

## Removal of Methylene Blue Dye from an Aqueous Solution by an Adsorption Technique Using Sulfonated Polystyrene as Three Low-cost Adsorbents

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In this study, three alternative techniques were used to recycle expanded polystyrene waste (WPS). Sulfonated polystyrene (PSS)-based materials (PSS-01, PSS-02, and PSS-03) were produced and employed as efficient and reasonably priced adsorbents. The findings demonstrated that the clearance efficiency of expanded polystyrene increased from 13.6% for pH = 3 to 21% at pH = 9. The removal capacity for sulfonated polystyrenes, which varied from 60% to 85% and 98% for PSS-01, PSS-02, and PSS-03, respectively, did not alter over the pH range. Furthermore, the removal effectiveness of the sulfonated polystyrenes was unaffected by increasing the starting dye concentration. However, for a methylene blue (MB) concentration of 200 mg l<sup>-1</sup>, the removal capacity employing PSS-02 significantly decreased and fell to less than 62%. The elimination rate of the dye by PSS-03 at the ideal contact duration of 15 min was more incredible than 98.2% at the ideal amount of 20 mg. Undoubtedly, the results showed that MB adsorption corresponded to the Langmuir isotherm for WPS and PSS-02 and the Freundlich isotherm for PSS-01 and PSS-03, and adsorption kinetic models for the three copolymers produced pseudo-second order. PSS-03's adsorption capability increased because of its hydrophilic sites and higher adsorbent surface area.

**Keywords:** Expanded polystyrene, Sulfonated polystyrene, Absorbents, Freundlich, Hydrophilic sites

### INTRODUCTION

One of the most significant environmental issues today is water contamination, which has been growing exponentially [1] since the rise of industrialization. Environmental issues are raised since numerous industries release varied amounts of dyeing wastewater directly into the environment (around 0.7 million metric tons annually [2-4]). The primary consumers of dyes are businesses that make textiles for clothing and food [5]. It is challenging to biologically cure synthetic dyes [6]. They are highly soluble in water, poisonous, carcinogenic, and weakly biodegradable [7]. Human health is impacted by dye contamination in wetness, strictly at insufficient quantities (1 mg l<sup>-1</sup>) [8,9]. One of the main obstacles to protecting the environment from

contamination is industrial wastewater treatment since it permits secure recycling within the ecosystem [7].

Various methods, such as coagulation and flocculation [10,11], oxidative decomposition [12], flotation [13], photocatalysis [14], electrochemical treatment [15], membrane [16,17], and adsorption treatment [18-23], are used to remove contaminants from wastewater. Resembling all these techniques, the latter one is the most useful because this technique is straightforward and effective due to its comfort, usefulness, low price, better performance [24], high effectiveness [25], low sludge generation, and speed [26].

Efforts include discovering more effective, economical, and ecologically benign adsorbents to remove impurities. Expanded polystyrene waste recycling is among the most acceptable choices because of its low price and high adsorption effectiveness. The dye adsorption process is carried out through interactions between dye molecules and

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the adsorbent and primarily includes hydrogen bonding, electrostatic bonding, and  $\pi$ - $\pi$  interactions [27]. Because of its excellent availability and chemical composition, sulfonated polystyrene is cheap and viable for cationic dye removal from aqueous solutions.

Many businesses, including those that produce silk and wood, use methylene blue (MB) dye extensively [28]. It is an extremely heat- and light-sensitive cationic dye. Environmental releases may hurt the ecosystem and human health [29,30]. As a result, MB needs to be taken out of the water. Numerous sorbents have so far been employed to clean MB wastewater [7,31]. In order to find effective and affordable sorbents, we researched several polystyrene sulfonate (PSS) derivatives. PSS is cheap and reacts with several chemicals thanks to its sulfur trioxide group ( $\text{SO}_3$ ).

The present work aims to study the recycling of waste-expanded polystyrene by three different methods to obtain modified copolymers. The obtained copolymers were used as adsorbents to remove methylene blue (a cationic dye) from wastewater. To improve the adsorption conditions, the effects of numerous experimental factors were investigated.

## EXPERIMENTAL

### Materials

Expanded polystyrene waste (WPS), sulfuric acid ( $\text{H}_2\text{SO}_4$  97% biochem), acetic anhydride ( $(\text{CH}_3\text{CO})_2\text{O}$ ), silver sulfate ( $\text{Ag}_2\text{SO}_4$  biochem), dichloromethane ( $\text{CH}_2\text{Cl}_2$  biochem), and Methylene Blue (MB) ( $\lambda_{\text{max}} = 665\text{nm}$ ).

### Methods

#### Preparation of the copolymer PSS-01.

Dichloromethane was used to dissolve WPS (5 g). After 15 min of stirring, 3 ml of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was added as a sulfonating agent [32]. After 4 h, the response was complete. Following that, distilled water was used to wash the copolymer that had been obtained and noted as PSS-01.

**Preparation of the copolymer PSS-02.** For PSS-02, 20 ml of sulfuric acid was used to dissolve 5 g of expanded polystyrene, and 0.02 g of  $\text{Ag}_2\text{SO}_4$  was added. At  $t = 1$  h, the reaction was heated to  $90^\circ\text{C}$  [33]. Thereafter, it was precipitated in weak sulfuric acid, cleaned with distilled water, and baked to dry.

#### Preparation of the copolymer PSS-03.

Dichloromethane was used to dissolve the polystyrene (5 g) in a 250 ml flask while it was being magnetically stirred. It was carefully added to the acetyl sulfate solution [34]. The system was then heated to  $T = 40^\circ\text{C}$  and closed after 4 hours, as noted in PSS-03.

### Characterization of Polystyrene Sulfonate

A Cary 600 Series FTIR spectrometer from Agilent Technologies was used to record infrared spectra. The samples of PS, PSS, and PSS-MB After adsorption, were analyzed in powder form to qualitatively describe the groupings.

According to the procedure outlined by Benabadji *et al.* [23], the zero-charge point ( $\text{pH}_{\text{PZC}}$ ) was determined using the batch equilibrium method.

