Article

Surface Modifications of Superparamagnetic Iron Oxide Nanoparticles with Polyvinyl Alcohol, Chitosan, and Graphene Oxide as Methylene Blue Adsorbents

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Abstract: Synthetic dye contamination of wastewater has long been a social issue, with adsorption being the most focused upon research technique among wastewater treatment. Using the co-precipitation method, superparamagnetic iron oxide nanoparticles (SPIONs) with the size of 13.6 ± 1.9 nm were synthesized. By adsorbing methylene blue (MB) on the modified surface of SPIONs using polyvinyl alcohol, chitosan, and graphene oxide, the entrapment efficiency at pH 7 can be up to 87.00 ± 0.16% after 13 days, and the highest MB loading capacity was 3.638 ± 0.009%, while the highest loading amount achieved was 36.385 ± 0.095 mg/g. The cumulative desorption capacity of the adsorbent at pH 3.8 was at its maximum at 8.94 ± 0.66% after 30 days. The results of the experiments indicated that the compound has a favorable impact on the adsorption of synthetic dyes; nevertheless, more research is needed to determine the ideal ratio, temperature, and pH levels for this chemical.

Keywords: methylene blue; adsorption; desorption; magnetic graphene oxide; nanocomposites

1. Introduction

Wastewater discharge, including eutrophication of waterbodies and deterioration of water quality, is one of the most concerning environmental issues. Due to their non-biodegradable properties, the main contributors of water pollution are 7 × 10^7 tons of synthetic dyes, which are generated globally per annum [1]. Textile dyes significantly limit the biochemical and chemical oxygen requirement, result in photosynthesis impairment and plant growth inhibition, gain access into the food chain, enable recalcitrance and bioaccumulation, and have the potential for toxicity, mutagenicity, and carcinogenicity [2–4].

Dye effluents can be treated in numerous ways, such as adsorption, ion exchange, flocculation, decantation, advanced oxidation processes, biodegradation, chemical precipitation, and other processes. Traditional treatment techniques have been effectively used on a variety of wastewaters. However, the traditional treatment techniques have been ineffective in industrial wastewater, due to lots of heavy metals, hazardous compounds, and coloring chemicals [5]. Among these techniques, adsorption is well-known to be a promising technique [6], due to its efficiency, low cost, and simple material handling [7]. Moreover, because they are highly effective, consume little energy, and are environmentally friendly, magnetic field-enhanced treatment approaches have been suggested to improve wastewater treatment operations [5]. Due to their large surface area, charge neutralization, and high absorption capabilities that can promote adsorption, magnetic nanoparticles have
been taken as a promising adsorbent for wastewater treatment. Their unique magnetic nature is also advantageous because it encourages high floc activity and separation simplicity by accelerating separation and settling when an external magnetic field is applied [7–9].

Conventional adsorbents used in dye removal can be activated carbon, graphene, graphene oxide (GO), and polymeric membranes, which have shown adequate performance in the process. The adsorption process depends heavily on the adsorbent and adsorbate properties. For instance, adsorbents with high surface area and strong interaction with a variety of anionic, cationic, or neutral dyes in aqueous media via electrostatic interactions brought on by the presence of polar functional groups containing oxygen, such as GO, have emerged over the past ten years as a next-generation material for wastewater treatment. For cationic dyes, such as methylene blue (MB), the substantially negative charge density of GO in aqueous solutions offers efficient adsorption sites. Effective recovery is challenging when using it in raw form because of its propensity to form stable colloids that prevent phase separation. However, the ability to create composite materials with distinctive capabilities for solid phase separation and adsorption exists when using polymers to immobilize GO. Much research has been conducted utilizing GO in cooperation with other compounds to evaluate the activity of the adsorbent on dye removal [10–12].

One of the most common magnetic nanomaterials are superparamagnetic iron oxide nanoparticles Fe₃O₄ (SPIONs) [13] due to their substantial specific surface area for component adsorption. Iron oxide nanoparticles display superparamagnetic properties because of their smaller size than iron oxide in its bulk state. At the nanoscale, superparamagnetism, a unique magnetic feature of ferromagnetic iron oxide, does exist [14–16]. Comparing the MB adsorption capacity of SPIONs to SPION@Carbon sheets, SPION/expanded graphite, SPION/GO, and SPION/MWCNT, the adsorption capacity can be 45.43 [17], 95, 76.2 [18], 280.26 [19], and 280.06 mg/g, respectively [20].

