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Modified waste polystyrene as a novel adsorbent for removal of methylene blue from aqueous media

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ABSTRACT

This research deals with the sequent sulfonation and magnetization of waste polystyrene to form a novel adsorbent. The novelty is assigned by an anionic surface that can adsorb cationic dye and by a magnetic property allowing it to be separated quickly and practically. The sulfonation was conducted using H_2SO_4 , and the magnetization was performed by the coprecipitation of Fe_3O_4 . The prepared adsorbents were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM) machines. The adsorption capacity was evaluated for the removal of methylene blue (MB) dye from aqueous media conducted by batch experiment. The contact time, adsorbent weight, and solution pH were optimized. The parameters of kinetic and isotherm adsorptions were also determined. The characterization data showed evidence that sulfonated magnetic polystyrene was successfully produced. The adsorbent with 50 wt% of Fe_3O_4 showed good adsorption capacity and separability effectiveness. The optimum condition of the adsorption of 10 mg/L MB in a 40 mL solution was reached by 15 mg of the adsorbent weight within 45 minutes and at pH 7 with an effectiveness of about 98%. The adsorption kinetics is best suited to a pseudo-second-order with an adsorption rate constant of $0.364 \text{ g mg}^{-1} \text{ min}^{-1}$ and is well explained by the Langmuir isotherm model with an adsorption capacity of 46.56 mg/g.

1. Introduction

Methylene blue (MB) is a cationic dye widely used for biological staining [1], as well as for coloring leather, paper, hair, cotton, and wool [2,3]. MB with a complex aromatic structure (Figure 1c) is less degradable in the environment. The presence of MB in an effluent, even at low concentrations, is

noticeable and unpleasant, as well as harmful to fish and other aquatic organisms [4,5]. The dye is less permeable to sunlight; it inhibits photosynthetic activity in aquatic ecosystems [2,4], which decreases the quality of the water system [4]. Further, when contact with such contaminant occurs, it can cause eye burns, genetic mutation, and dermatological diseases

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[1,6]. Therefore, the removal of such dye pollutants before being discharged into the environment is extremely important for human life and the protection of the environment. In recent years, the methods that have been established for removing MB from the aquatic system include photocatalytic degradation [7-10] and adsorption [11-15]. Because of its high stability against chemicals, MB cannot be degraded completely and forms secondary pollutants that may be more toxic [5]. On the other hand, it has been demonstrated that adsorption is a promising procedure due to its high efficiency, simple operation, no generation of secondary pollutants, and regeneration and reuse possibilities [3-5]. Accordingly, the adsorption of MB dye contaminants from wastewater has received a great deal of attention [4-6,11,12,16]. However, the high cost of the adsorbents is believed to be the main drawback of the adsorption method [1-3,17,18]. Therefore, there is a growing need to find low-cost and efficient non-conventional adsorbents to treat large volumes of wastewater. Such adsorbents can be fulfilled by bean peel waste [1], agricultural waste [2], ficus carica bast [3], potato waste [17], pine sawdust [13], guaran [19], and the waste of polymethyl methacrylate (PMMA) [18] for MB removal. In addition to the waste of PMMA, waste polystyrene is another polymer that has also been explored as an adsorbent in the sulfonation process [20-24]. But so far, there is a lack of reports on sulfonated waste polystyrene for MB removal. In the last decade, waste polystyrene has been found abundantly in the environment originating from the large disposal of Styrofoam cups, food trays, and electronic goods [20-24]. Waste polystyrene has characteristics such as stable chemical properties, large capacity, aging resistance, corrosion resistance, and non-degradability due to its light weight; it is recognized as a global environmental threat and waste management problem [21,24]. Chronic polystyrene

