show that St-g-P(AA)/P-AC composites were effective for MB dye adsorption from water solution and could be recycled.

**Keywords** Grafted polymer composite · *Pterocladia capillacea* · Activated carbon · Methylene blue dye · Adsorption isotherm · Adsorption kinetic

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## 1 Introduction

The pollution produced by dyeing effluent has been judged to be a serious hazard to aquatic life since the textile effluents contain bright colour, high chemical oxygen demand (COD), low biochemical oxygen demand (BOD), acidic pH, and other harmful pollutants [1–7]. Dye substances are hazardous to human health because they have the potential to produce mutagenesis and carcinogenesis [8, 9]. Dye substances also interfere with the natural biological processes in water bodies. There is substantial evidence that dyes harm the liver and the central nervous system [9–11].

Methylene blue (MB), a basic cationic dye, officially named 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride, has been extensively used in several applications such as dyeing cotton, paper, wool, silk, jute, and leather due to its low price and wide availability [12–14]. The MB dye structure's unique blue and red color in aqueous solution

and toluene, respectively, due to electrons delocalization from the conjugated  $\pi$ -bonds (chromophore group) are present [12, 15]. To date, there are various methods have been investigated for removing MB dye from water resources, such as coagulation and flocculation [16, 17], electrochemical [18], photocatalysis [19, 20], membrane filtration [21, 22], anaerobic or aerobic biodegradation treatment [23, 24], and adsorption [25–28]. The adsorption process is the most popular technique among these approaches. It has attracted a lot of interest because of its efficient procedures, high efficiency, lack of requirement for a vast application area, low costs, and absence of toxicity and bad consequences [14, 29–31]. Two crucial characteristics of an adsorption process are high adsorption and separation performance [26, 32]. As a result, creating a novel adsorbent with a high adsorption capacity is an exciting endeavor.

Recently, various developments in polymeric adsorbents have focused on using natural polysaccharides as treatment agents to eliminate water contamination [33, 34]. Due to their non-toxic nature and biodegradability, starch [35], chitosan [36], and gum [37] receive special consideration for usage as adsorbents in wastewater treatment. Starch is an abundant biopolymer derived from biodegradable agriculture, a low-cost material used especially to prepare green composites [38]. Starch can be chemically modified through oxidation, hydrolysis, esterification, etherification, and grafting, which can significantly improve the characteristics of the starch and allow it to be used for water treatment [9, 39]. The chemical grafting of vinyl monomer poly (acrylic acid) PAA onto starch (St) has increased much attention. Starch-grafted-poly(acrylic acid) (St-g-P(AA)) are becoming more significant due to their potential applications in the environment, agriculture, and biomedical [40]. It has been used as flocculants, ion exchangers, hydrogels, and superabsorbents, among other applications [41].

The development of St-g-P(AA) superabsorbent composites has been recognized. The addition of some additives or fillers into the St-g-P(AA) such as mica [42], attapulgite [43], kaolinite [44], Zeolite [45, 46], metals nanoparticles, or cellulose nanowhiskers [12], for instance, have been utilized in polymers preparation to achieve lower costs of production and higher properties. The study of the literature reveals that no comprehensive studies have been conducted on the application of the P-AC on St-g-P(AA) in the removal of MB dye from aqueous solution and the recovery qualities.

This study reports the synthesis of composites as a superabsorbent through the graft copolymerization reaction of starch and acrylic acid in the presence of *Pterocladia capillacea*-driven AC. The cross-linker used in this process was *N,N*-methylenebisacrylamide (NMBA), and the initiator was ammonium persulfate (APS). FT-IR, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), surface area analysis,

and thermal gravimetric analysis (TGA) were all used to describe the superabsorbent composites that were created. On the St-g-P(AA)/P-AC composite, the adsorption equilibrium of a cationic dye called methylene blue (MB) dye from artificial wastewater was examined in detail. To study adsorption isotherms, kinetics, and thermodynamics, the specific impacts that various parameters have on adsorption, such as pH, beginning dye concentration, contact time, adsorbent dose, and temperature, were investigated. Experiments involving adsorption and desorption were also carried out to determine whether the prepared composite could be reused.

## 2 Experimental

### 2.1 Materials

Acrylic acid (AA, Assy = 99%) was obtained from Merck Schuchardt OHG (Germany). Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Assy = 98%) was obtained from Oxford Lab Chem (Navghar Road, INDIA). *N,N'*-methylenebisacrylamide (MBA, Assy = 99%) were obtained from SIGMA (USA). Starch (Assy = 99.97%) was obtained from Qualikems Fine Chem Pvt. Ltd. (Nandesari, Vadodara, India), and Methylene blue (MB, Assy = 99%) from Honeywell Riedel-de Haën AG (SEELZE-HANNOVER, Germany) (Fig. 1). Hydrochloric acid (HCl, Assy = 30–34%) was obtained from SD Fine-Chem Limited (Mumbai, India). Sodium hydroxide (NaOH, Assy = 96%) was purchased from El Nasr Pharmaceutical Chemical Company (ADWIC, Egypt). *Pterocladia capillacea* was collected from the Mediterranean coast in Alexandria, Egypt.

#### 2.1.1 Synthesis of activated carbon from red algae *Pterocladia capillacea*

Red algae *Pterocladia capillacea* was cleaned using distilled water, dried in an oven, milled, crushed, and stored until used. Activated carbon from *Pterocladia capillacea* (P-AC) was synthesized by the stated activated method [47]. Briefly, the dried *Pterocladia capillacea* 10 g was soaked with a solution of 5 g ZnCl<sub>2</sub> for 24 h. Afterwards, the combinations

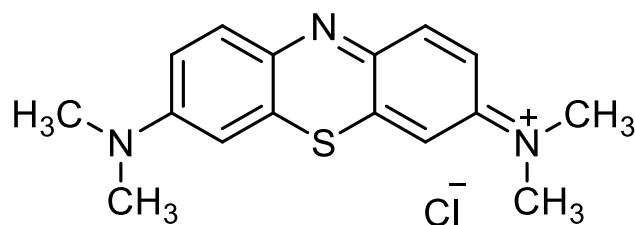


Fig. 1 Methylene blue structure

were heated to 110 °C for 24 h to remove excess water. Then, they were carbonized in a quartz tube with a holding time of 30 min at a temperature of 600 °C. After the activated carbon that had been obtained had been cooled to room temperature, washed with boiling water, and oven dried at 70 °C, it was subjected to a 2-h reflux in a soxhelt containing one million parts hydrochloric acid, after which it was filtered and washed with distilled water until the pH was neutral. The final result of P-AC was dried at 70 °C, then crushed and sieved to a particle size of less than 60 µm, and then it was stored in a dark glass bottle until it was needed.

## 2.2 Synthesis of St-g-P(AA)/P-AC composites

At 85 °C, starch (1 g) was distributed in distilled water (50 mL) and agitated for 30 min under an N<sub>2</sub> environment before cooling to 50 °C. To create free radicals, 1.0 g ammonium persulfate was added to the reaction mixture and agitated for 15 min [12]. Then, to complete the grafting reaction, precise amounts of (acrylic acid) AAc (7 g), MBA (1.0 g), and P-AC (0–10 wt % in relation to the sum weight of starch and AAc) were added to the reaction mixture and heated to 70 °C with stirring for 3 h. The St-g-P(AA)/P-AC (0–10%) composites were cooled to room temperature, filtered, and then extensively washed with distilled water to eliminate unreacted compounds. Totally, composites were crushed, sieved after being oven-dried to a consistent weight, and sieved to smaller than 100 µm.

## 2.3 Characterization

FTIR analysis was made using a VERTEX70 Spectrometer connected to platinum ATR unit model V-100, Germany. FTIR analysis was employed at 400 and 4000 cm<sup>-1</sup> wave-number range to study the formed chemical bonds and functional groups. The Brunner Emmett Teller (BET) surface areas were determined by N<sub>2</sub> adsorption–desorption isotherm using BELSORP-Mini II BEL equipment, Japan. Thermal analyzes were carried out using the SDT650-Simultaneous Thermal Analyzer device, USA, at a temperature range of 50 to 1000 °C, at a temperature increase rate of 5 °C/min. X-ray diffraction (XRD) patterns were obtained on a Bruker's X-ray diffractometer, Germany, (second generation Bruker 2D Phaser, X-ray diffractograms (XRD) run at 30 kV, in the range 2θ: 5–80°, with Cu Kα radiation (λ = 1.540598 Å). The morphological structure was performed using Scan Electron Microscope and Energy Dispersive X-ray Spectroscopy using JEOL-JSM-5300 LV, Tokyo, Japan. UV–visible spectra of MB dye before and after adsorption were recorded on PG spectrophotometer instrument model T80, UK. The point of zero charge (pH<sub>pzc</sub>) was determined as described by Shoaib et al. (2020). In brief, in nine flasks, 50 mg of St-g-P(AA)/P-AC adsorbent was added to a 50 mL 0.1 M NaNO<sub>3</sub> solution.

The pH (pH<sub>i</sub>) of the starting solution was changed from 2 to 10 by adding 0.1 M HCl or NaOH. The final pH (pH<sub>f</sub>) of the supernatant liquid was measured, and the difference between the beginning and final pHs (Δ pH = pH<sub>i</sub> – pH<sub>f</sub>) was plotted against the initial pH (pH<sub>i</sub>) [48]. The point where the curve intersected the x-axis is the composite's pH<sub>ZPC</sub> value [49] Bench-top pH/mV/temperature meter model JENCO-6173 was used for pH value adjustment. Bench-top laboratory incubator shaker JSSI-100 T JS Research Inc., Korea, was used for temperature effect studies.

## 2.4 MB dye adsorption and desorption tests

The adsorption study evaluated the MB dye removal capacity of the St-g-P(AA)/P-AC composites. Briefly, in a run of 250 mL conical flask, 20 mg of adsorbent was shaken in 100 mL of MB dye solution. The experimental design was done under shaking (ca. 200 rpm) at a controlled temperature (25 ± 2 °C). At chosen time intervals, a supernatant aliquot was collected and determined at λ<sub>max</sub> 665 nm. Using a plot of the calibration curve have linear regression equation (R<sup>2</sup> > 0.996) the MB dye solution concentrations were measured before and after adsorption. The capacity of adsorption of the St-g-P(AA)/P-AC samples for MB dye was obtained from the following Eq. (1):

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

where  $q_e$  is the MB dye adsorption capacity loaded adsorbent (mg/g),  $C_0$  and  $C_e$  represent the MB dye beginning and equilibrium concentrations (mg/L),  $m$  (g) is the amount of St-g-P(AA)/P-AC and  $V$  (L) is the MB dye solution volume.

Similar procedures were used to assess how specific parameters might affect the adsorption capacity: contact time (0 to 120 min), pH values (3 to 10), dose (5 to 25 mg for 100 mL dye solution), MB dye solution beginning concentration (60 to 140 mg/L), and temperature range (25 to 40 °C).