Besides combining SPIONs with carbon-based materials, SPIONs have been used in conjunction with multiple compounds as dye adsorbents such as superparamagnetic iron oxide nanoparticles with polyactic acid-polyethylene glycol diblock copolymer and graphene oxide, graphene oxide/polyvinyl alcohol/Fe₃O₄, superparamagnetic iron oxide nanoparticles (SPIONs) impregnated activated carbon, nano Fe₃O₄/polyvinyl alcohol/polyacrylamide hydrogel, and SPION/CS/GO. The polymer modification on SPIONs could greatly limit the aggregation and many of issues relating to the nanoparticles’ surface without an effect on the desired properties of the SPION. Moreover, the appropriate combination with the polymer may strongly enhance the properties of SPIONs [21–27].

One of the most common polymers used to enhance the properties of SPIONs is polyvinyl alcohol (PVA). PVA is one of the derivatives of vinyl polymer that is connected by only a C-C linkage. PVA has the polymer formula \([\text{CH}_2\text{CH(OH)}]_n\). PVA is a water-soluble and biodegradable polymer that can be used as a carrier in fertilizer and pesticide production [28]. In several studies, PVA has been used as a dye removal adsorbent when combined with various compounds such as PVA membrane functionalized by D-glucose and agar, peroxidase-immobilized buckypaper/polyvinyl alcohol, PVA@walnut shell powder, polyvinyl alcohol/magnesium peroxide, PVA/GO, and PVA/GO/Fe₃O₄ [27,29–33].

One of the most common polymers that has been utilized in conjunction with PVA is chitosan (CS). CS is mostly extracted from the shells of crustaceans including crabs, shrimp, krill, and prawns. These shells are defined as a large waste material resource in the seafood industry in the world; for instance, 200,000 tons of shrimp shells are withdrawn from the Thailand food industry annually [34]. As a result, CS is denoted as an eco-friendly, biocompatible substance that contributes to reducing production costs and as being an effective adsorbent for water and waste treatment. CS is a nontoxic and hydrophilic polymer, mostly due to its excellent processability. For instance, various studies have combined PVA and CS to make cast hydrogels or ion conductive membranes and to enable film-forming [35,36].

When the epoxy groups in GO are cross-linked with CS via the primary amino groups, secondary amines can be produced. Numerous studies have shown that GO may absorb MB
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by being encapsulated in a polymer matrix that contains CS [10,37–39]. CS is defined as one of the deacetylated derivatives of chitin which has the structure of linear polysaccharides consisting of N-acetyl-2 amino-2-deoxy-D-glucose linked with 2-amino-2-deoxy-D-glucose residues by β-1,4-glycosidic linkage. The primary protonated amine group on CS’s structure is responsible for the solubility properties that are applied for the formation of a water complex with an anionic polymer such as PVA [40]. CS has been noticed to be promising in wastewater treatment as an adsorbent; however, the stability of CS in an acidic environment is not good and may form gels below pH 5.5. Thus, the acid pollutants may lead to the limitation of CS as an adsorbent in eliminating dye or metal ions [41]. Lately, several studies on CS-based metals have been conducted using metals, metal oxides, magnetite, or bimetallics [42–45]. The research on removal of chromium in wastewater by chitosan-Fe\textsubscript{3}O\textsubscript{4} has been carried out. With the presence of magnetite nanoparticles, the chromium removal efficiency of CS–magnetite nanocomposites had reached 92.33% compared to approximately 29.4% of CS itself. It can be concluded that the noticeable efficiency in combining CS with SPIONs can be promising in wastewater treatment [46].