contamination adversely affects the central nervous system, manifesting symptoms such as depression, headache, fatigue, and weakness; it may also have minor effects on kidney function and blood [23,24]. Recently, conversion of the waste polystyrene into a sulfonated adsorbent has been intensively developed, which could change the hydrophobic surface into a negative surface [20-24]. The chemical structure of polystyrene and sulfonated polystyrene is exhibited in Fig.1a and Figure 1b. The negative surfaced adsorbent has attracted much attention and has been investigated to reduce the use of several cationic of heavy toxic metals such as Cd (II) [20-22], Hg(II) [23], and Pb(II) [22-24]. In general, recovery by filtration of the spent adsorbent at the end of the adsorption process is inconvenient and expensive for large scale applications. Thus, a great effort has been devoted to replacing the impractical separation, that is, the modification with Fe_3O_4 to form a separable/recoverable magnetic adsorbent [4-6,14,15,25-29]. In recent years, magnetic adsorbents have attracted much interest because they not only have high separation efficiency and reusability but also have a large adsorption capacity for contaminant removal, including activated montmorillonite [5], zeolites [25-27], waste iron mud [14], various waste biomasses [28,29], and polystyrene synthetic [29]. To our knowledge, very few reports of MB adsorption using magnetic polystyrene sulfonate prepared from the corresponding waste can be traced [29]. Therefore, the present paper aims to demonstrate the feasibility of using new adsorbents obtained by the sulfonation and magnetization of waste polystyrene to remove MB dye in water. The effects of various parameters such as adsorbent weight, contact time, and solution pH have been evaluated. The kinetic and isotherm adsorptions are also examined.

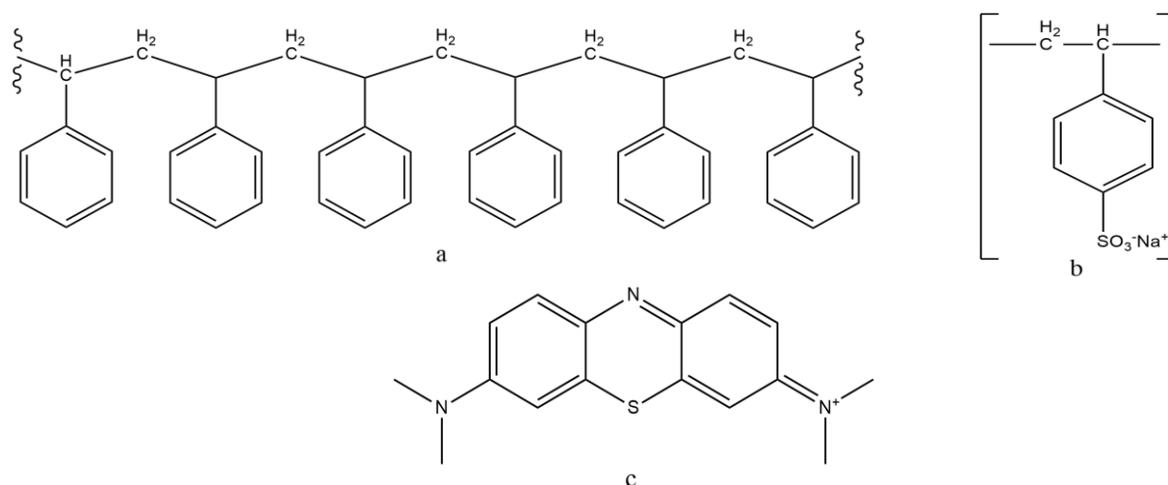


Fig. 1. The chemical structure of a) polystyrene, b) sulfonated polystyrene, and c) methylene blue.

2. Materials and methods

2.1. Chemicals

The waste polystyrene of disposed cups was crushed and sieved into a 100 mesh powder. The H₂SO₄ 96 wt%, FeCl₂, FeCl₃, NH₄OH, HCl, NaOH, N₂ gas, and methylene blue in the analytical grade were purchased from E. Merck and used without purification.

2.2. Preparation of magnetic polystyrene sulfonate adsorbent from styrofoam waste

The magnetic polystyrene sulfonate was prepared by sequential steps of the sulfonation of waste polystyrene and magnetization of the polystyrene sulfonate.

2.2.1. Sulfonation of the waste polystyrene

The sulfonation of waste polystyrene was conducted using a procedure previously reported with the following optimum conditions [18]. About 3 g of the 100-mesh waste polystyrene powder was mixed with 50 mL of concentrated H₂SO₄; the mixture was then heated at 55 °C accompanied by stirring within 90 mins. Then, the mixture was left at room temperature for 24 h. Finally, the sulfonated polystyrene adsorbent was separated from the solution by filtration using Whatman 42 filter paper and dried at 100–110 °C for 2 h. The dry adsorbent noted as polystyrene-SO₃ was stored in a desiccator before the magnetization process.