Scanning electron microscopy (SEM) (Hitachi TM-1000) was used to image PSS-03.

### Adsorption Kinetics

In the adsorption isotherm experiments, the obtained product was tested for efficiencies in the adsorption of the dye (Methylene Blue) for pH between 2 and 10 and at a constant stirring speed of 400 rpm ( $V_{\text{dye}} = 20$  ml,  $m_{\text{PSS}} = 20$  mg, and  $C_{\text{dye}} = 20$  to  $200$   $\text{mg l}^{-1}$ ) in the batch experiment. The influence of the contact time from 2 min to 2 h on the adsorption capacity of MB was studied. Finally, a UV-Vis spectrophotometer (OPTIZEN 1412 UV/VIS) was used to evaluate the resulting supernatant.

Using Eq. (1), it was possible to calculate the produced copolymers' adsorption capacity and efficiency based on the beginning and conclusive concentrations of MB in the solution.

$$q_e = \frac{(C_1 - C_2) V}{m} \quad (1)$$

Where

$C_1$  and  $C_2$ : the initial and final concentrations of MB solution.

$V$ : The volume of MB (l)

$m$ : The mass of PSS used (g)

### Polystyrene Sulfonated Regeneration

Following the adsorption tests, the utilized MB-loaded

materials were submerged in a 0.1 M HCl solution with constant stirring for 24 h to regenerate the adsorbent. As a desorption agent, the HCl solution was employed. Sulfonated polystyrene was then filtered out and subjected to distilled water washings until it attained a pH of zero. After five cycles, the adsorbent was regenerated.

## RESULTS AND DISCUSSION

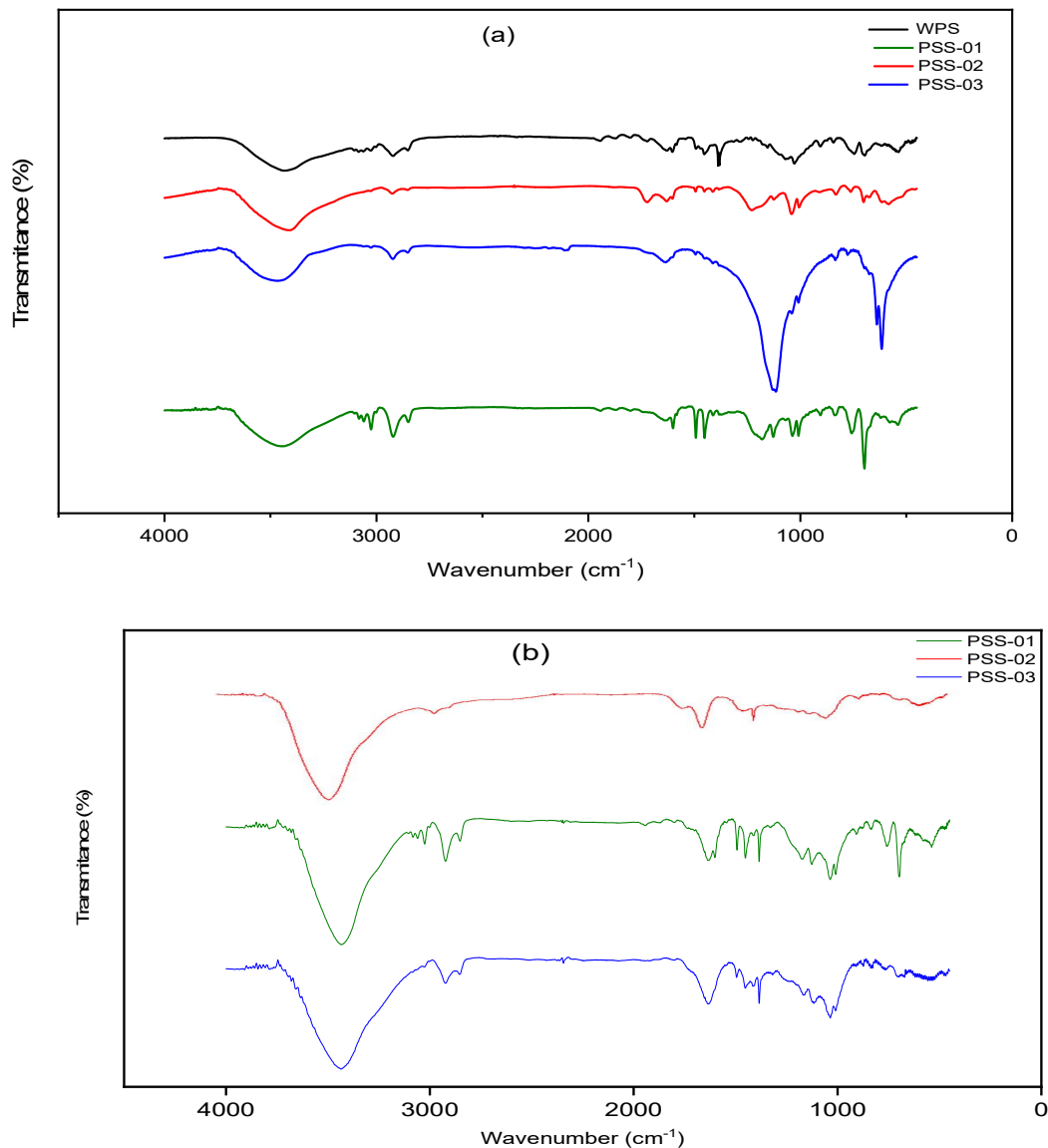
### Change Rate

The three copolymers used were synthesized,

characterized, and their DS (degree of modification) was calculated in our previous work [35]. The result obtained is 7% for PSS-01, 20% for PSS-02, and 13% for PSS-03.