The pH range between 6 and 8 is ideal for methylene blue (MB) adsorption. The isoelectronic point of MB could be at pH 7 to 8, when the functional group in the adsorbent has the greatest capacity to bind the dye [47,48]. Because many of the carboxyl and siloxane groups in the adsorbent connect with the H\textsuperscript{+} and become positively charged as a result, the H\textsuperscript{+} in solution will further weaken the bond between the adsorbent and the methylene blue at a lower pH. Hence, binding to the ion of the methylene blue dye becomes more challenging. This phenomenon decreases at pH 10 because there is free OH\textsuperscript{-} in the solution since the dye does not capture it. The colored base tends to be slightly negatively charged at the time of addition because the active group in the adsorbent, the carboxyl group, is partially positively charged. As a result, the dye and free OH\textsuperscript{-} ions compete for space on the surface of the adsorbent, decreasing the adsorbent’s ability to bind dye [49]. In addition, sewage normally has a pH range of 6 to 8, and hence the adsorption experiment in this study was performed with a pH of 7 [50,51].

Due to the greater likelihood that MB-adsorbed ions are desorbed in an acidic solution, several investigations have demonstrated that performing desorption at a pH below 4 was the most effective [32]. Moreover, the negative charges increase for pH over 3.65 as MB is a cation dye, which means the adsorption will increase much higher than pH 3.65 [53]. As a result, pH 3.8 ± 0.1 was selected in this research.

Hence, in this study, the composites of SPIION/PVA/CS/GO were synthesized and used as methylene absorbents. These adsorption and desorption experiments were carried out and the adsorption capacity, entrapment efficiency percent, loading capacity percent, and desorption kinetics were analyzed, in addition to the characterization of the composites using field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Barrett–Joyner–Halenda (BJH).

2. Materials and Methods

2.1. Materials

Iron(III) chloride hexahydrate (99% FeCl\textsubscript{3}·6 H\textsubscript{2}O), iron(II) chloride tetrahydrate (98% FeCl\textsubscript{2}·4H\textsubscript{2}O), ammonium hydroxide solution (NH\textsubscript{4}OH) (28 wt% NH\textsubscript{3} in H\textsubscript{2}O), sulfuric acid (98% H\textsubscript{2}SO\textsubscript{4}), potassium permanganate (KMnO\textsubscript{4}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), and hydrochloric acid (37% HCl) were purchased from Xilong Scientific Co., Ltd. (Shantou, China). Methylene blue trihydrate (98.5% MB), polyvinyl alcohol (PVA), chitosan (CS), and graphite (GR, particles sizes ≤ 30 µm fine powder 95%) were purchased from Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China). Glacial acetic acid (99.7% AA) was purchased from RCI Labscan (Bangkok, Thailand). All materials were used as received.
2.2. Synthesis

2.2.1. Synthesis of SPIONs

The co-precipitation approach was used to create SPIONs [53]. To begin, 500 mL of 0.7 M NH₄OH was produced and placed into a three-necked round bottom flask. The solution was stirred at room temperature. The first neck was completely covered. Then, nitrogen gas (N₂) was bubbled through the second neck of the flask into the solution. And the third neck was closed with a hole cover to allow oxygen to escape. Following that, 10.81 g of FeCl₃·6H₂O was dissolved in 40 mL of DI water and 3.97 g of FeCl₂·4H₂O in 10 mL of 2 M HCl. After mixing the two iron solutions, the entire 50 mL was added dropwise to the flask containing the 0.7 M NH₄OH solution. When the mixture turned black, the amount of stirring was lowered. In a N₂ environment, the reaction lasted 30 min. A neodymium magnet was used to capture the particles at the bottom of the flask. The supernatant was removed, and the particles were washed five times with DI water. The solution was dried in an oven at 80 °C for 24 h. The synthesis mechanism can be seen as following:

\[
\text{FeCl}_2 + 2\text{FeCl}_3 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 4\text{H}_2\text{O}
\]

2.2.2. Synthesis of GO

Graphite was oxidized using a modified version of the Hummers’ method to create GO powder [54,55]. Firstly, 75 mL of concentrated H₂SO₄ (98%) and 3 g of graphite powder were combined and agitated continuously for 15 min before adding 12 g of KMnO₄ every 10 min (0.75 g for each time) while maintaining a temperature below 20 °C in an ice bath. Then, 500 mL of deionized water was gradually added over a period of eight hours while the mixture was stirred at room temperature. Then, 5 mL of 30% H₂O₂ was added. GO was then separated by centrifugation for 5 min at 5000 rpm. The GO was dried in a vacuum oven at 70 °C for 24 h after being cleaned twice with DI water.