2.2.2. Magnetization of the polystyrene-SO₃

The magnetization of the polystyrene-SO₃ adsorbent with Fe₃O₄ was performed by the coprecipitation technique of Fe₃O₄ [24]. About 1.5 g of the polystyrene-SO₃ was suspended in 400 mL of the NH₄OH 0.5 mole/L solution. Then, the suspension was heated at 70 °C for 30 min; at the same time, it was added drop-wise with a 100 mL solution containing Fe(II) and Fe(III) ions with the mole ratio 1:2 under nitrogen gas and stirred for about 15 min until the black solid was produced. Then, the black solid was separated from the filtrate by contacting a magnet rod onto the outside wall of the flask. The recovered adsorbent was rinsed with deionized water up to neutral pH and dried at 70 °C for 2 h. The black solid was ground and sieved to get a 200-mesh powder. The black powder was noted as polystyrene-SO₃/Fe₃O₄ with 50 wt% of the Fe₃O₄ fraction. The same procedure was duplicated for polystyrene-SO₃ as weight 3.0 g and 4.5 g to obtain polystyrene-SO₃/Fe₃O₄ with 33.3 wt% and 25.0 wt% of Fe₃O₄ fractions, respectively. The adsorbents obtained were notified as polystyrene-SO₃/Fe₃O₄(50), polystyrene-SO₃/Fe₃O₄(33.3), and polystyrene-SO₃/Fe₃O₄ (25), following the fractions of Fe₃O₄.

2.2.3. Characterization of magnetic polystyrene sulfonate adsorbents

The samples characterized were polystyrene-SO₃/Fe₃O₄ with 50, 33.3, and 25 of the Fe₃O₄ fractions, and the waste polystyrene as well as polystyrene-SO₃ for comparison. The FTIR spectra

were recorded on a Shimadzu 8210 FTIR spectrophotometer. The XRD patterns were scanned by a Shimadzu 6000X X-ray diffractometer equipped with Cu K α radiation. The SEM images were taken using JSM-6510LA SEM. The separable effectiveness of polystyrene-SO₃/Fe₃O₄ adsorbents, represented by turbidity, was measured by a turbidimeter (LaMotte 2020 17999-EX2). The adsorption capacity of the adsorbents was evaluated for MB adsorption. The Fe₃O₄ fraction that gave the best separability and adsorption capacity can be found from the separation and adsorption studies. This adsorbent was then used to examine MB dye removal.

2.2.4. Adsorption of methylene blue by magnetic polystyrene sulfonate adsorbent

The batch adsorption experiment was conducted in an Erlenmeyer flask filled with 15 mg polystyrene-SO₃/Fe₃O₄(50) adsorbent and 40 mL methylene blue 10 mg/L at pH 7; it was magnetically stirred under a constant rate (150 rpm) and at a constant room temperature (30 °C) for 45 min. The magnetic adsorbent was separated from the MB solution by contacting a magnetic rod to the outside wall of the flask. The concentration of MB left in the solution was determined by a UV-Visible spectrophotometer (Evolution 201-Thermo scientific) at 665 nm of the wavelength. The same procedure was repeated for the adsorbents of polystyrene-SO₃/Fe₃O₄(33.3) and polystyrene-SO₃/Fe₃O₄(25) to find the best fraction. To obtain the optimum condition, the above procedure was repeated by applying various contact times (5, 10, 15, 30, 45, 60, 75, 90, and 120 min), adsorbent weights (1, 5, 10, 15, 20, 25, 30, 35, and 40 mg), MB solution pHs (2, 3, 4, 5, 6, 7, 8, 9, and 10), and MB solution concentrations (10, 20, 40, 80, and 100

mg/L). When one variable was changed, the others remained constant. The kinetic study was performed using the adsorption data from the various contact times, while the adsorption isotherm was verified based on the adsorption data obtained from the variation of the initial MB concentrations. The formulas expressing the first-order and second-order adsorptions and the corresponding curves were plotted by following previous reports [2,21]. The reaction order and rate could be determined from the slope and intercept. For the determination of the best fitting isotherm model, the Langmuir and Freundlich models were investigated by constructing the related curves based on the adsorption data from the initial MB concentrations [2], the adsorption isotherm parameters could then be verified.