Desorption experiments: the samples consumed in the adsorption experiments with a MB dye solution beginning concentration (100 mg/L) and 15 mg St-g-P(AA)/P-AC dose were collected and then dried at 70 °C. The MB dye loaded on the adsorbent samples was desorbed using 0.1 M HCl as an eluent. 15 mg of MB dye-loaded composites was obscured in elution media (100 mL) under shaking at 25 ± 1 °C for 2 h. The eluted MB dye per gram of adsorbent ( $q_{des}$ ) from the concentration of MB desorbed ( $C_{des}$ ) in the solution was calculated by using the following Eq. (2):

$$q_{des} = C_{des} \frac{V}{m} \quad (2)$$

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 the MB dye desorbed ( $q_{des}$ ) to the MB adsorbed ( $q$ ) using this Eq. (3):

$$\% \text{ Desorption} = \frac{q_{des}}{q} \times 100 \quad (3)$$

For regeneration and desorption experiments, samples were shaken in 0.1 M NaOH solution for 30 min and cleaned several times with distilled water. It was necessary to carry out this process to deprotonate the functional groups that had been formed due to the desorption step. To determine whether or not the composites have a chance of functioning effectively as practical MB dye adsorbents, samples were subjected to three successive adsorption–desorption cycles.

Error analysis functions coefficient of determination ( $R^2$ ), and average percentage errors (APE%) function were applied to investigate the power of the isotherm models fitted by the nonlinear regression method [50]. The Average percentage errors (APE%) were determined using Eq. (4):

$$APE (\%) = \frac{100}{N} \times \sum_{i=1}^N \left| \frac{q_{e, isotherm} - q_{e, calc}}{q_{e, isotherm}} \right|_i \quad (4)$$

## 3 Results and discussion

### 3.1 Characterization

#### 3.1.1 FTIR analysis

FTIR spectra were displayed for P-AC, St-g-P(AA)/P-AC0%, and St-g-P(AA)/P-AC7.5%, respectively (Fig. 2). For P-AC, the bands at 3795 and 3195  $\text{cm}^{-1}$  represent bonding and non-bonding OH groups on their surface [51]. Figure 2a shows these band locations of aldehydes, ketones, quinones, and carboxylated groups which can all be identified by the peak of C=O that is located at 1590  $\text{cm}^{-1}$  [52, 53]. In addition, there were peaks at 1190  $\text{cm}^{-1}$  that represented C–O stretching vibrations [54], and bands at 886–756  $\text{cm}^{-1}$  indicated  $\text{H}_2\text{PO}_4^-$ ,  $\text{PO}_4^{2-}$ , disulfide, or aromatic structures. In the meantime, the band at a frequency of 467  $\text{cm}^{-1}$  may indicate metal oxide or aromatic structures.

Starch spectra Fig. 2b showed O–H stretching peak at 3290, C–H symmetric stretching peak at 2926, and C=O stretching peak at 1641  $\text{cm}^{-1}$ . At 1148 and 997  $\text{cm}^{-1}$ , the C–O–C triplet band stretching absorption was also visible. New peaks developed in the spectrum after the grafting of acrylic acid [St-g-P(AA)/P-AC0%] (Fig. 2c). These peaks included an acrylic C=O stretching band at 1709  $\text{cm}^{-1}$ , acrylic acid symmetric and asymmetric COO stretching at 1541 and 1444  $\text{cm}^{-1}$  and a weak peak at 3187  $\text{cm}^{-1}$  owing to water molecules. The peak at 2935  $\text{cm}^{-1}$  is due to C–H symmetric stretching. The grafting of acrylic acid

onto starch was validated by this knowledge. This confirmation is backed up by previous reports of starch graft copolymerization with acrylic acid [44, 55]. FTIR spectra for St-g-P(AA)/P-AC7.5% (Fig. 2d) and St-g-P(AA)/P-AC0% (Fig. 2c) were similar. FTIR peaks intensities are very small when compared to intensities of the St-g-P(AA), which explains the similarity of the figures between St-g-P(AA)/P-AC7.5% and St-g-P(AA)/P-AC0% (Figs. 2c and 2d). The present at 1700, 1540, and 1443  $\text{cm}^{-1}$  were assigned to C=O<sup>−</sup> and COO<sup>−</sup>, which corroborated the composite's formation.

#### 3.1.2 Pore structure analysis

Figure 3a displays the adsorption–desorption isotherms of nitrogen at 77 K on St, St-g-P(AA)/P-AC0%, St-g-P(AA)/P-AC5%, St-g-P(AA)/P-AC7.5%, and St-g-P(AA)/P-AC10%. According to the IUPAC categorization [56], a type III isotherm with notable H3 hysteresis loops suggests that the pores are of low energy, homogeneous solid surface that possesses mesoporosity. As long as the interactions between the adsorbent and the adsorbate are modest, it can be found in mesoporous or microporous adsorbents. In addition, the BJH desorption pore size distributions are displayed in Fig. 3b. These distributions include St, St-g-P(AA)/P-AC0 percent, St-g-P(AA)/P-AC5%, St-g-P(AA)/P-AC7.5%, and St-g-P(AA)/P-AC10%. It can be noted that the pores between 2 and 30 nm were dominant for all; that is, both mesopores and macropores are present [57].

The porous structure parameters of St, St-g-P(AA)/P-AC0%, St-g-P(AA)/P-AC5%, St-g-P(AA)/P-AC7.5%, and St-g-P(AA)/P-AC10% are summarized in Table 1.

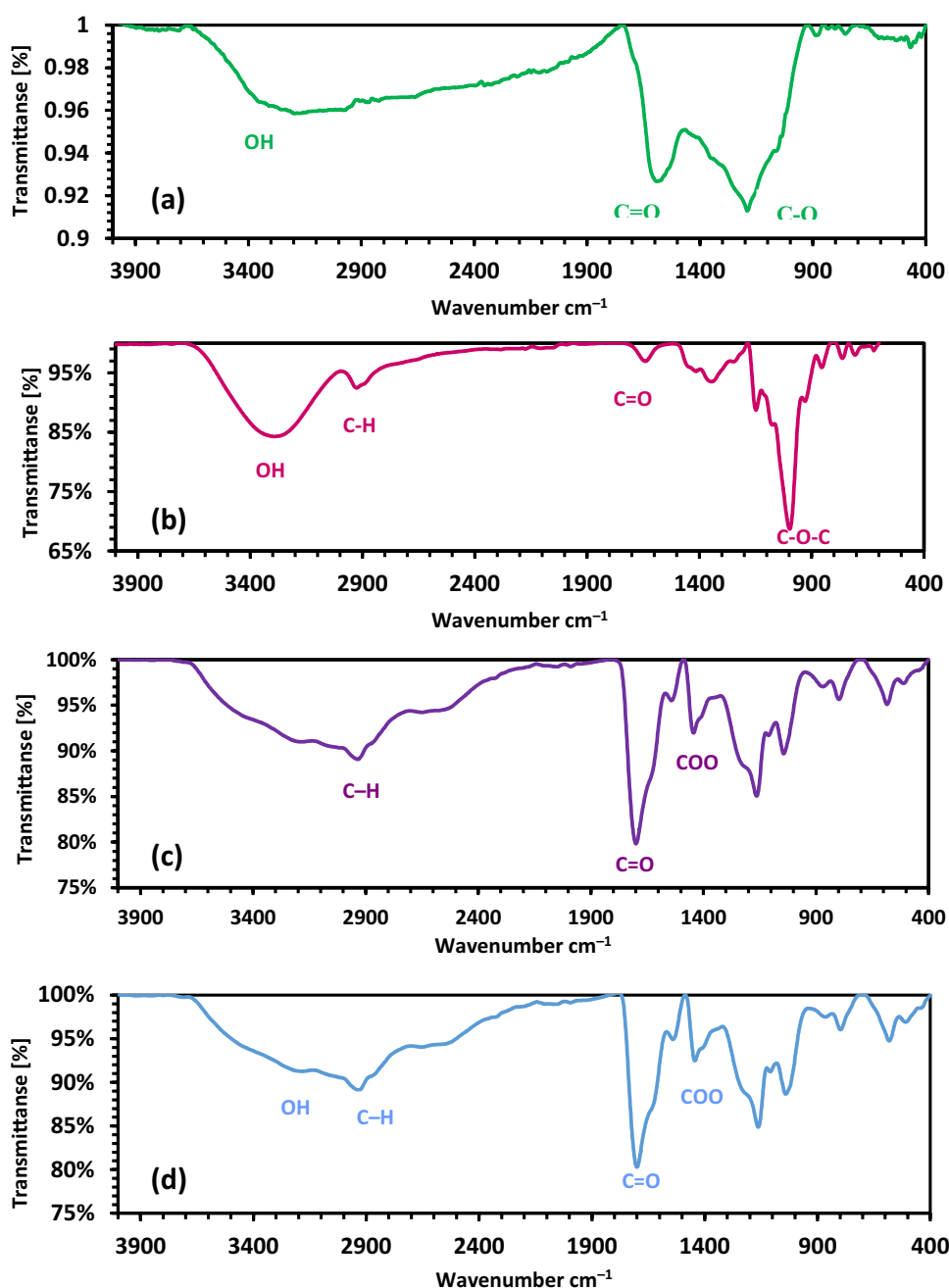
#### 3.1.3 Thermal analysis

Thermal properties of the St-g-P(AA)/P-AC0%, and St-g-P(AA)/P-AC7.5% were studied, and their corresponding thermograms are exemplified in, Fig. 4(a, b) and Table 2. Both St-g-P(AA)/P-AC0%, and St-g-P(AA)/P-AC7.5% composite showed three stages of decomposition, and the total weight loss was 78.92 and 77.12%, respectively, which indicated that the presence of P-AC in the network of the composite led to an increase in thermal stability. The initial weight loss occurs due to the hydrophilic polymer's water loss [58]. The second and third weight loss is due to the degradation of starch in graft copolymer [59] and polymer chain and matrix [31], respectively.

#### 3.1.4 XRD analysis

The XRD results of P-AC, St, St-g-PAA/P-AC0%, and St-g-PAA/P-AC7.5% were presented in Fig. 5. There

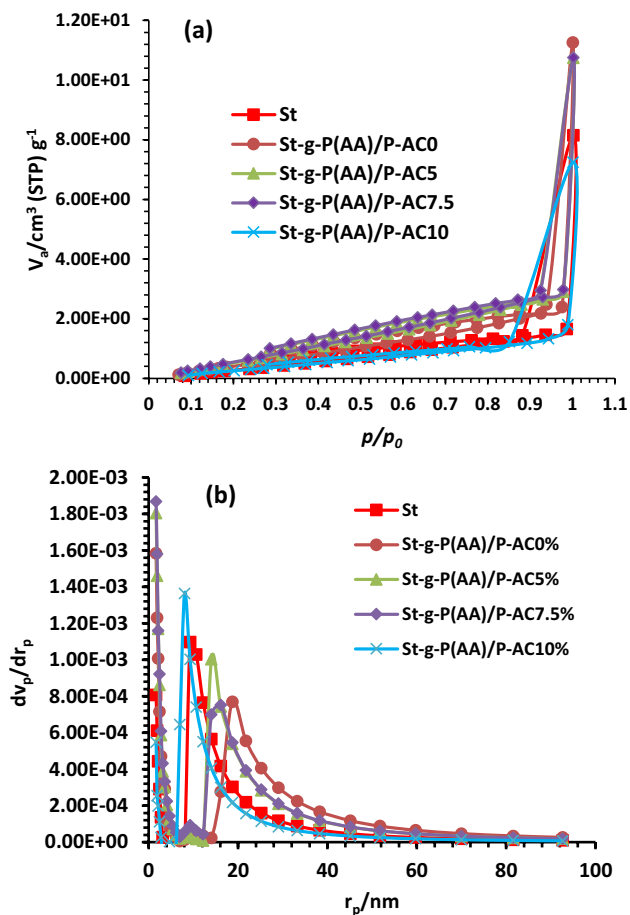
**Fig. 2** FT-IR spectra image of P-AC (a), St (b), St-g-P(AA)/P-AC0% (c), and St-g-P(AA)/P-AC7.5% (d)



were sharp peaks in XRD patterns of pure starch (St) and P-AC. Afterwards, graft copolymerization St-g-PAA, the sample displayed a broad peak without characteristics peaks, which indicated that the crystal structure of the starch was damaged [55] and confirmed its amorphous nature [26]. Similar results were also reported by Saberi et al. (2019) and Shi et al. (2012) [26, 55]. The peak intensity of the original properties of P-AC was diminished as a result of its incorporation into the polymerization process, which caused damage to the peaks' original forms.