2.2.3. Synthesis of SPION/PVA/CS/GO

In this study, 0.5 g of PVA powder was mixed with 97 mL of distilled water for 2 h at 70 °C, then 3 mL of acetic acid and 0.5 g of CS powder was added, and the solution was stirred for 2 more hours. The combination was then given 1 g of SPION and 2 g of GO, with each component being sonicated for 30 min before, and the mixture was stirred continuously for an hour for every added step. For one day, the product was dried at 80 °C in the oven to collect the solid nanoparticles.

2.3. Characterization

The field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) can confirm the successful construction of the SPION/PVA/CS/GO material. The FE-SEM images can show the morphology of the material. The FTIR can confirm the type of iron oxide nanoparticles and the bonding of SPION/PVA/CS/GO. And the XRD analysis can show that the iron oxide nanoparticles have characteristics of superparamagnetic iron oxide nanoparticles. If an iron nanoparticle exhibits superparamagnetism, it can be verified using a vibrating sample magnetometer (VSM). Barrett–Joyner–Halenda (BJH) can be used to determine the surface area, pore size, and pore volume.

2.4. Determining the Adsorption Capacity of Methylene Blue on SPION/PVA/CS/GO

To construct the calibration curve for the adsorption, the MB solution with three concentrations at 0.015, 0.020, and 0.025 mg/mL was quantified with the quantity of nanoparticles for 13 days at room temperature. Then, 30 mg of dried SPION/PVA/CS/GO and 50 mL of pH 7 MB solution was mixed in a 50 mL falcon tube and left at room temperature for 13 days. UV-Vis spectrometry (Jasco V-730, scan speed 100 nm/min, data
interval 1 nm, response 0.96 s, filter exchange step) was used to determine the amount of methylene blue present every day. This process was performed three times.

2.5. Determining the Desorption Capability of the Methylene Blue on SPION/PVA/CS/GO

Neodymium magnets were used to remove the aliquot from each falcon tube following the adsorption experiment. Each falcon contained loaded nanoparticles and was filled with 50 mL of deionized water which had pH = 3.8. At room temperature, the desorption experiment was conducted, and each day the concentration of methylene blue was measured by UV-Vis spectrometry. UV-Vis spectrometry (Jasco V-730, scan speed 100 nm/min, data interval 1 nm, response 0.96 s, filter exchange step) was used to determine the amount of methylene blue present. The aliquot was put back into the falcon tube after being subjected to the UV-Vis spectrometry analysis. Every 7 days, the solution in falcons was changed back to pH 3.8 deionized water (MB-free) again. This process was carried out three times in 30 days.

2.6. Theory

The loading amount at time was calculated by the equation [24]:

\[ Q_t = \frac{(C_0 - C_t)V}{m} \]  

(1)

The loading capacity (%LC) was calculated by the following equation [24,56]:

\[ %LC = \frac{\text{Weight of MB adsorbed on the particles (mg)}}{\text{Weight of particles (mg)}} \times 100 \]  

(2)

The entrapment efficiency (%EE) was calculated by the following equation [24,56]:

\[ %EE = 100 \times \frac{\text{Weight of MB adsorbed on the particles (mg)}}{\text{Weight of MB initially fed (mg)}} \]  

(3)

The experimental data can be used to calculate the adsorption kinetic studies to define the order of kinetic models by plotting \( Q_t \) vs. \( t \) (in days) and using the nonlinear regression following these equations.

The experimental data are used for calculating the adsorption kinetics. The model of adsorption kinetics can be either pseudo-first order or pseudo-second order kinetics and fitted with the equations shown in Table 1.

Table 1. The pseudo order kinetics equations and plots [57].