### FTIR Characterization

All three techniques were sulfonated satisfactorily. Figure 1a shows the S-O bands not present in the polystyrene waste's spectra. Each sample is thought to include bonded sulfur trioxide groups based on observing an S-O band at  $1050\text{ cm}^{-1}$  and  $1180\text{ cm}^{-1}$  [34]. It is possible that some chemical bonds were broken during the production of the



**Fig. 1.** Infrared spectra (FTIR) for (a) PS, PSSs, and (b) PSS-MB after adsorption.

sulfonated polystyrene because a few peaks in the PSS spectra have slightly differing intensities. The alterations in the PSS's functional groups brought on by the MB dye adsorption were further confirmed by re-analyzing FTIR, as shown in Fig. 1b. The relationship between the out-of-plane bending vibration of N-H and the stretching vibration of  $-\text{CH}_2$ , which are indicators that MB dye was adsorbed on the PSS surface, and the shift of a minor peak at  $1100\text{ cm}^{-1}$  and the emergence of bands at  $800\text{ cm}^{-1}$  after MB adsorption [36].

### Determination of the $\text{pH}_{\text{PZC}}$ of the Copolymers Used

To calculate  $\text{pH}_{\text{PZC}}$ , the  $f(\text{pHi})$  curve's point of intersection with the  $\text{pH}_f - \text{pH}_i = 0$  axes is projected onto the  $x$ -axis. Figure 2 demonstrates that PSS-03 has a  $\text{pH}_{\text{PZC}}$  of 4.10 as opposed to PSS-01 and PSS-02, which have  $\text{pH}_{\text{PZC}}$  values of 5.58 and 3.84, respectively. The surfaces of the materials will therefore be positively charged with pH solutions below  $\text{pH}_{\text{PZC}}$ , which may result in anionic attraction. On the other side, the material surfaces will be negatively charged if the pH solution is higher than  $\text{pH}_{\text{PZC}}$ .

### Adsorption Studies

**Effect of contact time.** As seen in Fig. 3, batch studies were carried out at pH 6.2 using 20 ml of a 20 ppm MB solution and 20 mg of various adsorbents at intervals of 5 to 200 min. Compared with polystyrene waste, which does not affect adsorption, PSS-03, PSS-01, and PSS-02 gave positive results, with efficiencies of up to 48.9, 32.46, and 12% dye removal, respectively, at around 10 min. This is due to the free adsorption sites on the surface of the adsorbent. After 20 min, which is the equilibrium time for PSS-03, dye removal was recorded at 98% for PSS-03, 56% for PSS-01, and 21% for PSS-03, with no adsorption for polystyrene waste, which was around 20%.

### Effect of pH

Studies have been done on how pH affects the elimination of methylene blue (Fig. 4a). The degree of ionization of the adsorbate in the solution, the surface charge of the adsorbent, and the dissociation of different functional groups on the adsorbent's active sites are all significantly influenced by the pH of the solution [37]. The adsorption efficiency increases with increasing pH from 2 to 10. The MB adsorption mechanism may result from hydrogen bonding and

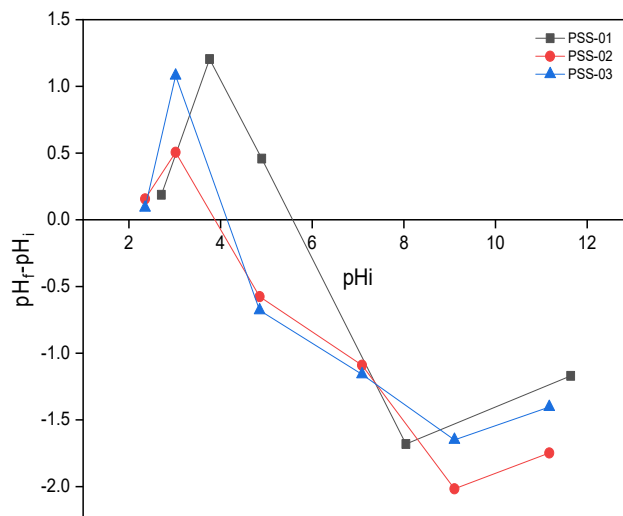


Fig. 2. Represents the  $\text{pH}_{\text{PZC}}$  value of the copolymers used.

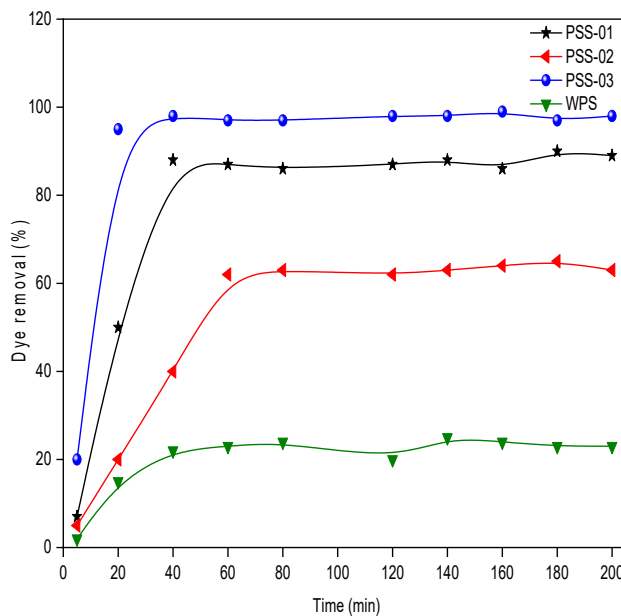
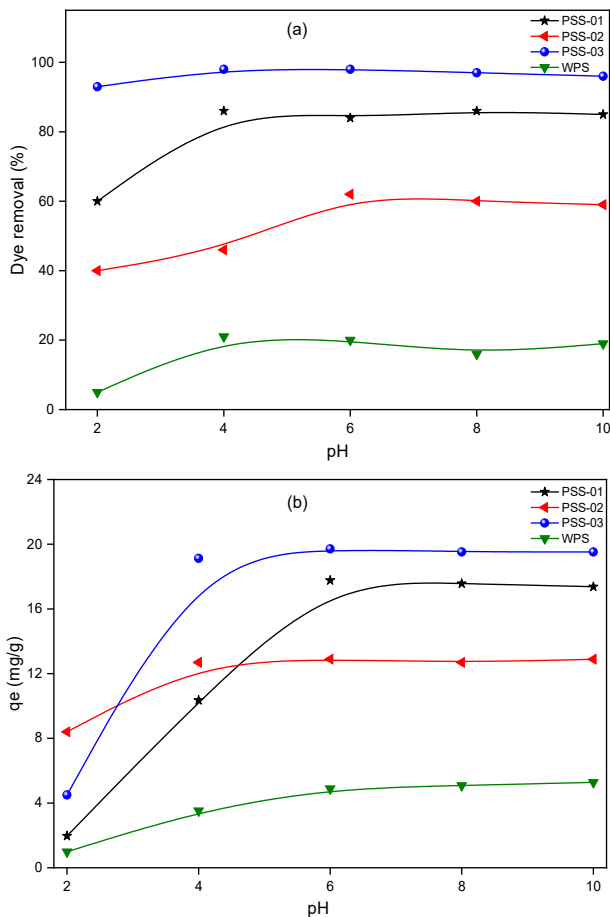