3. Results and discussion

3.1. Characterization of the prepared adsorbent

3.1.1. FTIR and XRD data

For confirming the sulfonation of the waste polystyrene and the magnetization of the sulfonated polystyrene, their FTIR spectra have been recorded and are demonstrated in Figure 2A. In the spectra of the polystyrene, several absorbances are observed at the wavenumbers as follows. The absorbance at 3440 cm⁻¹ belongs to OH, 3024 cm⁻¹ is related to the unsaturated aromatic C-H stretching vibrations, 2924 cm⁻¹ corresponds to CH₂ bending vibration, 1492 cm⁻¹ is attributed to the aromatic ring, 1451 cm⁻¹ is assigned to CH₂, and 905, 837, 754 cm⁻¹ represents various substitutions of the benzene ring of the polystyrene [22].

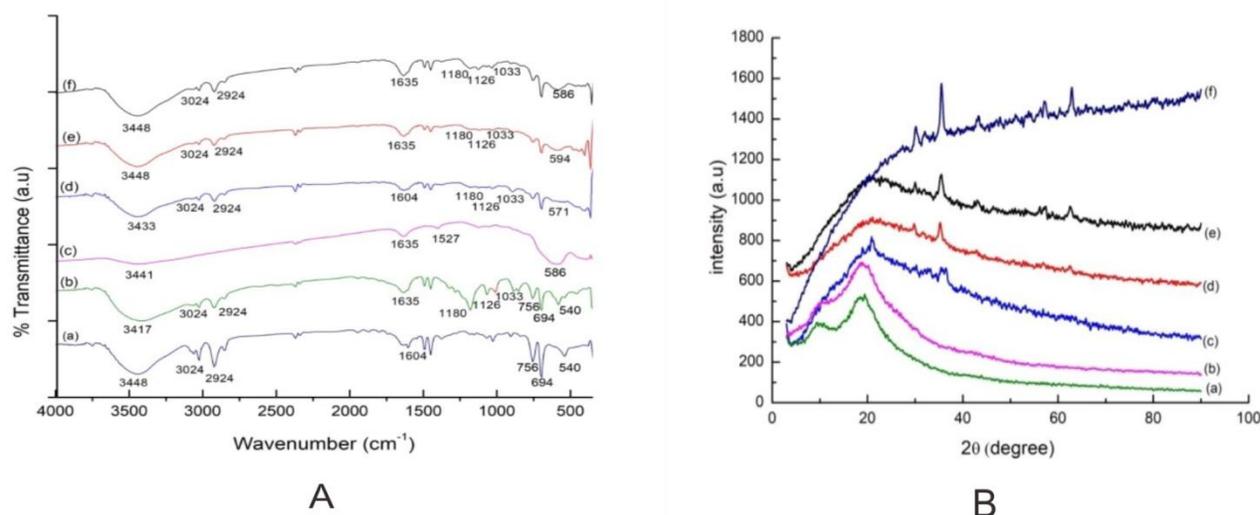


Fig.2. A) The FTIR spectra and B) The XRD patterns of a) polystyrene, b) polystyrene -SO₃, c) Fe₃O₄, d) polystyrene -SO₃/Fe₃O₄(25), e) polystyrene -SO₃/Fe₃O₄(33.3), and f) polystyrene -SO₃/Fe₃O₄(50).

The characteristic FTIR absorbances of sulfonated polystyrene are the same as the peaks for polystyrene, with the addition of peaks located at 1126, 1180, 1033, 1126, and about 830 cm⁻¹. Similar data was also observed by other studies [18,22]. It is suggested that the absorption at 1126 cm⁻¹ represents a sulfonate anion attached to a benzene ring [18]. The vibration of the S-O bond at 1180 cm⁻¹ is observed as very broadband [18,22,23]. Furthermore, the absorption at 1033 cm⁻¹ is related to the symmetric stretching vibration of the SO₃H groups. Then, the absorption at 1126 cm⁻¹ verifies a sulfonate anion attached to a benzene ring [18,22,23]. The substitution of the sulfonic groups to the aromatic ring of polystyrene appears at wavenumber approximately from 830 cm⁻¹ to 850 cm⁻¹ [18,22,23]. It is evidence that sulfonation of the waste polystyrene has successfully occurred. The FTIR spectra of Fe₃O₄ show several peaks around 3441, 1635, 1527, and 586 cm⁻¹. The band at 586 cm⁻¹ corresponds to the Fe-O stretching band, which is a characteristic peak of Fe₃O₄ [5]. The peaks at 1635 and 3441 cm⁻¹ are attributed to the hydroxyl groups of water adsorbed on the surface [5,25]. The FTIR spectra of polystyrene-SO₃/Fe₃O₄ are seen as a combination of the absorption peaks belonging to polystyrene sulfonate and that of Fe₃O₄. Additionally, there are shifts of bands at 586 cm⁻¹ into 591 cm⁻¹ and at 1033 cm⁻¹ into 1035 cm⁻¹ due to the interaction of Fe-O with the polystyrene. Hence, the formation of the polystyrene-SO₃/Fe₃O₄ adsorbent may be verified. A similar finding was