### 3.1.5 SEM and EDX analyses

The surface morphological features of St-g-P(AA)/P-AC0%, St-g-P(AA)/P-AC7.5%, and MB- St-g-P(AA)/P-AC7.5% were examined by SEM study. A very rough surface and appearance of voids were cleared for St-g-P(AA)/P-AC0% composite (Fig. 6a). When P-AC was incorporated (Fig. 6b), St-g-P(AA)/P-AC7.5% the surface roughness was expressively decreased due to the partial fill-up of the voids by P-AC a smooth surface was appeared compared to untreated composite (Fig. 6a). This morphological analysis revealed



**Fig. 3** St, St-g-P(AA)/P-AC0%, St-g-P(AA)/P-AC5%, St-g-P(AA)/P-AC7.5%, and St-g-P(AA)/P-AC10%. **a**  $\text{N}_2$  gas adsorption-desorption isotherms, **b** BJH desorption pore size distributions

that P-AC was successfully incorporated into the polymeric matrix. After the MB dye adsorption on St-g-P(AA)/P-AC7.5% (Fig. 6c), the morphology of the composite has significantly changed. It should be observed that after MB adsorption, the composite became rougher.

Figure 7 shows the elemental composition of St-g-P(AA)/P-AC0%, and St-g-P(AA)/P-AC7.5% adsorbents, it was calculated that St-g-P(AA)/P-AC0, and St-g-P(AA)/P-AC7.5 contained about 40.95 and 42.24 wt % of carbon, 52.19 and 50.69 wt % of oxygen, 4.44 and 3.91 wt % of nitrogen, and 2.41 and 3.15 wt % of sulfur, respectively. Sulfur and Nitrogen are predicted in the EDX spectra of St-g-P(AA)/P-AC0% comes from APS, and MBA, which were the free radical initiator and cross-linked in the polymerization reaction, respectively. The wt % of sulfur increased due to the presence of sulfur in the P-AC as described in Shoaib et al. (2020) [47].

### 3.1.6 Points of zero charge ( $\text{pH}_{\text{PZC}}$ )

The electrical charge nature in the adsorbent and adsorbed particles directly influences the physical adsorption process reported for St-g-P(AA)/P-AC7.5% composites. Hence,  $\text{pH}_{\text{PZC}}$  gives useful information on adsorption of St-g-P(AA)/P-AC7.5% at specific conditions of pH [12]. The  $\text{pH}_{\text{PZC}}$  is the pH required to affect a net zero charge on a solid surface if there isn't any particular sorption. The  $\text{pH}_{\text{PZC}}$  of adsorbent St-g-P(AA)/P-AC7.5 surface was found to be about 2.3 (Fig. 8). So, it can be assumed that when  $\text{pH} > 2.3$  the surface will be charged negative, and so favor cationic MB dye specimens adsorption [60].

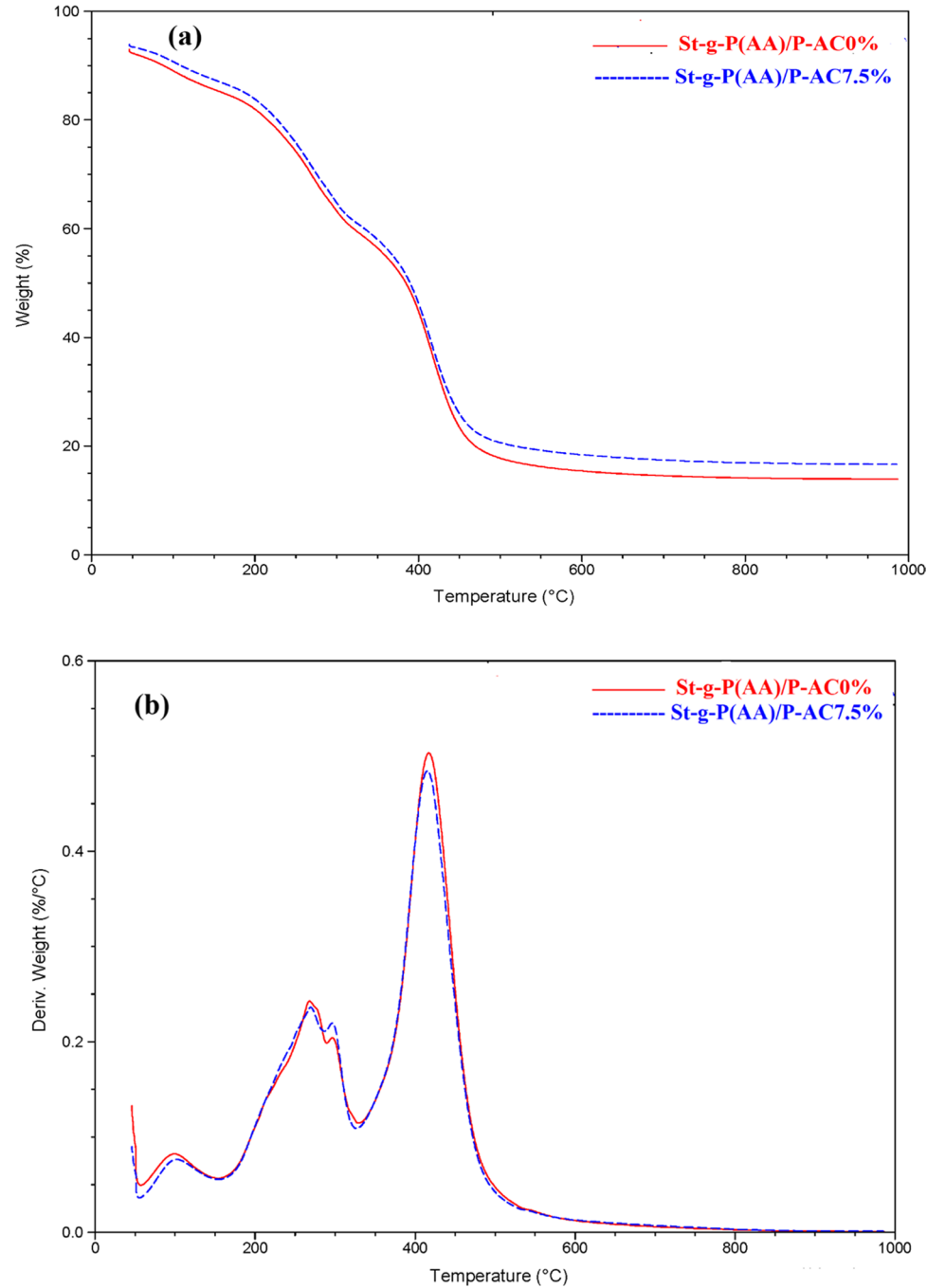
## 3.2 Sorption study

Utilizing a variety of thermodynamic and kinetic analyses, such as the impact of pH, composite mass, beginning MB dye concentrations, the effect of temperature and thermodynamics, and other significant factors, an evaluation of the rate and adsorption capacity of MB dye from aqueous solution is carried out. This evaluation determines how well the MB dye can remove itself from the solution.

**Table 1** The parameters of porous structure of St, St-g-P(AA)/P-AC0%, St-g-P(AA)/P-AC5%, St-g-P(AA)/P-AC7.5%, and St-g-P(AA)/P-AC10%

| Sample            | BET                                             |                                  |                               |                                                 | BJH desorption                            |                                  |                                                            |
|-------------------|-------------------------------------------------|----------------------------------|-------------------------------|-------------------------------------------------|-------------------------------------------|----------------------------------|------------------------------------------------------------|
|                   | $a_{s,\text{BET}}$<br>( $\text{m}^2/\text{g}$ ) | $V_m$ ( $\text{cm}^3/\text{g}$ ) | Mean pore<br>diameter<br>(nm) | Total pore volume<br>( $\text{cm}^3/\text{g}$ ) | Pore volume<br>( $\text{cm}^3/\text{g}$ ) | Average pore<br>diameter<br>(nm) | Pore-specific<br>surface area<br>( $\text{m}^2/\text{g}$ ) |
| St                | 2.92                                            | 0.6714                           | 6.64                          | 0.0049                                          | 0.0114                                    | 9.25                             | 1.9197                                                     |
| St-g-P(AA)/P-AC0  | 3.58                                            | 0.8233                           | 12.92                         | 0.0116                                          | 0.0146                                    | 1.66                             | 2.4621                                                     |
| St-g-P(AA)/P-AC5  | 5.29                                            | 1.2149                           | 7.94                          | 0.0105                                          | 0.0142                                    | 1.66                             | 2.8816                                                     |
| St-g-P(AA)/PAC7.5 | 5.27                                            | 1.2108                           | 7.94                          | 0.0105                                          | 0.0141                                    | 1.66                             | 2.9547                                                     |
| St-g-P(AA)/P-AC10 | 2.00                                            | 0.4598                           | 6.54                          | 0.0033                                          | 0.0105                                    | 8.03                             | 1.8728                                                     |

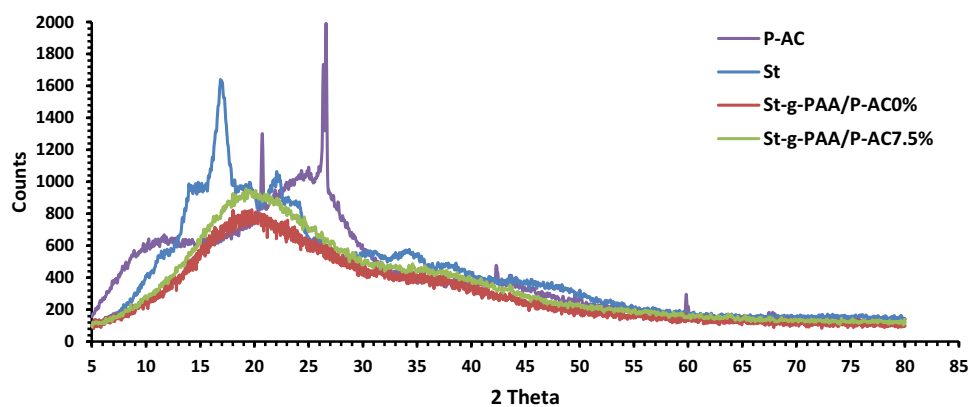
**Fig. 4** TGA (a) and DTA (b) of St-g-P(AA)/P-AC0% and St-g-P(AA)/P-AC7.5%