Fig. 3. Time effect on the adsorption of MB on different materials used.

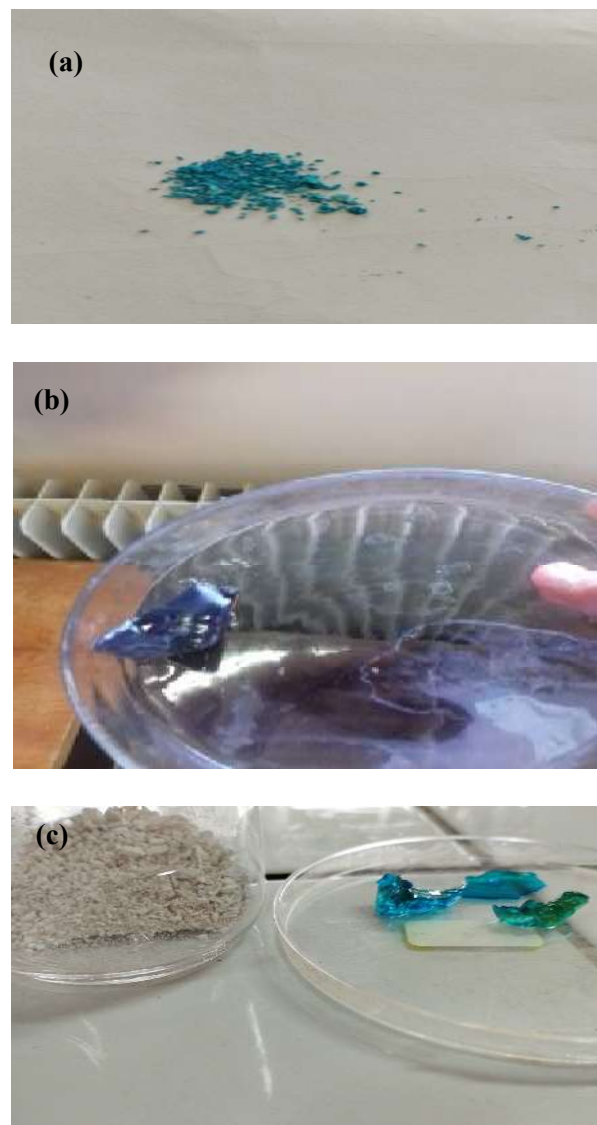
electrostatic interactions between the negatively charged groups on the sulfonated polystyrenes and the cationic MB. The proposed adsorbent, PSS, includes sulfur trioxide groups. The protonation potential of these groups decreases progressively with increasing pH. Consequently, the negative

charges on PSS increase with increasing pH. Alternatively, due to electrostatic repulsion between  $H^+$  from PSS and positively charged sulfur, the lowest percentage of MB removal occurs at  $pH < pH_{PZC}$ . MB removal increases with pH up to pH 6 and remains constant over the rest of the pH range studied. The electrostatic interaction between  $OH^-$  and the positively charged sulfur of MB results in a high percentage of removal under basic conditions ( $pH > pH_{PZC}$ ). For PSS-01, the clearance rate rose from 60% at  $pH = 3$  to 81% at  $pH = 9$ , and for the amount of adsorbed dye  $q_e$  ( $mg\ g^{-1}$ ) increased from 6.001 to 17.41  $mg\ g^{-1}$  (Fig. 4b), and for PSS-02, from 40% at  $pH = 3$  to 59% at  $pH = 9$ . However, PSS-03 could adsorb the dye with a 96 and 98% capacity at pH 3 to 9, and the amount of dye adsorbed  $q_e$  ( $mg\ g^{-1}$ ) reached a maximum value of 19.4 ( $mg\ g^{-1}$ ).