also reported previously [5,25].

3.1.2. XRD data

To detect the formation of Fe₃O₄ on the sulfonated polystyrene, their XRD patterns were recorded and are presented in Figure 2B. The figure exhibits the amorphous patterns for unsulfonated and sulfonated waste polystyrene, which are common patterns for polymers [21]. In contrast, a crystalline XRD pattern is demonstrated by Fe₃O₄, with observable peaks appearing at 30.09°, 35.36°, and 43.21° that are associated with the (220), (311), (400), (422), (511) and (440) phase, respectively [14,25,27]. In the XRD pattern of polystyrene-SO₃/Fe₃O₄, the amorphous pattern belonging to the polystyrene and the crystalline peaks from Fe₃O₄ are also observed. Additionally, it is observable that the intensity of the crystalline peaks increases with an increasing fraction of Fe₃O₄ since the intensity is proportional to the amount of the respective crystal. This data implies that Fe₃O₄ has been impregnated onto a polystyrene-SO₃ structure. Some studies have also found similar results [14,26,27].

3.1.3. SEM data

Figure 3 demonstrates the SEM images of polystyrene, polystyrene-SO₃, Fe₃O₄, and polystyrene-SO₃/Fe₃O₄. It is observable that polystyrene has a sheet appearance, while the polystyrene-SO₃ looks like a large flake resulting from the polymer destroyed during the sulfonation process under strong conditions. A similar result

has also been reported previously [18,21]. For Fe_3O_4 , it is seen as small particles with less uniform size. The adsorbent of polystyrene- $\text{SO}_3/\text{Fe}_3\text{O}_4(50)$ is observed as a large flake covered by small particles

of Fe_3O_4 . This appearance verifies the formation of magnetic Fe_3O_4 impregnated on the polystyrene- SO_3 , which shows a good agreement with the previous data.

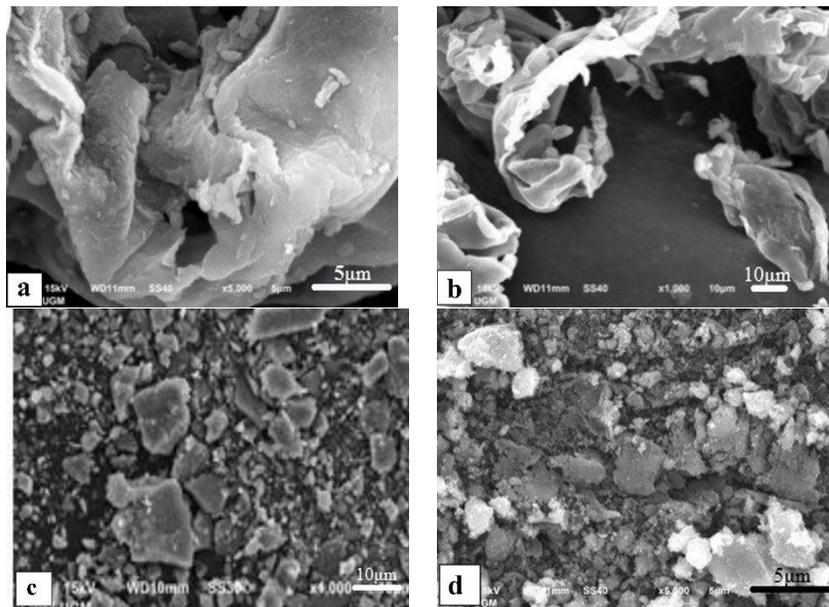


Fig. 3. The SEM images of a) waste polystyrene, b) polystyrene- SO_3 , c) Fe_3O_4 , and d) magnetic polystyrene- $\text{SO}_3/\text{Fe}_3\text{O}_4(50)$.