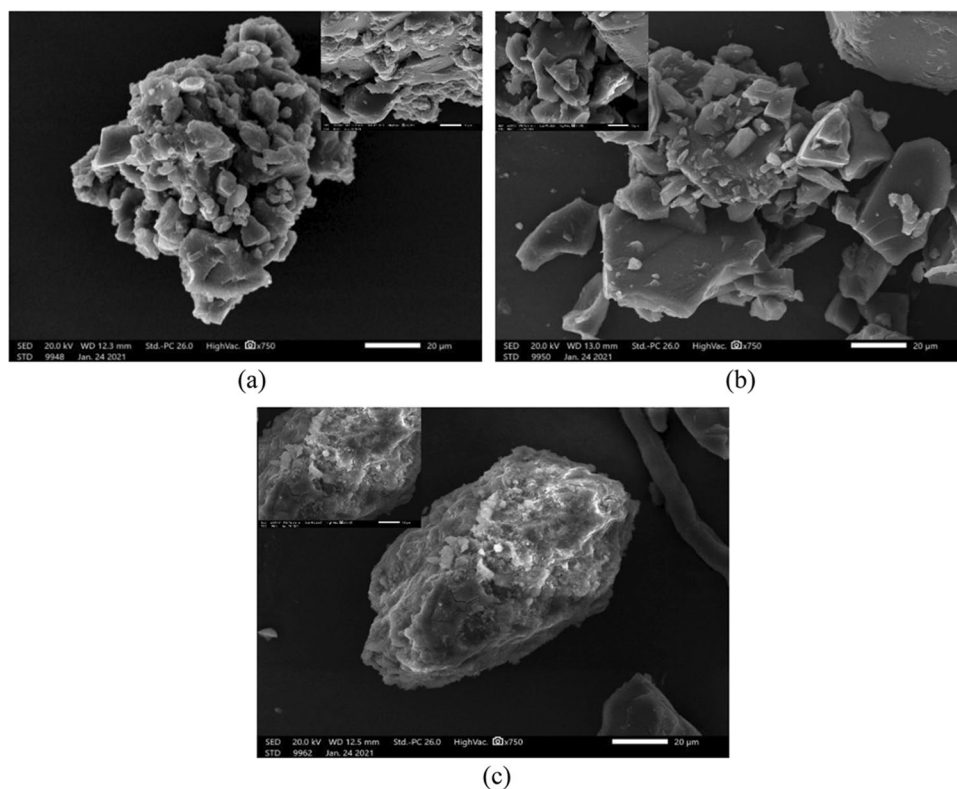
**Table 2** The weight loss %, and specific decomposition temperatures of St-g-P(AA)/P-AC0, and St-g-P(AA)/P-AC7.5 reads from thermogravimetric analysis (TGA) and DTA plot, respectively

| Weight loss stage | St-g-P(AA)/P-AC0       |                 |                                | St-g-P(AA)/P-AC7.5     |                 |                                |
|-------------------|------------------------|-----------------|--------------------------------|------------------------|-----------------|--------------------------------|
|                   | TGA                    |                 | DTA                            | TGA                    |                 | DTA                            |
|                   | Temperature range (°C) | Weight loss (%) | Decomposition temperature (°C) | Temperature range (°C) | Weight loss (%) | Decomposition temperature (°C) |
| First             | 45.8–143.1             | 6.837%          | 98.45                          | 46.0–154.4             | 6.620%          | 99.22                          |
| Second            | 143.1–332.6            | 27.40%          | 267.48                         | 154.4–326.9            | 26.37%          | 269.10                         |
| Third             | 331.5–986.3            | 44.80%          | 417.61                         | 326.9–989.1            | 44.14%          |                                |

**Fig. 5** XRD of P-AC, St, St-g-PAA/P-AC0%, and St-g-PAA/P-AC7.5%



**Fig. 6** SEM image of St-g-P(AA)/P-AC0% (a), St-g-P(AA)/P-AC7.5% (b), and MB-St-g-P(AA)/P-AC7.5% (c)

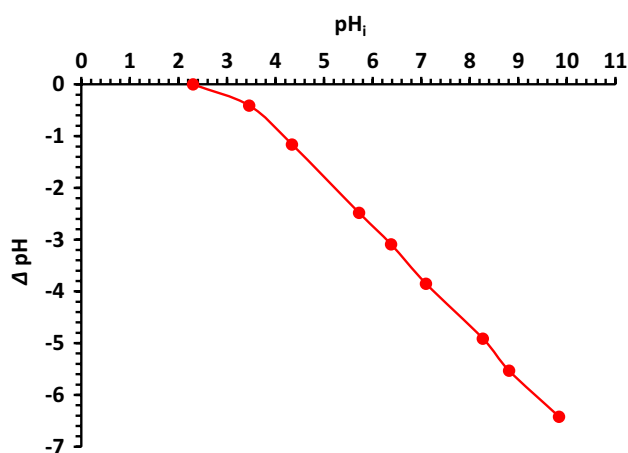
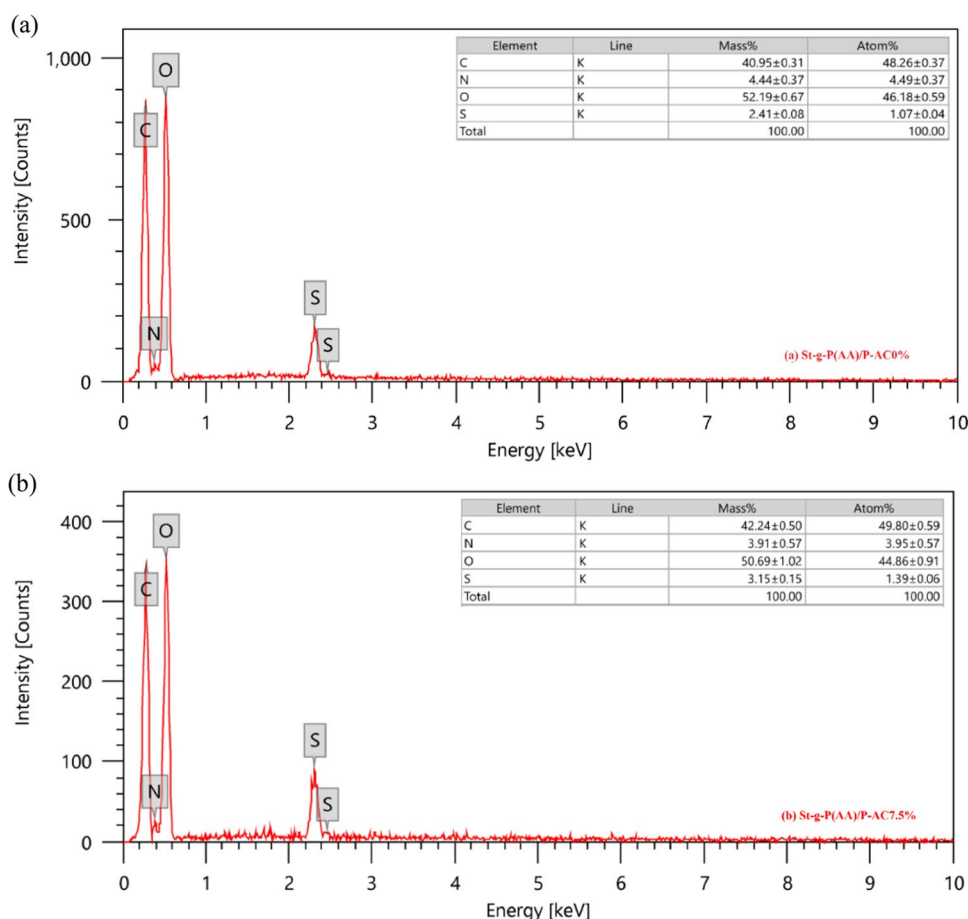


### 3.2.1 Impact of P-AC addition to St-g-P(AA) on MB dye adsorption at different pH

The impact of the addition P-AC to St-g-P(AA) 0–10% on removal of MB dye was tested at [MB] = 100 mg/L, pH = 8, dose = 20 mg, contact time = 120 min, and shaking speed = 200 rpm. Figure 9 shows that P-AC has some effect on MB dye adsorption capacity. The maximum MB adsorption capacity increased with an increase in %P-AC to 496.29 mg/g obtained by St-g-P(AA)/P-AC7.5%, which increased by 30 mg/g after adding 7.5% of P-AC then slightly decreased after addition 10% of P-AC. This can be explained by the matrix's greater porosity as a result of the presence

of P-AC, facilitating interaction between both polymeric chains and MB molecules. The enhancement of crosslinking spots within the matrix is responsible for the small decrease in MB adsorption property [61, 62]. The hydroxyl groups of P-AC engage strongly with the carboxylic groups of PAAc, as previously observed [55, 56], reducing the number of carboxylate groups accessible to interact with MB dye molecule due to hydrogen bonds [62–64]. Overall, these answers indicate that all of the composites have excellent MB dye removal properties, which is critical for treating wastewater contaminated with dyes. The composite which has the maximum amount of MB dye adsorption was used to perform the batch experiment.

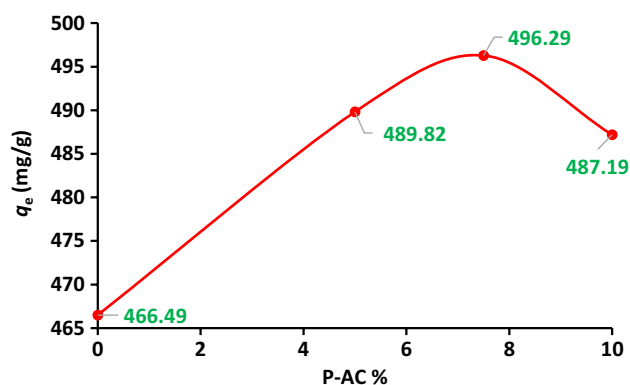
**Fig. 7** EDX image of St-g-P(AA)/P-AC0% (a) and St-g-P(AA)/P-AC7.5% (b)



**Fig. 8**  $pH_{pzc}$  of St-g-P(AA)/P-AC7.5% adsorbent by pH drift method.

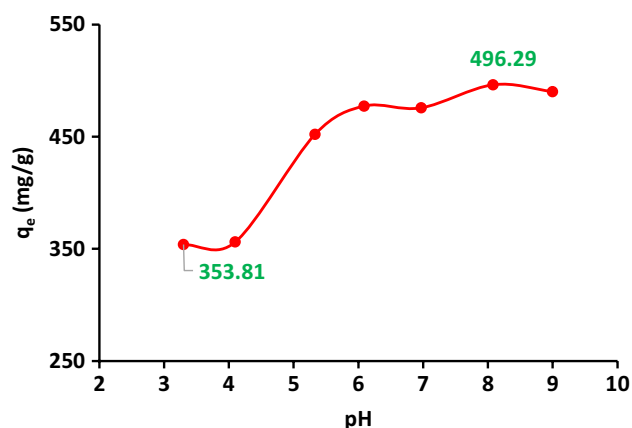
### 3.2.2 Influence of pH

As presented in Fig. 10, the MB dye adsorption on St-g-P(AA)/P-AC7.5% as a function of pH at  $[MB] = 100 \text{ mg/L}$ , dose = 20 mg, temperature =  $25 \pm 2^\circ\text{C}$ , shaking = 200 rpm, and contact time = 120 min] increases with the increasing



**Fig. 9** The amount of MB dye that was absorbed by the composites as a function of the amount of P-AC present (adsorbent dosage of 20 mg, MB concentration of 100 mg/L, pH of 8, solution volume of 100 mL, contact period of 120 min, and temperature of  $25 \pm 2^\circ\text{C}$ )

of the pH where, the maximum and minimum capacity of adsorption reaches 353.81 and 496.29 mg/g at pH 3 and 8, respectively. The weakened MB dye adsorption removal % reaches around 70% at pH 3 and pH 4 due to the  $H^+$  ions contend with the cationic MB dye molecules for sites of adsorption, and the absence of electrostatic attraction due to