<table>
<thead>
<tr>
<th>Model</th>
<th>Equations</th>
<th>Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonlinear</td>
<td>( Q_t = Q_e \left(1 - e^{-kt}\right) )</td>
<td>( Q_t ) vs. ( t )</td>
</tr>
<tr>
<td>Linear</td>
<td>( \log(Q_e - Q_t) = \log Q_e - \left(\frac{k_1}{2.303}\right)t )</td>
<td>( \log(Q_e - Q_t) ) vs. ( t )</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonlinear</td>
<td>( Q_t = \frac{k_2Q_e^2}{1 + k_2Q_e t} )</td>
<td>( Q_t ) vs. ( t )</td>
</tr>
<tr>
<td>Linear Type I</td>
<td>( t/Q_t = \left(\frac{1}{k_1Q_e}\right)\frac{1}{t} + \frac{1}{Q_e} )</td>
<td>( t/Q_t ) vs. ( t )</td>
</tr>
<tr>
<td>Linear Type II</td>
<td>( \frac{1}{Q_t} = \left(\frac{1}{k_1Q_e}\right)\frac{1}{t} + \frac{1}{Q_e} )</td>
<td>( \frac{1}{Q_t} ) vs. ( t )</td>
</tr>
<tr>
<td>Linear Type III</td>
<td>( Q_t = Q_e - \left(\frac{1}{k_2Q_e}\right)Q_t )</td>
<td>( Q_t ) vs. ( Q_t )</td>
</tr>
<tr>
<td>Linear Type IV</td>
<td>( \frac{Q_t}{Q_e} = k_2Q_e^2 - k_2Q_e Q_t )</td>
<td>( \frac{Q_t}{Q_e} ) vs. ( Q_t )</td>
</tr>
</tbody>
</table>
The pseudo-first order model illustrates that the change in concentration is proportional to the time variable which only depends on the concentration. The pseudo-first order was applied mostly for the initial stage in the process of adsorption rather than a long time span as with second order. As mentioned, the rate-limiting step was denoted as the adsorption and applied for the prediction in behavior for a long period of time. In the second-order process, the rate of adsorption was based on the adsorption capacity instead of the adsorbate concentration [57].

For the nonlinear pseudo-first order model, the values can be obtained by plotting $Q_t$ vs. $t$ (in days) with nonlinear regression. On the other hand, the second-order model, by plotting $\frac{1}{Q_t}$ vs. $t$, $\frac{1}{k_2}$ and $\frac{1}{k_2}$ can be calculated by $\frac{y-{\text{intercept}}}{\text{slope}}$ and slope, respectively. Therefore, in this study, the model of pseudo-second order will be analyzed by linear and nonlinear regression; the model or pseudo-first order will be analyzed by nonlinear regression due to the long span of adsorption.

Another kinetics model that can be considered is the simplified Elovich model for $\alpha\beta \gg 1$ which can be expressed as follows [57,58]:

$$Q_t = \beta \ln(\alpha \beta) + \beta \ln t \quad (4)$$

A plot of $Q_t$ vs. $\ln t$ will determine the $\frac{1}{\beta}$ and $\frac{1}{\beta} \ln(\alpha \beta)$ value as the slope and the $y$-intercept, respectively. Therefore, $\ln(\alpha)$ can be calculated by the equation $\ln(\alpha) = \frac{y{-\text{intercept}}}{\text{slope}}$.

The desorption kinetics study can be carried out using the zeroth order, while the research on the isotherm is performed by the Korsmeyer–Peppas (KP) and the Higuchi as shown in Table 2 [59].

**Table 2. Desorption kinetic equations.**

<table>
<thead>
<tr>
<th>Model</th>
<th>Linear</th>
<th>Nonlinear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeroth order</td>
<td>$M_t = k_0 t$</td>
<td>$M_t = k_0 t$</td>
</tr>
<tr>
<td>Korsmeyer–Peppas</td>
<td>$\log\left(\frac{M_t}{M_\infty}\right) = \log(k_{KP}) + n_{KP} \log(t)$</td>
<td>$\frac{M_t}{M_\infty} = (k_{KP})(t^{n_{KP}})$</td>
</tr>
<tr>
<td>Higuchi</td>
<td>$\log(M_t) = \log(k_H) + 0.5 \log(t)$</td>
<td>$M_t = k_H t^{1/2}$</td>
</tr>
</tbody>
</table>

The zeroth order model illustrates that the release rate of MB does not depend on the concentration of MB since there is only the presence of the rate constant $k_0$ and released mass fraction at time $t$ as $M_t$.