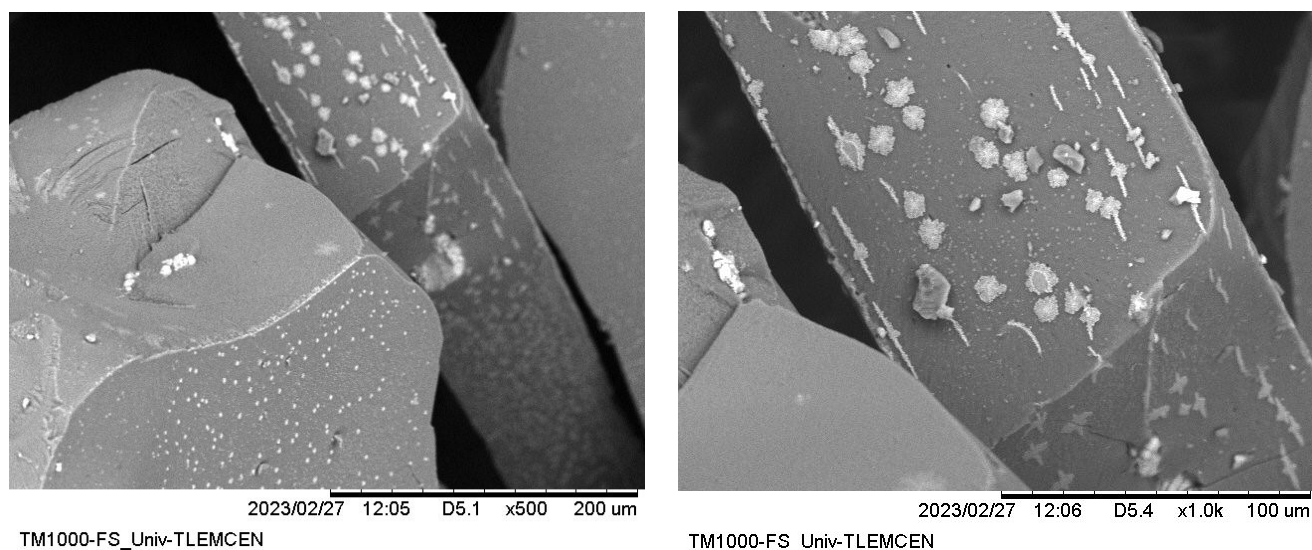


**Fig. 4.** pH effect on the adsorption of MB onto PSS-01, PSS-02, and PSS-03 copolymers. (a) removal dye and (b)  $q_e$ .

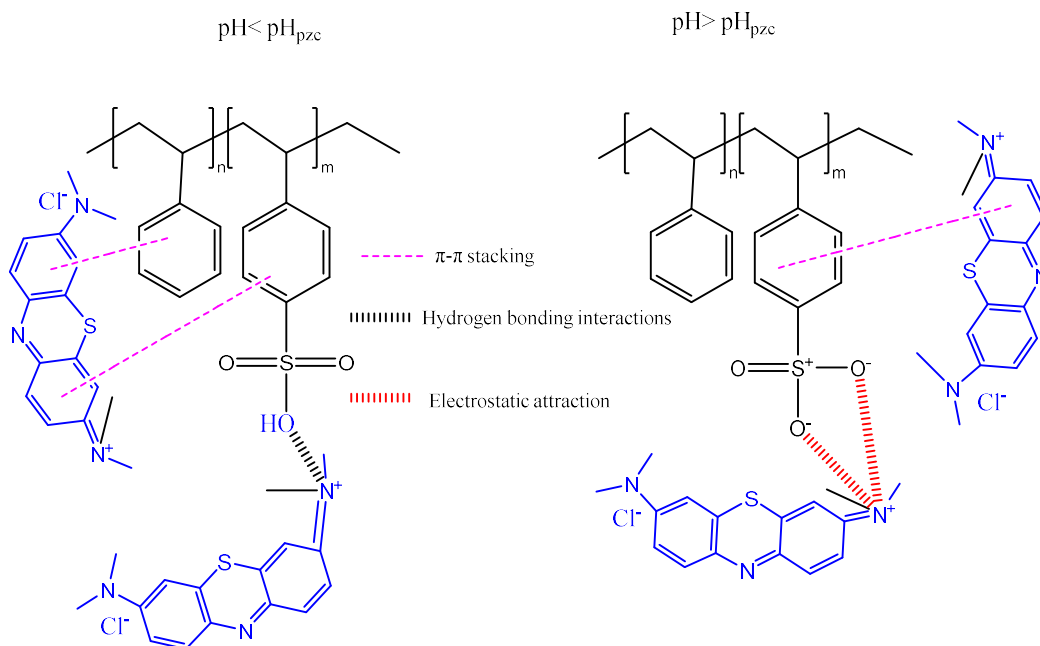
The degree of modification, the surface of each polymer (which are shown in Figs. 5a and 5b of PSS-01 and PSS-02, respectively, and Fig. 5c of PSS-03 after adsorption), the presence of silver material in PSS-02, which prevents dye adsorption, and the zero-charge pH ( $pH_{PZC}$ ), are the causes of the differences between the three polymers. In order to observe the morphologies of PSS-03, scanning electron microscopy images were obtained (Fig. 6). Figures 6a and 6b show that the surface of PSS-03 is smooth and flat with intense relief.



**Fig. 5.** Shows PSS-01, PSS-02, and PSS-03 after dye adsorption. (a) PSS-01, (b) PSS-02, and (c) PSS-03.



**Fig. 6.** SEM images of PSS-03.



**Fig. 7.** Adsorption mechanism for sulfonated polystyrene.

The electrostatic and hydrogen bonding interactions between the opposite charge groups of the three materials of PSS and MB may cause MB's plausible adsorption mechanism. Sulfur trioxide and hydroxyl groups are present in the suggested adsorbent, PSS. As the pH rises, the protonation potential of the hydroxyl and sulfur trioxide

groups gradually diminishes. As a result, as pH rises, so do the negative charges on PSS. Therefore, electrostatic interactions between the opposite charge groups of PSS and MB were in charge of the adsorption process (Fig. 7). The cationic MB can compete with the hydrogen ions (H<sup>+</sup>) and  $\pi$ - $\pi$  interaction in the water for the free functional on the PSS

at subordinate pH, which gives more smallish adsorption as opposed to this case where there are additionally hydrogen ions ( $H^+$ ) in the solution. Since unionized hydroxyl groups are often visible at low pH levels, weaker connections between the unionized hydroxyl and the positively charged MB, known as hydrogen bonding interactions, are seen. Therefore, due to electrostatic interactions, the cationic MB adsorption on negatively charged PSS may be more effective at high pH.

### Adsorbent Dosage Impact

Choosing the proper sorbent dosage is one of the most crucial factors. According to the findings shown in Fig. 8a, increasing the sorbent dose from 10 mg to 50 mg consistently produced MB removal efficiencies of around 97% and 86% for PSS-03 and PSS-01, respectively. After reaching a steady state at 20 mg copolymer, adding different sorbent dosages had no additional impact on MB adsorption. Even when the sorbent concentration is raised in the instance of PSS-02, the removal effectiveness of MB remains poor (the removal rate is roughly 68% at 50 mg).