3.2. Adsorbent activity in the MB removal

3.2.1. Influence of Fe_3O_4 fraction in the adsorbent

The effect of the Fe_3O_4 fraction on the adsorption and adsorbent separation effectiveness is displayed in Figure 4. The figure illustrates that magnetization of the polystyrene- SO_3 adsorbent could noticeably enhance the adsorption capacity, and the improvement is proportional to the Fe_3O_4 fraction. It is implied that the presence of Fe_3O_4 possessing a high surface area has contributed to the active surface for adsorption [25] that

extended the surface area of the adsorbent. A similar finding has also been reported [25–27]. The figure also reveals that the higher fraction of Fe_3O_4 results in a decrease in the turbidity or increases the clarity of the solution from the magnetic separation due to the effective recovery. This trend is promoted by the existence of Fe_3O_4 providing magnetic property to the adsorbent, which allows the adsorbent to be separated easily. The solution after adsorbent magnetic separation is seen to be clearer compared to before separation, as demonstrated in Figure 4.

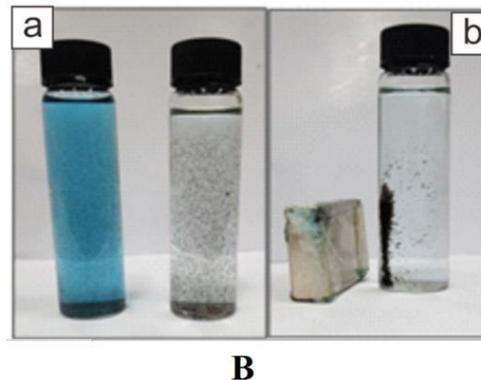
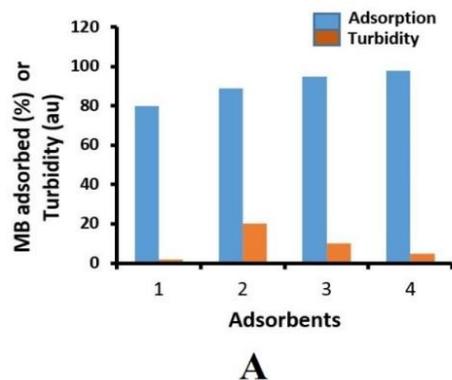


Fig. 4. A) The effect of Fe_3O_4 fraction on the effectiveness of the adsorption and adsorbent separation of 1) polystyrene- SO_3 , 2) polystyrene- $\text{SO}_3/\text{Fe}_3\text{O}_4(25)$, 3) polystyrene- $\text{SO}_3/\text{Fe}_3\text{O}_4(33.3)$, and 4) polystyrene- $\text{SO}_3/\text{Fe}_3\text{O}_4(50)$. B) The appearance of MB solutions: a) before and b) after adsorbent separation by magnet rod.

3.2.2. Influences of the contact time, adsorbent weight, and solution pH

The adsorption results conducted in various contact times are illustrated in Figure 5. A trend is seen where the expanding time can raise the adsorption, but a time longer than 45 min does not influence the adsorption. Fast adsorption in the early stages is associated with a larger concentration gradient, which can lead to higher driving forces and higher availability of vacant active surfaces in the adsorbent [25]. At a contact time of more than 45 min, the lower adsorption rate is due to the depletion of vacancies in the adsorbent and dye concentrations. In particular, the decrease in the adsorption rate towards the end of the experiment

indicates that MB may be formed as a monolayer on the adsorbent surface [3]. This trend is consistent with other studies [3,5,28]. The adsorption of MB on the polystyrene-SO₃/Fe₃O₄ with various masses is presented in Figure 5. Increasing adsorbent weight sharply improves the adsorption, and when using a larger mass than the optimal level, the adsorption does not depend on the adsorbent weight. This is mainly due to the enrichment in the number of active sites available on the adsorbent surface. The excessive adsorbent provides a much more active surface, but because all the adsorbate (MB) has been attached to the adsorbent, no further adsorption took place. The same finding has also been obtained in [2,4,18].