The Higuchi model gives information about the release of the MB from the insoluble matrices (planar system). The model is clarified by the function of the square root of time. The model especially fits with the use of polymers that do not swell when interacting with water.

The “Power law” or Korsmeyer–Peppas model describes the release of the adsorbate from polymeric matrices, which is developed from the Higuchi model. The study of MB release is easier with the Korsmeyer–Peppas model when the release mechanism is not well-known or there are several release phenomena included [60].

The intraparticle diffusion rate can be calculated using Weber’s intraparticle diffusion model [61,62]:

$$Q_t = 1 + k_i t^{1/2} \quad (5)$$

where $k_i$ and $I$ are the intraparticle diffusion rate constant (mg g$^{-1}$ min$^{-1/2}$) and constant (mg g$^{-1}$), respectively. By plotting $Q_t$ vs. $t^{1/2}$, $k_i$ and $I$ can be obtained via the value of the linear slope and $y$-intercept, respectively. If $I = 0$, the adsorption process is the intraparticle diffusion.
The chi-square test was computed for the adsorption kinetic models to evaluate which kinetic model the experimental data best suited. Following are the steps to calculate the chi-square test:

\[
\chi^2 = \sum_{i=1}^{m} \left( \frac{Q_{l,exp} - Q_{l,calc}}{Q_{l,calc}} \right)^2
\]

(6)

The \( \chi^2 \) value will help to determine the similarity of isotherm theory and the experimental data. The smaller \( \chi^2 \) is, the closer the data from the theory is to the experimental data.

3. Results and Discussion

3.1. Characterization of SPION/PVA/GO

According to the FE-SEM, FTIR, and XRD, the SPION/PVA/CS/GO material was effectively manufactured. The FE-SEM images allow for the visualization of the material’s morphology. The FTIR can be used to confirm the type of iron oxide nanoparticles and the bonding of SPION/PVA/CS/GO. The iron oxide nanoparticles may also have shown superparamagnetic iron oxide nanoparticle characteristics, according to the XRD analysis. Additionally, the BJH and VSM can be used to assess the pore size and magnetic type of the SPION, respectively.

3.2. FE-SEM Analysis

For the investigation and analysis of micro- and nanoparticle imaging characterization of solid objects, scanning electron microscopes (SEMs) are among the most frequently used instruments. One microscope that uses electrons with a negative charge in place of light is the FE-SEM. A field emission source releases these electrons [63]. By moving in a zigzag motion, electrons scan the object. The iron oxide nanoparticles (IONPs) were characterized by FE-SEM (Hitachi SU8000), as shown in Figure 1.

Figure 1. (a) FE-SEM image of IONPs in 200 nm. (b) The normal size distribution of IONPs.

The combination of the materials was clearly depicted in the figure, and the agglomeration was evident, similar to a prior study, which might be avoided by employing an ultrasonic probe. The size distribution (as shown in Figure 1b) and average size of IONPs were calculated from the FE-SEM picture, ImageJ software, and Origin software, and were found to be 13.6 ± 1.9 nm, which is consistent with earlier publications [64–66].

As shown in Figure 2a–d, the morphology of IONPs/PVA/CS/GO can be seen. As the figure was zoomed out, the SPION cluster can be seen clearer. Moreover, the layers of GO sheets in the background can be seen as well. Hence, from Figure 2, IONPs can be seen...
dispersing on GO. However, the polymers (PVA and CS) could not be seen clearly. This leads to the XRD and FTIR analysis to confirm the existence of PVA and CS in the composite.

**Figure 2.** FE-SEM images of IONPs/PVA/CS/GO 1:1:2 at (a) 200 nm, (b) 200 mm, (c) 1 µm, (d) 500 mm.

### 3.3. XRD Analysis

For the primary characterization of material parameters such as crystal structure, crystallite size, and strain, X-ray diffraction (XRD) was employed. The X-ray diffractograms of IONPs, as shown in the diagram (Figure 3), demonstrated that the nanoparticles exhibit peaks at 2θ positions of 18.80°, 30.25°, 35.58°, 43.22°, 53.69°, 57.18°, and 62.79° that correlate to magnetite, which led to the conclusion that IONPs were SPIONs. These peaks correspond to their *hkl* indices of (220), (311), (400), (422), (511), and (440), which is similar to the literature [67–69]. When comparing the other materials’ diffractograms in Figure 3 with the corresponding peaks, SPIONs, polymers, and GO have successfully combined.