### Influence of Temperature

This effect was studied between  $T = 10\text{--}45\text{ }^\circ\text{C}$  with 0.02 g of PSS, 15 min of contact time, and a pH of about 6.2. As shown in Fig. 8b, increasing the temperature from 10 to

$45\text{ }^\circ\text{C}$  did not impact the amount of MB removed because the percentage removal for PSS-03 remained constant, thanks to the great stability of this material, as proved in our article [35]. For PSS-01, there is a very small increase in adsorption, but in general, it also remains almost constant.

### An impact of the Initial MB Concentration

As the adsorption of blue methylene on PSS was examined at various initial pigment concentrations (10 to 60 ppm), all other variables were kept constant (Fig. 9). When the initial dye concentration was increased from 10 to 50 ppm or from 10 to 60  $\text{mg g}^{-1}$  for PSS-03, the highest sorbent, the adsorption capacity of the aqueous phase increased for each of the three sorbents. The dye and adsorbent reacted more strongly when the initial dye concentration increased [38]. In other words, as the initial pigment concentration rises, so does the driving force required to overcome the mass transfer resistance of the dye between the solution and the adsorbent surface [39].

### Adsorption Kinetic Models

First- and second-order pseudo-kinetic models were examined to determine the appropriate adsorption mechanism for the MB pigment on the three copolymers employed.

The kinetic equation of pseudo-first order is [40]:

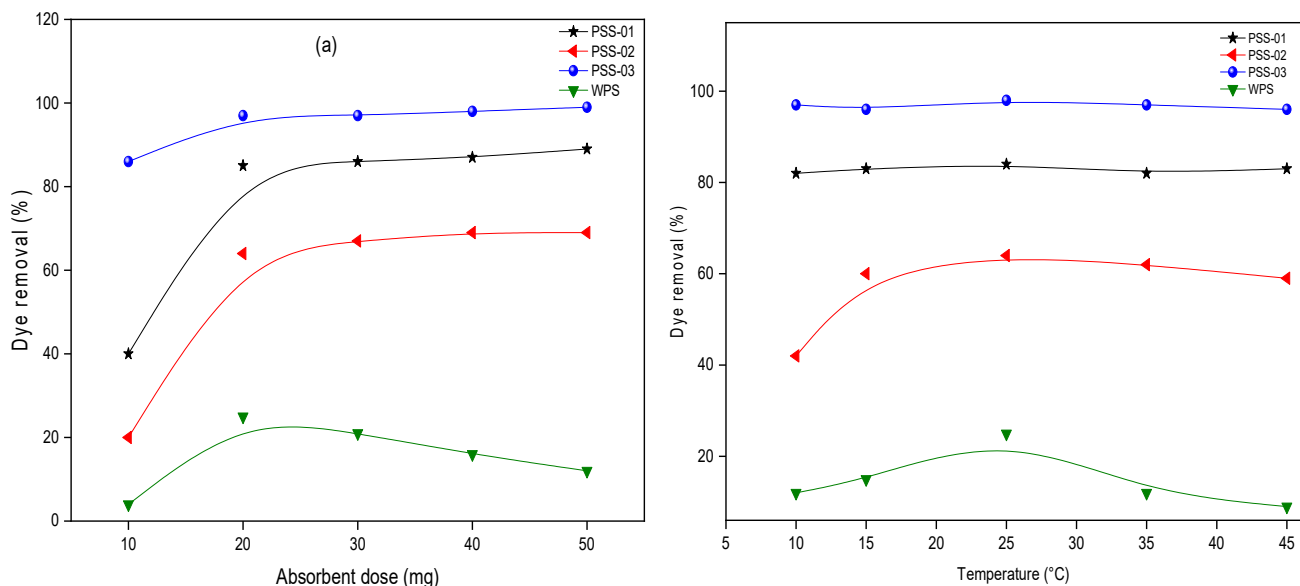


Fig. 8. (a) effect of adsorbent dose and (b) temperature on elimination of MB.

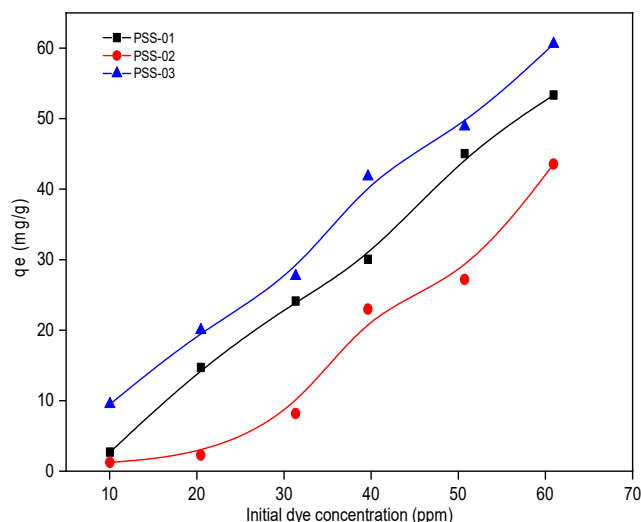


Fig. 9. Effect of initial dye concentration.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Where  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the amounts of dye adsorbed onto the copolymers at equilibrium and time  $t$ , respectively, and  $k_1$  is the adsorption rate constant ( $\text{min}^{-1}$ ).

The kinetic equation of pseudo-second order is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $k_2$  is the constant rate for the pseudo-second-order model.

Figures 10a and 10b display the adsorption kinetic diagrams. Table 1 displays the rate parameters and correlation coefficients for both models.