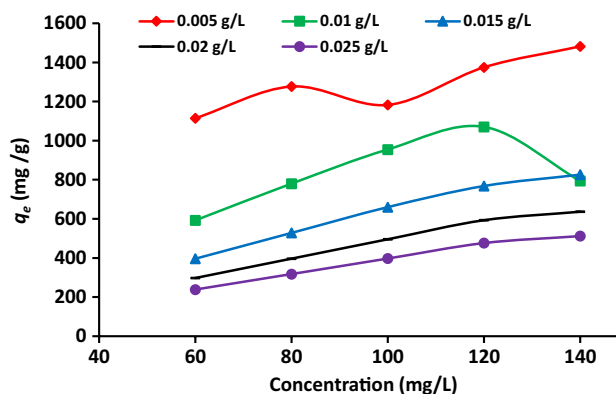


**Fig. 10** Impact of solution pH on the MB dye capacity of adsorption (100 mg/L) onto St-g-P(AA)/P-AC7.5% (0.02 g/100 mL) at  $25 \pm 2$  °C

most portions of composite carboxylic groups is in  $-\text{COOH}$  protonated form, also, reduction anionic sites on the adsorbent surface. Otherwise, when a solution pH of  $\geq 5$ , the MB adsorption removal % reaches 90–99% at pH 8 where  $\text{H}^+$  ions and MB molecules had no competition for the carboxylated groups of PAAc, favouring MB adsorption. In addition, the excessive number of  $-\text{COO}^-$  ions contained by the composite creates repulsive forces, which cause the polymeric matrixes to expand. Overall, matrix expansion increases MB adsorption and causes liquid uptake [12]. Such results suggest strongly that composite St-g-P(AA)/P-AC7.5% as proficient MB adsorbents in a pH wide range (pH 5–9). Therefore, pH 8 was used as the preferred pH for all the experiments' work due to achieving maximum adsorption capacity.

### 3.2.3 Influence of initial MB dye concentration

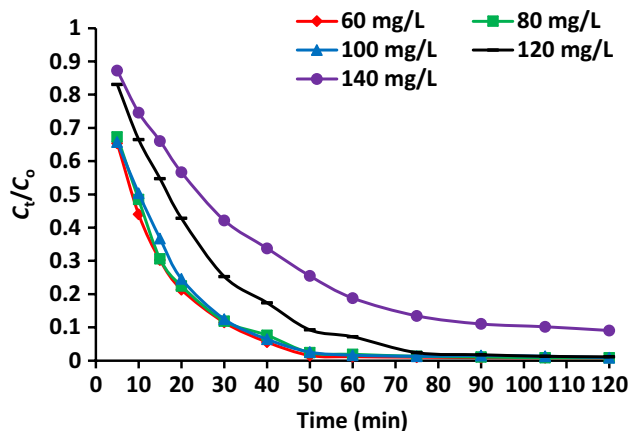
Adsorption studies were operated at beginning concentrations of MB dye ranging from 60 to 140 mg/L with St-g-P(AA)/P-AC7.5% doses (0.005, 0.01, 0.015, 0.02 and 0.025 g/L) (Fig. 11). The data referred that the increased MB dye adsorption capacity of St-g-P(AA)/P-AC7.5% increases the beginning concentration of MB dye. The adsorption capacity of St-g-P(AA)/P-AC7.5% at dose 0.005 g/L–0.025 g/L increased from 1114.59 to 1482.00 mg/g and 238.55 to 511.91 mg/g, respectively, when the MB dye primary concentration increases from 60 to 140 mg/L. On the other hand, the MB dye removal percent was inversely proportional with MB dye concentrations, which clearly suggested that MB dye adsorption from its aqueous solution was dependent on its primary concentration in addition to a reduction of active surface size with an increase in MB dye concentration [53].



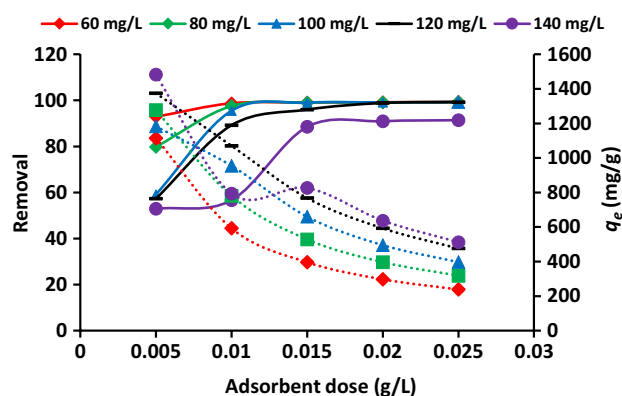
**Fig. 11** The relationship between the amounts of MB dye adsorbed at equilibrium and its beginning concentration using different doses of St-g-P(AA)/P-AC7.5%

### 3.2.4 Impact of contact time

MB dye removal by St-g-P(AA)/P-AC7.5% at different shaking intervals was estimated by consuming MB dye with concentrations of 60, 80, 100, 120, and 140 mg/L. Figure 12 shows the concentration variations of MB dye in external solution in reference to the primary concentration vs time. The concentration of MB dye in the external solution decreases until it reaches equilibrium. As a result of being adsorbed in the composite, the concentration of MB dye in the solution dropped. After achieving the equilibrium (50 min for concentration 60, 80, 100 mg/L), 60 min for concentration 120, 140 mg/L), the concentration of MB dye in the solution is stable and the St-g-P(AA)/P-AC7.5% gets saturated ( $C_t/C_0 = 0.02$ ). Desorption may occur with the passage of time, implying that the composite may progressively



**Fig. 12** The impact of contact time on the concentration of MB dye in the external solution using St-g-P(AA)/P-AC7.5% (0.02 g/100 mL) at a temperature of  $25 \pm 2$  °C and a pH of 8.0



**Fig. 13** Effect of mass (g) of St-g-P(AA)/P-AC7.5% concentration on  $q_e$  of MB ( $C_0$ : 60–140 mg/L, pH 8.0, agitation speed: 200 rpm and temperature:  $25 \pm 2$  °C)

desorb a limited number of adsorbed MB dye back to the solution [40].

### 3.2.5 Effect of St-g-P(AA)/P-AC7.5% dose

The effect of the adsorbent dose of St-g-P(AA)/P-AC7.5% on MB dye adsorption was performed by changing the adsorbent dose (0.005 to 0.025 g/L) and five different initial MB dye concentrations from 60 to 140 mg/L at pH 8 (Fig. 13). It is observed that the increase in the amount of the hydrogel St-g-P(AA)/P-AC7.5% resulted in a rise in MB removal with a maximum of 99.40%. So, there is a decrease in the equilibrium adsorption capacity ( $q_e$ ) of MB dye. Raising the sorbent dosage increased the amount of sorbent functional groups, surface area, and pore volume available for MB dye adsorption on the St-g-P(AA)/P-AC7.5% surface may be able to explain this outcome. This finding is in line with previous studies [65, 66].

### 3.2.6 Adsorption kinetics

The kinetic adsorption data of MB dye onto St-g-P(AA)/P-AC7.5% were processed to understand and predict the nature of the process of adsorption. Table 3 summarized the three linear equations of kinetic models that had been employed to understand the reaction mechanism [67–69], i.e., pseudo-first-order (PFO) Eq. (5), pseudo-second-order (PSO) Eq. (6), and intraparticle diffusion (IPD) models Eq. (7). Kinetics parameters, coefficients of determination  $R^2$ , and the statistic average percentage errors APE%, were summarized in Tables 4 and 5 for different initial MB dye and St-g-P(AA)/P-AC7.5% concentrations. Figure 14a, b displayed the PFO and PSO kinetics models of MB dye adsorption onto St-g-P(AA)/P-AC7.5%. Table 4 shows that (A) for the PFO kinetic model, the  $q_{e(\text{exp})}$  values are in agreement with the predicted  $q_{e(\text{th})}$  values more than the PSO. (B) The rate

**Table 3** Summary of the linear kinetic models PFO, PSO, and IPD parameters

| Models | Linear equation                                                          | Parameters                                                                                                                                      | Description                                                                                                                                                                                                                                                 | Ref      |
|--------|--------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| PFO    | $\log(q_e - q_i) = \log(q_e) - \frac{k_1}{2.303} t$ (5)                  | $q_e$ (mg/g): adsorption capacity at equilibrium; $q_i$ (mg/g): adsorption capacity at time $t$ ; $K_1$ (L/mg): rate constant of PFO adsorption | The sorption rate based on the sorption capacity                                                                                                                                                                                                            | [67]     |
| PSO    | $\left(\frac{t}{q_i}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (6) | $k_2$ (g/mg min): second-order constants<br>$h$ (mg/g min): initial sorption rate, $h = k_2 q_e^2$                                              | Examine the nature of binding between MB dye and St-g-P(AA)/P-AC7.5% either physical or chemical adsorption                                                                                                                                                 | [50]     |
| IPD    | $q_i = K_{\text{dif}} t^{1/2} + C$ (7)                                   | $C$ (mg/g): the intercept related to the thickness of the boundary layer; $K_{\text{dif}}$ (mg/g min <sup>1/2</sup> ): IPD rate constant        | The first phase in the process involves the movement of molecules of the solute from the aqueous medium to the surface of the adsorbent. The second step involves the movement of molecules of the adsorbate into the pores of the adsorbent (slow process) | [59, 60] |

**Table 4** Comparison of kinetics parameters of PFO and PSO kinetic model values for different initial MB dye and St-g-P(AA)/P-AC7.5% concentrations