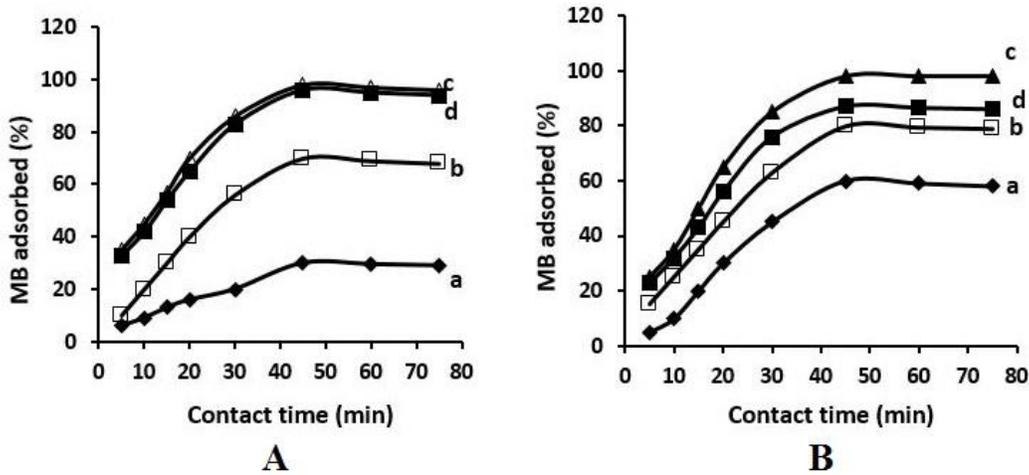


Fig. 5. The influence of contact time, adsorbent mass (in Fig.5 A a : 5 mg, b : 10 mg, c : 15 mg, d : 25 mg), and solution pH (in Fig 5B, a : 3, b : 5, c : 7, d : 9) on the MB adsorption.

The influence of the solution pH on the adsorption effectiveness is shown in Figure 5B. Alteration of solution pH reveals a positive effect on the adsorption, but at pH higher than 7, the opposite effect is observed. At the low pH, the sulfonate group is protonated by an H⁺ ion present in excess to form an uncharged surface [21], and most of the MB exists in a non-ionic form [13], which inhibits the interaction between MB and the adsorbent. The protonation of the sulfonate group decreases by increasing the pH up to 7, permitting a more negative surface of polystyrene-SO₃/Fe₃O₄. The cationic MB also grew gradually, which promoted higher adsorption. By raising the pH further, the anionic OH in the solution may be in excess that could interact with the cationic MB [13], which declined the number of MB adsorbed.

3.2.3. The adsorption kinetic and isotherm models

The most common models used to study adsorption kinetics are pseudo-first-order and pseudo-second-order kinetic models [5]. A linear plot of log (q_e-q_t) versus time was analyzed for the pseudo-first-order model. The pseudo-second-order model was determined based on a plot of t/q_t versus time. The curves are presented in Fig. 6a and 6b. The slopes and intercepts of the pseudo-first-order and pseudo-second-order models of the curves were used to calculate the maximum MB uptake capacity (q_e in mg/g) and the rate constant (k), as presented in Table 1. Based on the correlation factor, the pseudo-second-order model (R²=0.998) was well fitted compared to the pseudo-first-order one (R²= 0.396) with the adsorption experiment.

The pseudo-second-order kinetic model confirmed that the rate-limiting step was chemisorption, involving valence forces through sharing or exchanging electrons [3]. The pseudo-second-order of the adsorption was a multi-step process involving adsorption on the external surface and diffusion into the interior [3]. Many studies have

reported the same trend [2,3,5,6,14,28]. From the curves, it was found that the maximal adsorption capacity (q_e) of polystyrene-SO₃/Fe₃O₄ was as much as 25.585 mg/g (Table 1), which is close to the capacity of corn husk biosorbent [2] and magnetic iron-mud [14].