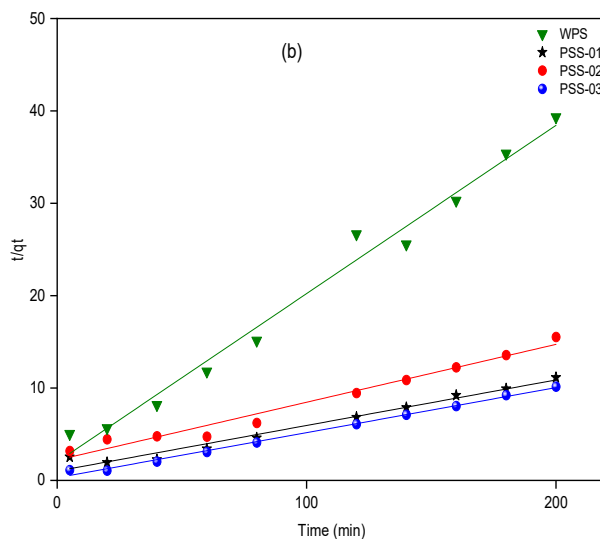
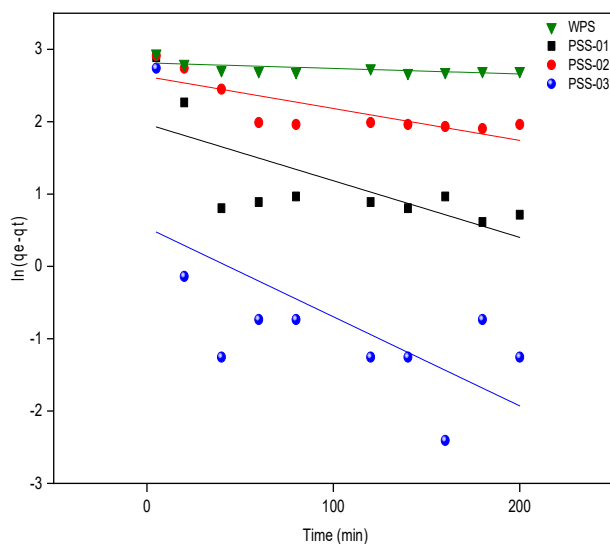


Fig. 10. Kinetic model for the adsorption of MB on different copolymers (a) pseudo-first and (b) pseudo-secondary order.

Table 1. Pseudo-first and Pseudo-second Order Kinetic Parameters for MB Adsorption on Copolymers

Adsorbent	$q_e$ (exp) ( $\text{mg g}^{-1}$ )	Pseudo-first order			Pseudo-second order		
		$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (cal) ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{min}^{-1}$ )	$q_e$ (cal) ( $\text{mg g}^{-1}$ )	$R^2$
WPS	12.60	$7.6 \cdot 10^{-4}$	16.60	0.645	0.00165	5.49	0.929
PSS-01	18.15	0.0078	7.149	0.711	0.00239	20.28	0.989
PSS-02	13.27	0.0044	13.790	0.809	0.00178	15.97	0.989
PSS-03	19.9	0.012	1.709	0.633	0.00808	20.54	0.999



From the results obtained, it is clear that the R<sup>2</sup> values are shallow and the calculated q<sub>e</sub> values are much lower than the corresponding experimental values for the pseudo-first-order model. Therefore, this model needed to be more suitable for modeling the MB adsorption process on the three adsorbents. However, the pseudo-second-order model had the highest correlation coefficient (R<sup>2</sup>). This suggests that the adsorption of MB on the three adsorbents agrees with the pseudo-second-order kinetic model and represents a chemical process. Furthermore, the q<sub>e</sub> estimated by the pseudo-second-order kinetic model was very close to the experimentally determined q<sub>e</sub>. These data show that MB's adsorption kinetics strongly depend on the available active adsorption sites. [41,42].

### Adsorption Isotherm

At pH = 6 and with 0.02 g/20 ml of the copolymer, adsorption isotherms were investigated for starting dye concentrations of 50, 100, 150, and 200 ppm. In most cases, isotherms are used to depict the adsorption mechanisms. The Freundlich and Langmuir models were fitted to the experimental data. According to the Langmuir model, an even monolayer of adsorbate molecules should cover the surface of the adsorbent. When the surface approaches the saturation point, where maximal surface adsorption is attained, the sites are occupied, and no more sorption can occur [43]. The Langmuir Eq. (4) is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}K_L} \quad (4)$$

Where:

C<sub>e</sub>: the concentration of equilibrium of MB (mg l<sup>-1</sup>)

q<sub>e</sub>: the amount of MB adsorbed on the adsorbent (mg g<sup>-1</sup>)

K<sub>L</sub>: the adsorption constant of Langmuir (l mg<sup>-1</sup>)

q<sub>max</sub>: the adsorbent ability to form monolayers (mg g<sup>-1</sup>)

According to the Freundlich model, adsorption takes place on heterogeneous surfaces. [44,45]. Freundlich's Eq. (5) is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where K and n are the adsorption capacity and intensity-related Freundlich constants.

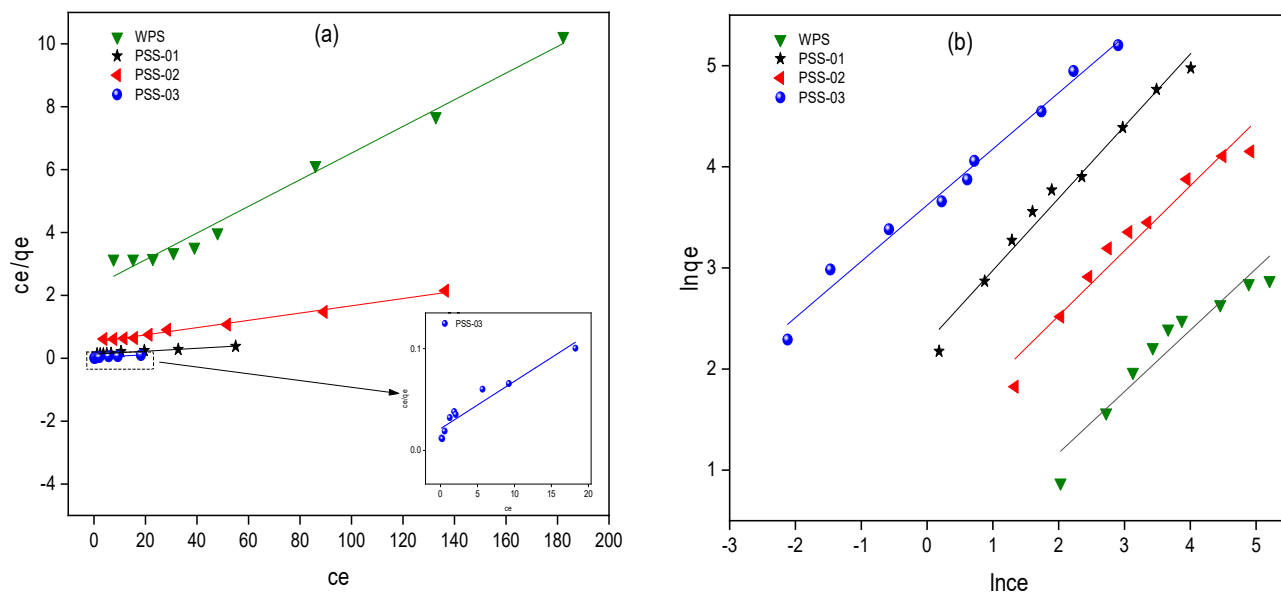
The exchange resin's sorption capacity can be determined this way using the Freundlich and Langmuir models. According to Figs. 8a and 8b, the Langmuir parameters in Table 2 represent the MB's adsorption onto sulfonated polystyrene. This demonstrates that, despite being very comparable, the maximum adsorption capacity differs; PSS-03 has the highest adsorption capacity, followed by PSS-01 with 215.5 mg g<sup>-1</sup> and PSS-02 with 86.43 mg g<sup>-1</sup> and 23.58 mg g<sup>-1</sup> for waste. This variance is brought on by the change rate and each polymer's form. This demonstrates that the Langmuir model is best for the final three polymers.