| Composite Conc (g/L) | MB dye Conc. (mg /L) | $q_e$ exp | First-order kinetic model |                   | Second-order kinetic model |               |                   |       |       |
|----------------------|----------------------|-----------|---------------------------|-------------------|----------------------------|---------------|-------------------|-------|-------|
|                      |                      |           | $q_e$ (calc.)             | $k_1 \times 10^3$ | $R^2$                      | $q_e$ (calc.) | $k_2 \times 10^3$ | $H$   | $R^2$ |
| 0.005                | 60                   | 1114.59   | 1479.11                   | 35.01             | 0.970                      | 2500.00       | 0.003             | 20.75 | 0.742 |
|                      | 80                   | 1276.74   | 2646.06                   | 49.05             | 0.728                      | 2500.00       | 0.004             | 26.18 | 0.933 |
|                      | 100                  | 1182.65   | 1362.39                   | 24.18             | 0.958                      | 2000.00       | 0.006             | 24.21 | 0.852 |
|                      | 120                  | 1375.03   | 1661.12                   | 26.02             | 0.990                      | 5000.00       | 0.001             | 17.76 | 0.237 |
|                      | 140                  | 1482.00   | 1807.17                   | 24.64             | 0.975                      | 3333.33       | 0.002             | 21.79 | 0.875 |
| 0.01                 | 60                   | 592.44    | 569.25                    | 51.36             | 0.971                      | 714.29        | 0.068             | 34.84 | 0.984 |
|                      | 80                   | 780.35    | 885.52                    | 40.07             | 0.935                      | 1000.00       | 0.034             | 34.48 | 0.992 |
|                      | 100                  | 954.86    | 2015.58                   | 56.65             | 0.780                      | 1250.00       | 0.020             | 31.95 | 0.988 |
|                      | 120                  | 1070.57   | 1534.26                   | 38.23             | 0.930                      | 2000.00       | 0.006             | 23.70 | 0.949 |
|                      | 140                  | 793.56    | 1028.49                   | 26.02             | 0.935                      | 2000.00       | 0.003             | 11.11 | 0.871 |
| 0.015                | 60                   | 396.23    | 251.13                    | 59.88             | 0.898                      | 434.78        | 0.236             | 44.64 | 0.994 |
|                      | 80                   | 528.21    | 675.46                    | 70.47             | 0.997                      | 625.00        | 0.103             | 40.16 | 0.990 |
|                      | 100                  | 660.01    | 615.89                    | 57.34             | 0.983                      | 769.23        | 0.103             | 60.98 | 0.997 |
|                      | 120                  | 768.02    | 914.32                    | 40.07             | 0.979                      | 1000.00       | 0.028             | 27.78 | 0.987 |
|                      | 140                  | 826.02    | 977.91                    | 37.54             | 0.992                      | 1111.11       | 0.023             | 28.01 | 0.993 |
| 0.02                 | 60                   | 297.54    | 256.86                    | 78.53             | 0.975                      | 322.58        | 0.418             | 43.48 | 0.998 |
|                      | 80                   | 396.55    | 348.18                    | 70.01             | 0.986                      | 434.78        | 0.276             | 52.08 | 0.997 |
|                      | 100                  | 495.57    | 302.76                    | 55.96             | 0.902                      | 555.56        | 0.199             | 61.35 | 0.997 |
|                      | 120                  | 593.13    | 871.16                    | 61.49             | 0.984                      | 714.29        | 0.061             | 31.35 | 0.987 |
|                      | 140                  | 636.60    | 797.26                    | 43.07             | 0.991                      | 833.33        | 0.034             | 23.36 | 0.989 |
| 0.025                | 60                   | 238.55    | 174.30                    | 74.62             | 0.968                      | 256.41        | 0.570             | 37.45 | 0.997 |
|                      | 80                   | 317.79    | 214.04                    | 76.23             | 0.914                      | 344.83        | 0.467             | 55.56 | 0.999 |
|                      | 100                  | 397.11    | 191.96                    | 63.33             | 0.884                      | 434.78        | 0.341             | 64.52 | 0.997 |
|                      | 120                  | 476.22    | 564.29                    | 69.55             | 0.991                      | 555.56        | 0.138             | 42.55 | 0.994 |
|                      | 140                  | 511.91    | 1442.12                   | 83.60             | 0.759                      | 625.00        | 0.078             | 30.30 | 0.995 |
| %APE                 |                      | 0.33      |                           | 2.04              |                            |               |                   |       |       |

**Table 5** Kinetics parameters of IPD kinetic model values for different initial MB dye and St-g-P(AA)/P-AC7.5% concentrations

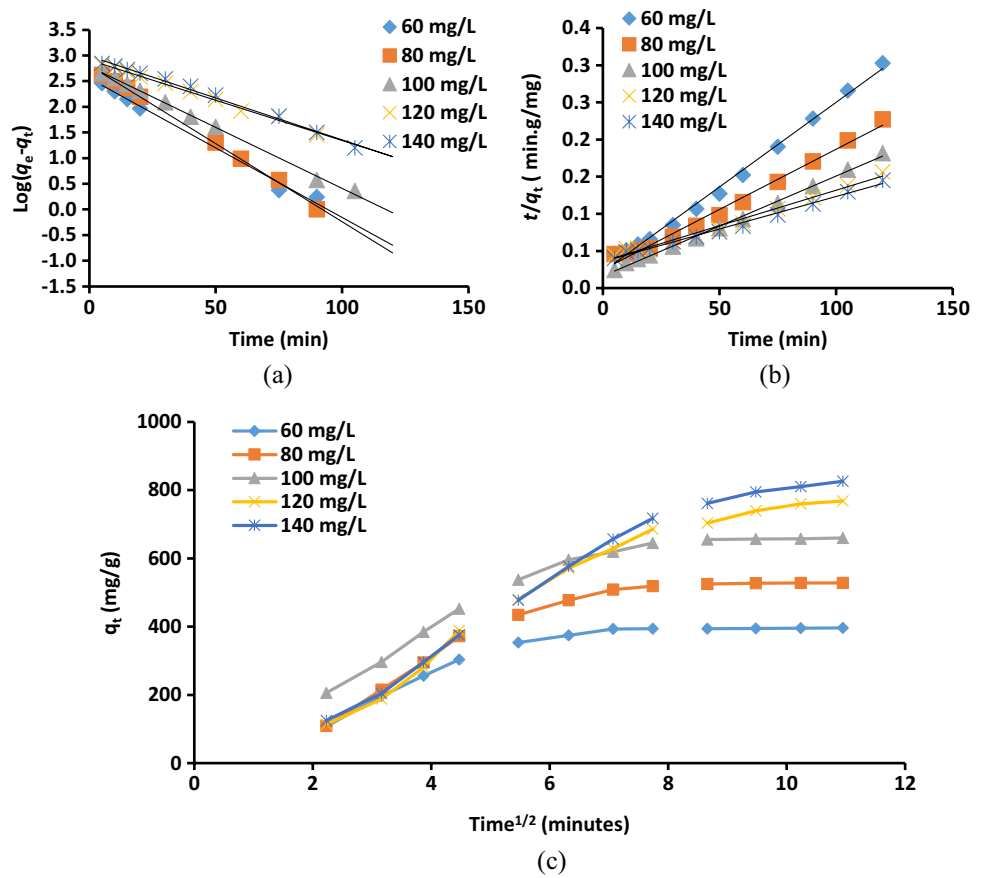
| Composite Conc. (g/L) | MB (mg /L) | Intraparticle diffusion |          |       |                  |          |       |                  |          |       |
|-----------------------|------------|-------------------------|----------|-------|------------------|----------|-------|------------------|----------|-------|
|                       |            | First stage             |          |       | Second stage     |          |       | Third stage      |          |       |
|                       |            | $K_{\text{dif}}$        | $C$      | $R^2$ | $K_{\text{dif}}$ | $C$      | $R^2$ | $K_{\text{dif}}$ | $C$      | $R^2$ |
| 0.005                 | 60         | 153.65                  | − 296.51 | 0.899 | 138.97           | − 175.21 | 0.897 | 64.62            | 420.62   | 0.900 |
|                       | 80         | 168.58                  | − 286.31 | 0.993 | 186.00           | − 438.14 | 0.890 | 94.97            | 266.79   | 0.904 |
|                       | 100        | 64.44                   | 51.16    | 0.835 | 179.54           | − 563.87 | 0.960 | 114.88           | − 70.80  | 0.980 |
|                       | 120        | 136.71                  | − 250.61 | 0.983 | 187.35           | − 440.80 | 0.995 | 107.37           | 192.23   | 0.994 |
|                       | 140        | 119.51                  | − 169.36 | 0.931 | 219.81           | − 655.47 | 1.000 | 145.23           | − 106.14 | 0.999 |
| 0.01                  | 60         | 115.77                  | − 158.41 | 0.989 | 44.41            | 237.08   | 0.998 | 4.33             | 544.62   | 0.984 |
|                       | 80         | 105.46                  | − 83.35  | 0.872 | 66.02            | 172.76   | 0.960 | 29.28            | 465.22   | 0.949 |
|                       | 100        | 104.12                  | − 69.46  | 0.951 | 116.34           | − 92.84  | 0.998 | 42.67            | 503.16   | 0.854 |
|                       | 120        | 130.27                  | − 204.28 | 0.996 | 135.63           | − 180.89 | 0.999 | 57.45            | 453.92   | 0.952 |
|                       | 140        | 66.02                   | − 98.77  | 0.947 | 115.20           | − 355.40 | 0.994 | 83.53            | − 113.53 | 0.989 |
| 0.015                 | 60         | 87.21                   | − 83.65  | 0.998 | 18.83            | 253.46   | 0.916 | 1.00             | 385.04   | 0.963 |
|                       | 80         | 116.81                  | − 153.21 | 0.999 | 37.87            | 232.74   | 0.960 | 1.62             | 511.10   | 0.824 |
|                       | 100        | 110.99                  | − 46.22  | 0.997 | 46.28            | 291.67   | 0.967 | 2.04             | 637.31   | 0.955 |
|                       | 120        | 121.69                  | − 175.31 | 0.968 | 89.82            | − 6.11   | 0.994 | 28.31            | 464.21   | 0.939 |
|                       | 140        | 112.62                  | − 136.43 | 0.988 | 106.22           | − 99.34  | 0.997 | 27.87            | 523.83   | 0.970 |
| 0.02                  | 60         | 59.43                   | − 24.72  | 0.992 | 14.10            | 191.38   | 0.917 | 0.28             | 294.57   | 0.900 |
|                       | 80         | 82.53                   | − 52.13  | 0.992 | 18.83            | 250.95   | 0.943 | 0.81             | 387.95   | 0.909 |
|                       | 100        | 91.89                   | − 37.16  | 0.998 | 24.41            | 308.79   | 0.937 | 0.94             | 484.40   | 0.450 |
|                       | 120        | 106.81                  | − 137.34 | 0.999 | 50.02            | 178.68   | 0.967 | 3.36             | 557.05   | 0.953 |
|                       | 140        | 94.32                   | − 121.77 | 0.998 | 72.59            | 6.76     | 1.000 | 12.99            | 495.71   | 0.954 |
| 0.025                 | 60         | 51.67                   | − 29.46  | 0.972 | 9.53             | 166.46   | 0.907 | 0.21             | 236.22   | 0.984 |
|                       | 80         | 60.36                   | − 3.10   | 0.990 | 14.38            | 209.76   | 0.933 | 0.13             | 316.35   | 0.712 |
|                       | 100        | 85.94                   | − 49.52  | 0.995 | 12.93            | 300.59   | 0.787 | 0.58             | 390.59   | 0.883 |
|                       | 120        | 100.57                  | − 106.85 | 1.000 | 24.69            | 276.52   | 0.981 | 1.50             | 460.20   | 0.838 |
|                       | 140        | 92.04                   | − 102.23 | 0.999 | 48.18            | 116.05   | 0.993 | 5.27             | 455.64   | 0.912 |
| %APE                  |            | 0.38                    |          |       |                  |          |       |                  |          |       |

constant of PFO adsorption increases with increased MB dye concentration and St-g-P(AA)/P-AC7.5% doses. (C)  $R^2$  values are greater than 0.990 for PFO kinetics model. So, the PFO kinetic model is more adequate to describe the adsorption process of MB dye onto St-g-P(AA)/P-AC7.5%. Douven et al. (2015) and Tan and Hameed (2017) [70, 71] defined the range of PFO models validity only under either of these two sets of conditions: (i) control of the reaction and Henry regime adsorption or (ii) control of the reaction and high dose of adsorbent.