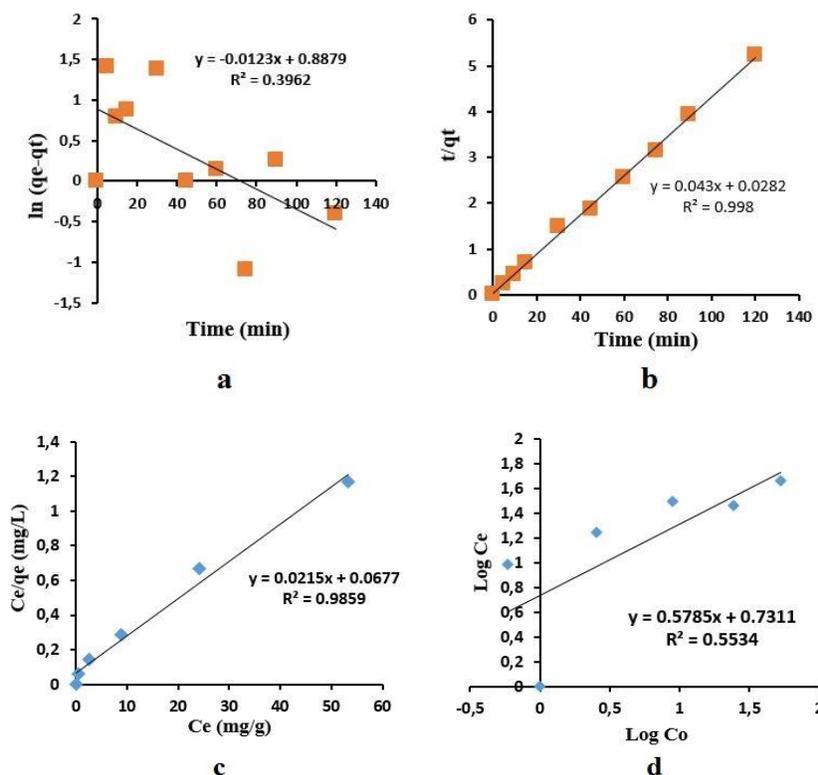


Fig. 6. The adsorption kinetic as a) pseudo-first-order and b) pseudo-second models and adsorption isotherm as c) Langmuir and d) Freundlich models.

The Langmuir and Freundlich models were verified to describe the adsorption isotherm. For the Langmuir adsorption model, a curve of (C_e/q_e) versus C_e was drawn, while $\log C_e$ versus $\log C_o$ was constructed for the Freundlich model, giving straight lines as demonstrated in Figure 6 c and 6d. The values of the Langmuir and Freundlich constants for MB dye uptake on the polystyrene adsorbent are given in Table 1. The table shows that

the R^2 value of the Langmuir constant is 0.9859, which is higher than the R^2 value of the Freundlich one, which is 0.5534, suggesting that the Langmuir isotherm provides the best description of the experimental data. This implies that MB molecules are identically adsorbed on the active surface of the polystyrene-SO₃/Fe₃O₄ adsorbent to form a monolayer. Some studies of MB adsorption have also concluded similar results [2,14].

Table 1. The adsorption kinetics and isotherm parameters of the MB on polystyrene-SO₃/Fe₃O₄.

Parameter	Kinetic study		Adsorption isotherm	
	Pseudo –first order	Pseudo –second order	Langmuir model	Freundlich model
R^2	0.3962	0.9968	0.9859	0.5534
Q_e (mg/g)	213.45	25.585	46.512	
k	0.0123	0.0364 min ⁻¹		
K (mg g ⁻¹)			0.318	5.384
n				1.728

4. Conclusions

It is concluded that the separable adsorbent of magnetic polystyrene-SO₃/Fe₃O₄ with a higher adsorption capacity for methylene blue removal has been successfully prepared from waste polystyrene. The adsorption capacity and separable effectiveness of the adsorbent are influenced by the Fe₃O₄ fraction, and a 50 wt% of the fraction shows the best compromising separability and adsorption capacity. The adsorption of MB on polystyrene-SO₃/Fe₃O₄(50) is controlled by contact time, adsorbent dose, and solution pH. The highest adsorption is reached by applying 15 mg of the adsorbent in a 40 ml solution of 10 mg/L MB for 45 min at pH 7, which was around 98% removal. The kinetic study reveals that the adsorption can be well described by the pseudo-second-order reaction with $k = 0.0364 \text{ g mg}^{-1} \text{ min}^{-1}$. The adsorption has the best agreement with the Langmuir adsorption isotherm model, with a maximum capacity of 46.512 mg/g.

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