The findings show that the Freundlich model best fits the experimental data and that multilayer adsorption occurs on the surfaces of the three copolymers used. For the PSS-03 and PSS-01 adsorbents, the Freundlich model's correlation coefficient (R<sup>2</sup>) is significantly higher than the Langmuir model's correlation coefficient (R<sup>2</sup>) (Figs. 11a and 11b).

Additionally, for PSS-01, PSS-02, and PSS-03 in that order, the 1/n values of the Freundlich equation were 0.71, 0.64, and 0.55, which are calculated in Table II. This suggests that the MB dye was quickly absorbed. A normal Freundlich isotherm is indicated by a ratio of 1/n less than 1, whereas a value greater than 1 denotes cooperative adsorption.

**Table 2.** For the Three Adsorbents, the Freundlich, and Langmuir Parameters for the Adsorption of MB

Adsorbent	Langmuir			Freundlich		
	q <sub>m</sub> (mg g <sup>-1</sup> )	K <sub>L</sub> (l mg <sup>-1</sup> )	R <sup>2</sup>	K <sub>F</sub> (l g <sup>-1</sup> )	1/n	R <sup>2</sup>
WPS	23.58	0.018	0.99	0.95	0.60	0.95
PSS-01	215.5	0.035	0.98	9.60	0.71	0.99
PSS-02	86.43	0.022	0.99	3.46	0.64	0.97
PSS-03	216	0.216	0.95	37.35	0.55	0.99



**Fig. 11.** Plots illustrating the isotherm for MB adsorption (a) Langmuir plot and (b) Freundlich plot.

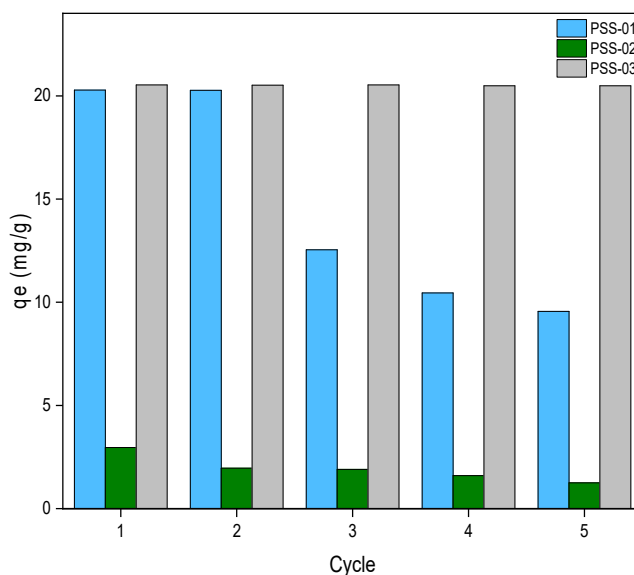
The Langmuir and Freundlich models therefore provide a definitive explanation of the kinetic adsorption data.

### The Regeneration of Sulfonated Polystyrenes

Excellent and promising adsorbent should, in general, be able to be recycled and reused in order to satisfy the demand for cheapness [46]. Moreover, it must have a large capacity for adsorption. Figure 12 demonstrates that PSS-03 still displayed a high adsorption capacity after five dye adsorption-desorption cycles, in contrast to PSS-01, which displayed a high regeneration capacity after no more than two cycles, and PSS-02, which displayed no regeneration, indicating that this polyelectrolyte can be recycled for dye removal. As a result of the aforementioned findings, it is possible to draw the conclusion that the stable and reasonably priced sulfonated polystyrene created in this study can be employed as a successful adsorbent for the removal of MB from an aqueous solution.

### CONCLUSION

The sulfonated polystyrenes were successfully prepared by recycling polystyrene waste using three different methods and have unique adsorbent characteristics such as environmental friendliness, subordinate price, and snappy



**Fig. 12.** Regeneration study of the materials used.

preparation. The copolymers made from the PSS-03 produced showed enhanced surface chemistry and a high specific surface area in their physicochemical properties. The findings showed that a dose of PSS-03 of 0.04 g, an MB solution at pH 6, and a time of 15 min are the optimal adsorption settings for maximal MB elimination. According

to the findings, the PSO kinetic model predicted the adsorption kinetics well. However, the Langmuir model best described the equilibrium results, with a maximum monolayer adsorption capacity of 142.5 mg g<sup>-1</sup> for blue methylene dye adsorption on PSS. According to the study's findings, PSS-03 can be employed as a water adsorbent to successfully remove synthetically charged pigments.

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