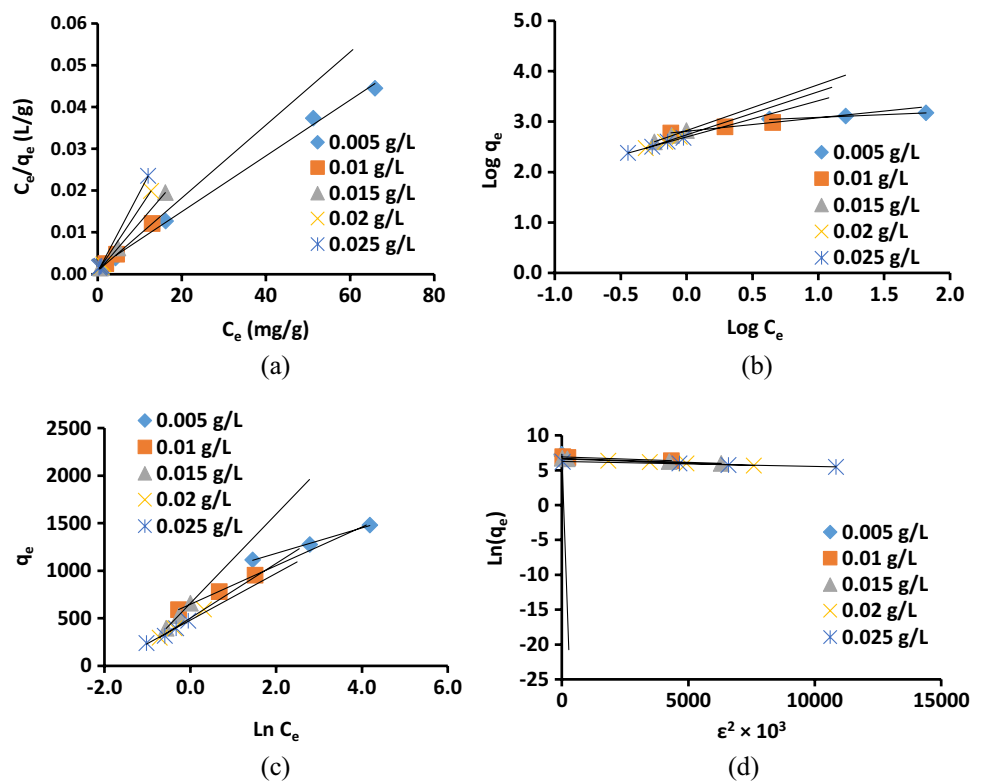
Intraparticle diffusion is the process of components transfer from the solution bulk to the solid phase. Figure 15c reveals that the IPD adsorption plots are not linear throughout the entire time range selected and could be divided into three linear regions. The three regions were completed within 20, 60, and 120 min. According to the research that has been conducted, the first region would be characterized by the external surface adsorption, in which the MB dye molecules diffuse through the bulk solution to the external surface of

the adsorbents, or the boundary layer diffusion of MB dye molecules [72], with the second region being dominated by the IPD. The decrease in the concentration of MB dye in the aqueous phase, as well as the reduction in the number of active sites that are available for adsorption, causes the IPD to begin to slow down in the final region [73]. This is due to the fact that the last region also contains fewer active sites. There was not a single plot of IPD that crossed the origin, which indicates that intraparticle diffusion was not only a rate-controlling step but also participated in the process C1,2,3,0 (Fig. 14c). Table 5 displays the values of  $k_{\text{dif}}$  and  $C$ , as well as the correlation coefficients, for each of the three locations in which the linear fitting of the kinetic data was performed. Where for the second region, the values of  $k_{\text{dif}}$  are directly proportional to MB concentration and inversely proportional with St-g-P(AA)/P-AC7.5% doses. Also, the values of  $C$  are considered directly proportional with St-g-P(AA)/P-AC7.5% doses and inversely proportional with MB concentration. A negative  $C$  value could be clarified by the dual impacts of both

**Fig. 14** Kinetic models: **a** PFO, **b** PSO, and **c** IPD of MB dye (60–140 mg/L) adsorbed onto St-g-P(AA)/P-AC7.5% (0.015 g/L) at pH 8 and temperature ( $25 \pm 2$  °C)



**Fig. 15** Isotherm models Linear Langmuir (a), Freundlich (b), Temkin isotherms (c), and D-R isotherm (d) of MB dye (60–140 mg/L) adsorbed onto St-g-P(AA)/P-AC7.5% (0.005 – 0.025 g/L)



film diffusion and surface reaction control [71, 74]. By comparing the statistic average percentage errors APE% values for the data presented in Tables 4 and 5, the PFO order was lower than PSO and IPD model, thereby indicating that PFD kinetic model verdicts the adsorption rate of MB dye onto St-g-P(AA)/P-AC7.5% under the studied conditions.

### 3.2.7 Adsorption isotherm, distribution coefficient, and average percentage errors analysis (APE %)

Adsorption isotherms were applied to explain the adsorption result by Langmuir [75], Freundlich [76], Temkin [77], and Dubinin–Radushkevich (D–R) isotherms [78–80] for MB dye concentration of 60–140 mg/L onto adsorbed St-g-P(AA)/P-AC7.5% (0.005–0.025 g/L) (Fig. 15). Table 6 illustrates the details of each linearized isotherm models and the associated parameters.

Based on the correlation coefficient ( $R^2$ ) values and the low error value (APE%), it can be assumed that the best isotherms model fitness arrangement for adsorptive removal of MB dye by St-g-P(AA)/P-AC7.5% as

Freundlich isotherm < Dubinin–Radushkevich > Langmuir < Temkin. According to the Langmuir model, the adsorption of MB dye takes place on a homogenous surface by monolayer adsorption, and no interaction takes place between the different adsorbed species [81]. The maximum monolayer capacity ( $q_m$ ) was 1428.57 mg/g at a dose of 0.005 g/L. On calculating the separation factor,  $R_L$  using followed equation [ $R_L = 1/(1 + K_a C_o)$ ]. Commonly, the value of  $R_L > 1$  adsorption is unfavorable,  $R_L = 1$  adsorption is linear,  $0 < R_L < 1$  adsorption is favorable, and  $R_L = 0$  adsorption is irreversible [14]. It was further confirmed that the isotherm is favorable, as  $R_L$  value equals 0.0367.

Meanwhile, Freundlich isotherm [76] suggested the adsorption process of MB dye based on a sorption heterogeneous surface. The value of  $n$  provides an indication of the degree to which there is a non-linear relationship between the concentration of the solution and adsorption as follows: If the value of  $n$  is equal to one, then the adsorption process is linear; if  $n$  is less than one, then the adsorption process is chemical; and if  $n$  is greater than one, then the adsorption process is a beneficial physical process [50]. The  $n$  value was

**Table 6** Langmuir, Temkin, Freundlich, and Dubinin–Radushkevich isotherm parameters, correlation coefficients ( $R^2$ ), and average percentage errors analysis (APE %) for MB dye adsorption onto St-g-P(AA)/P-AC7.5% composite at pH 8

| Model                | Linear equation                                                  | Eq. No. | Description                                                                                                                                                                                                                                                                                 | Isotherm parameters          | Value               | $R^2$  | APE%   |
|----------------------|------------------------------------------------------------------|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|---------------------|--------|--------|
| Langmuir             | $\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} \times C_e$ | 8       | $q_e$ (mg/g): amount of adsorbate adsorbed per unit weight of adsorbent<br>$q_m$ (mg/g): maximum adsorption capacity<br>$K_a$ (L/mg): adsorption equilibrium constant that is related to the apparent energy of sorption<br>$C_e$ (mg/L): equilibrium adsorbate aqueous phase concentration | $q_m$ (mg/g)<br>$K_a$ (L/mg) | 1428.57<br>0.44     | 0.9966 | 0.1397 |
| Freundlich           | $\log q_e = \log K_f + \frac{1}{n} \log C_e$                     | 9       | $K_f$ ((mg/g): Freundlich constant<br>$n$ : heterogeneity factor                                                                                                                                                                                                                            | $KF$ (mg/g)<br>$1/n$         | 957.41<br>0.10      | 0.9999 | 0.0001 |
| Temkin               | $q_e = B \ln A + B \ln C_e$                                      | 10      | $B = (RT/b)$ : Temkin constant;<br>$b$ : heat of adsorption(J/mole)<br>$R$ : universal gas constant (8.314 J/K.mol)<br>$T$ : absolute temperature (K)<br>$A$ : related to the heat of sorption binding constant (L/g)                                                                       | $A$ (L/g)<br>$b$ (J/mole)    | 898.88<br>18.44     | 0.997  | 0.8235 |
| Dubinin–Radushkevich | $\ln q_e = \ln q_m - K \epsilon^2$                               | 11      | $q_m$ : monolayer adsorption capacity (mg/g)<br>$K$ : constant related to the adsorption energy [ $\text{mol}^2/\text{kJ}^2$ ]<br>$E = 1/\sqrt{(2K)}$ : mean free energy of sorption (kJ/mol)<br>$\epsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$ : Polanyi potential                     | $q_m$ (mg/g)<br>$E$ (kJ/mol) | 1724.1682<br>0.0694 | 0.9923 | 0.1378 |

greater than unity, signifying that the adsorption process is favorable with higher values of  $n$  indicating the adsorption process is physical.

The Temkin isotherm model [77] makes the assumption that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. This model also assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorb. This model also operates under the premise that the adsorption process is typified by a distribution of binding energies that is consistent throughout. The Temkin sorption potentials, denoted by letter  $A$ , are 898.88 L/mg, while the heat of adsorption, denoted by letter  $b$ , is 18.44 J. The low  $b$  values that were reported in this experiment imply that the sorbent and the sorbate do not interact strongly with one another.

On the other hand, the D–R isotherm was also utilized to evaluate the porosity of apparent free energy and the adsorption characteristics [78–80]. It is possible to apply it to the explanation of adsorption on surfaces that are either homogenous or heterogenous [82]. The maximum capacity  $q_m$  obtained for the adsorption of MB dye is 1724.17 mg/g which is higher than the  $q_m$  obtained from the Langmuir isotherm model. The values of  $E$  calculated are 0.0694–2.6726 kJ/mol. Ion-exchange processes tend to have bonding energies that fall within the range of 8–16 kJ/mol on average, denoting physical processes play a significant role in the adsorption process of MB dye by the St-g-P(AA)/P-AC7.5% composite. Freundlich, Temkin, and D-R isotherm models basically stand true for the adsorption phenomenon observed for St-g-P(AA)/P-AC7.5%.

### 3.2.8 Thermodynamic study

MB dye removal % onto St-g-P(AA)/P-AC7.5% as a reaction temperature function was valued in the temperature ranges 25–40 °C to determine the thermodynamic parameters such as Gibbs free energy ( $\Delta G$ , J/mol), enthalpy change ( $\Delta H$ , J/mol) and entropy change ( $\Delta S$ , J/K mol) using Van't Hoff equations (Eqs. (12, 13, 14)) [83]:

$$\Delta G = -RT \ln K_d \quad (12)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

where  $K_d$  is the distribution coefficient ( $K_d = q_e/C_e$ , L/g), and  $T$  (K) and  $R$  (8.314 J/mol K) are the absolute temperature and the universal gas constant, respectively. The

**Table 7** Thermodynamic parameters of the MB dye adsorption onto St-g-P(AA)/P-AC7.5%

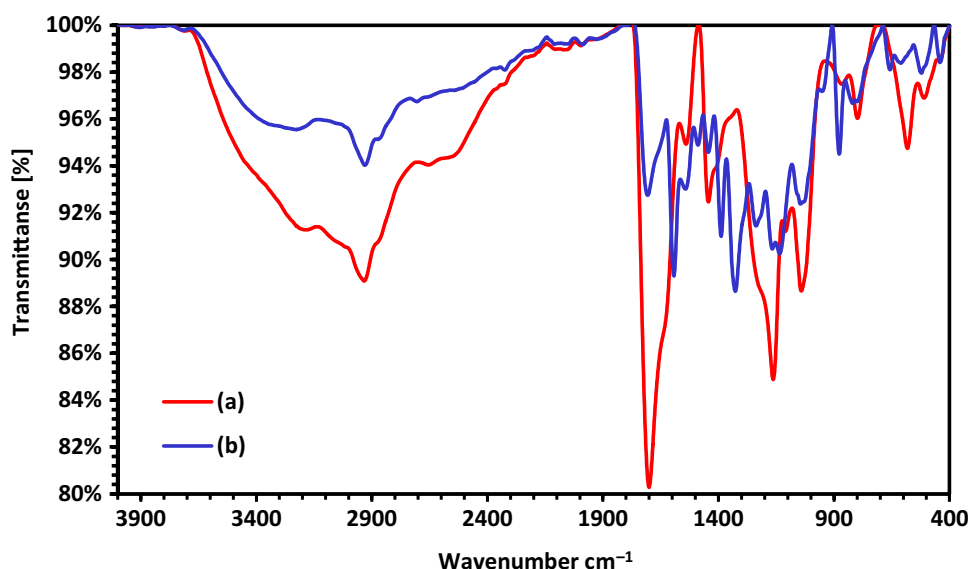
| $T$ (K) | $\Delta G$ (KJ/mol) | $\Delta H$ (KJ/mol) | $\Delta S$ (J/K mol) |
|---------|---------------------|---------------------|----------------------|
| 298     | −16.0731            | −19.6909            | −12.1401             |
| 303     | −16.0124            |                     |                      |
| 308     | −15.9517            |                     |                      |
| 313     | −15.891             |                     |                      |

values of  $\Delta H$  and  $\Delta S$  were determined based on the plot of  $\ln K_d$  vs  $1/T$ , and a summary of their findings can be found in Table 7. According to Table 7, all of the  $\Delta G^\circ$  values were negative, and their absolute values decreased as the temperature increased; as a result, the MB dye adsorption process on St-g-P(AA)/P-AC7.5% was an unintentional one. The presence of an exothermic process was substantiated by the fact that the MB dye adsorption on St-g-P(AA)/P-AC7.5% had a negative 19.6909 kJ/mol value for the  $\Delta H^\circ$  parameter. The value of the change in enthalpy, denoted by  $\Delta H^\circ$ , was less than 84 kJ/mol, which indicates that physisorption was the process that took place [84, 85]. During the process of adsorption, the value of entropy, denoted by the symbol  $\Delta S^\circ$ , was found to be negative (−12.1401 J/K.mol), which reflects a decrease in the amount of randomness at the interface between the solid and the solution.

### 3.2.9 Mechanism of adsorption.

Figure 16 displays the FTIR spectra of the adsorbents, St-g-P(AA)/P-AC7.5%, which were acquired before and after the adsorption trials. This method is appropriate for gaining an understanding of the mechanism underlying MB adsorption [12]. The FTIR spectra of MB-St-g-P(AA)/P-AC7.5% (Fig. 16) showed that the bands of St-g-P(AA)/P-AC7.5% at 3187, 1700, 1540, 1163, 1041, and 510  $\text{cm}^{-1}$  are blue and moved into 3228, 1707, 1543, 1167, 1045, and 522  $\text{cm}^{-1}$ , respectively, accompanied by intensity decreasing; as a result of MB dye adsorption, new peaks at 2109, 1989, 1593, 1489, 1388, 1327, 1238, 1135, and 441  $\text{cm}^{-1}$  appeared. Such behavior originated due to the formation of (1) bonds between the sulfur atoms in MB dye heterocycles and the OH groups found in the St-g-P(AA)/P-AC7.5%; (2) hydrogen bonds between the negatively charged groups in the St-g-P(AA)/P-AC7.5% and unsaturated MB dye dimethylamino groups. To finish, the band allocated to the vibration modes attributed to methylene groups (at 2934  $\text{cm}^{-1}$ ) moved to 2930  $\text{cm}^{-1}$ , indicating that hydrophobic contacts were engaged in addition

**Fig. 16** FTIR analysis of St-g-P(AA)/P-AC7.5% (a) and MB-St-g-P(AA)/P-AC7.5% (b)



to electrostatic interactions between MB and St-g-P(AA)/P-AC7.5%. As a consequence, the phenomenon known as MB adsorption in the St-g-P(AA)/P-AC7.5% is assumed to be caused by a combination of electrostatic interactions, hydrogen bonds, and hydrophobic interactions.

### 3.2.10 Regeneration studies

To discover the economic feasibility and reusability of St-g-P(AA)/P-AC7.5% adsorbents, desorption studies of MB from loaded St-g-P(AA)/P-AC7.5% adsorbents were performed using 0.1 N HCl as an eluted medium. So, ~60% of the MB previously adsorbed onto was desorbed after three cycles. As shown in Fig. 17a, the maximum desorption (ca. 67.23%) was verified for the first use of the adsorbents.

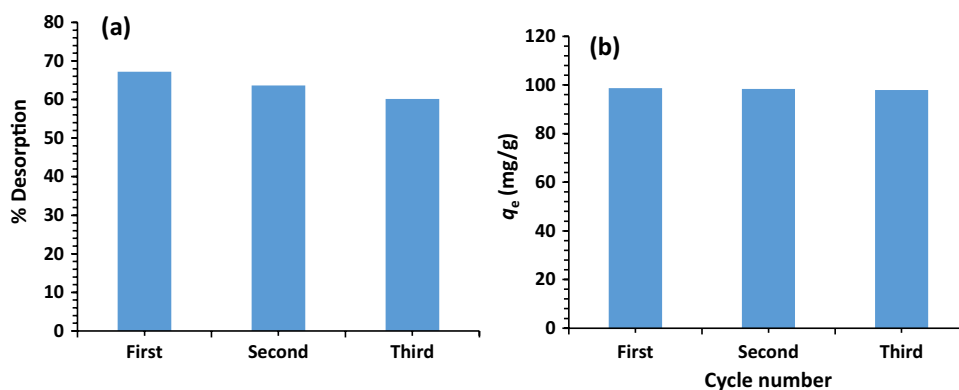
Three consecutive adsorption/desorption cycles with the regenerated St-g-P(AA)/P-AC7.5% composite were

performed. The amount of adsorption presented remained steady throughout the cycles, with only a minor drop (1%) after three cycles. (Fig. 17b), indicating that it might be utilized as a long-term MB removal method. This finding is in line with previous studies [62] where it experienced only a slight drop after regeneration cycles.

#### 3.2.11 Analysis of the outcomes of the current investigation in comparison to those of earlier studies

To justify the viability of the prepared St-g-P(AA)/P-AC7.5% as effective adsorbents for MB dye removal at different conditions, the adsorption capacity was compared with different adsorbents (Table 8). The prepared composite showed highly adsorption capacity equal to 1482 mg/g than other adsorbents, followed by Freundlich isotherm, pseudo-first-order kinetic model, and adsorption was exothermic.

**Fig. 17** a MB dye desorption % from St-g-P(AA)/P-AC7.5%; b Regeneration of St-g-P(AA)/P-AC7.5%



**Table 8** Different adsorbents' capabilities for MB dye adsorption were measured and compared across various experimental circumstances

| Adsorbent                                                     | pH  | T (°C) | Contact time (h) | $q_m$ (mg/g) | Isotherm   | Kinetics                                              | $\Delta H$  | Ref        |
|---------------------------------------------------------------|-----|--------|------------------|--------------|------------|-------------------------------------------------------|-------------|------------|
| Chitosan-g-PAAc/vermiculite10%                                | 7   | 30     | 4                | 1685.56      | Langmuir   | Pseudo-second order                                   | -           | [86]       |
| Fe <sub>3</sub> O <sub>4</sub> -PAAc-co Poly(sodium acrylate) | 7   | 25     | 24               | 246.1        | Langmuir   | Pseudo-second order                                   | Endothermic | [87]       |
| NaAlg-g-p(AA-co-St)/organo-I/S                                | 4   | 30     | 3                | 1843.46      | Langmuir   | Pseudo-second order                                   | -           | [88]       |
| Starch-g-PAAc/CNWs5%                                          | 5   | 33     | 1                | 1918.8       | Langmuir   | Pseudo-second order                                   | -           | [12]       |
| Starch/rice husk ash                                          | 5   | 33     | 1                | 1906.3       | Langmuir   | Pseudo-second-order model and intraparticle diffusion | Endothermic | [62]       |
| Starch/humic acid                                             | 5.5 | 25     | 24               | 110          | Langmuir   | Pseudo-second order                                   | Exothermic  | [89]       |
| Starch/monolithic porous rectorite                            | 5   | 30     | 2                | 277          | Langmuir   | Pseudo-second order                                   | -           | [90]       |
| chitosan-g-poly(acrylic acid)/montmorillonite (CTS-g-PAA/MMT) | 6.5 | 30     | 2                | 1859         | Langmuir   | Pseudo-second order                                   | -           | [61]       |
| St-g-P(AA)/P-AC7.5%                                           | 8   | 25     | 2                | 1482         | Freundlich | Pseudo-first order                                    | Exothermic  | This study |

## 4 Conclusion

Starch-g-poly(acrylic acid)/*Pterocladia capillacea*–activated carbon (St-g-PAA/P-AC) composites were prepared and characterized by FTIR, BET, XRD, TGA, EDX, and SEM. In addition, we describe the removal of MB dye from artificial wastewater using St-g-PAA/P-AC composites. The maximum MB dye adsorption capacity achieved at composites dose 0.02 mg/L, MB dye (100 mg/L), pH 8, 120 min obtained with the composite at 7.5 wt.% of P-AC, 496.29 mg/g. Batch experimental for MB dye adsorption operated at MB dye beginning concentration (60–140 mg/L), temperature (25–40 °C), pH (3–10) and contact time (0–120 min). The adsorption isotherms data were arranged for MB dye adsorptive removal by St-g-P(AA)/P-AC7.5% as Freundlich isotherm <Dubinin-Radushkevich> Langmuir> Temkin based on the coefficient of determination values ( $R^2$ ) and the low value of APE%. The maximum monolayer capacity ( $q_m$ ) was 1428.57 mg/g at a dose of 0.005 g/L from Langmuir isotherm. The adsorption kinetics data were correlated with pseudo-first-order with  $R^2$  values greater than 0.990 model where  $q_{e(\text{exp})}$  values are in agreement with the predicted  $q_{e(\text{th})}$  values more than the PSO. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) showed that the MB dye adsorption occurred physisorption, exothermic, and spontaneously in nature. Based on these results, the prepared St-g-PAA/P-AC composites can effectively be considered potential adsorbents to MB dye removal from industrial effluent and have good recycling capability.

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**Author contribution** The practical portion was led by Dr. Amany G. M. Shoaib, who also wrote the first draft. Professor Dr. Ahmed El Nemr oversaw the actual work, edited the article, and then submitted it. The work was overseen by Professor Mamdouh S. Masoud, Professor Mohamed S. Ramadan, Amany El Sikaily, and Dr. Safaa Ragab.

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**Data availability** The datasets used in this investigation are accessible for review upon request from the corresponding author of the paper.

## Declarations

**Consent to participate.** Not applicable.

**Competing interests** The authors declare no competing interests.

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