The average size of the particles was determined to be 11.65 nm using Scherrer’s equation $D = k\lambda / \beta \cos \theta$ with 2θ specified at 35.58°, constant k of the crystal at 0.89, and lambda $\lambda$ at 0.154 [70]. It can be inferred from that result that the average particle size of the samples falls between 11.64 and 15.5 nm, corresponding to the FE-SEM analysis (13.6 ± 1.9 nm) and other publications [64–66].
3.4. FTIR Analysis

FTIR is an effective instrument to quantitate and determine the functional groups of the nanoparticles, which confirm the final structure of the material. After synthesizing SPION/PVA/CS/GO, the sample was analyzed by FT-IR analysis (Bruker Sensor 27, Ettlingen, Germany) as given in Figure 4 and Table 3.

As shown in Figure 4 and Table 3, the peaks of SPIONs, PVA, CS, and GO were analyzed. The intensity of O-H stretching was outstanding because of the low concentration of the diluted component in water. Nevertheless, the distinguished peak of each component can be identified such as the vibration Fe-O of SPIONs, CH$_2$ asymmetric stretching of PVA, N-H primary bend of CS, and C-O-C stretching of GO.

The FTIR spectra of SPIONs presented four different peaks at 3412, 1622, 1402, and 579 cm$^{-1}$ which correspond to OH stretching, carboxyl C=O stretching, CH$_3$ deformation, and vibration Fe-O, respectively.
Table 3. FTIR spectra of SPION, PVA, CS, GO, and SPION/PVA/CS/GO.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Peaks (cm(^{-1}))</th>
<th>Functional Group</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPION</td>
<td>3412</td>
<td>O-H stretching</td>
<td>[71,72]</td>
</tr>
<tr>
<td></td>
<td>1622</td>
<td>Carbonyl C=O stretching band</td>
<td>[71,72]</td>
</tr>
<tr>
<td></td>
<td>1402</td>
<td>CH(_3) deformation</td>
<td>[71,73]</td>
</tr>
<tr>
<td></td>
<td>579</td>
<td>Vibration Fe-O</td>
<td>[74]</td>
</tr>
<tr>
<td>PVA</td>
<td>3416</td>
<td>O-H stretching</td>
<td>[75–77]</td>
</tr>
<tr>
<td></td>
<td>2920</td>
<td>CH(_2) asymmetric stretching</td>
<td>[75–77]</td>
</tr>
<tr>
<td></td>
<td>1738</td>
<td>C=O carbonyl stretching</td>
<td>[75–77]</td>
</tr>
<tr>
<td></td>
<td>1267</td>
<td>C-H wagging</td>
<td>[75–77]</td>
</tr>
<tr>
<td></td>
<td>1097</td>
<td>C-O stretching</td>
<td>[75–77]</td>
</tr>
<tr>
<td>CS</td>
<td>3437</td>
<td>O-H stretching</td>
<td>[78,79]</td>
</tr>
<tr>
<td></td>
<td>1647</td>
<td>C-O (amide) and N-H primary amine bends</td>
<td>[78,79]</td>
</tr>
<tr>
<td></td>
<td>1379</td>
<td>C-O starch in the primary alcoholic group</td>
<td>[78,79]</td>
</tr>
<tr>
<td></td>
<td>1082</td>
<td>Free amino group -NH(_2) at glucosamine C(_2) position</td>
<td>[78,79]</td>
</tr>
<tr>
<td>GO</td>
<td>3409</td>
<td>O-H stretching</td>
<td>[51,80–82]</td>
</tr>
<tr>
<td></td>
<td>1628</td>
<td>Carboxyl C=O stretching band</td>
<td>[51,80–82]</td>
</tr>
<tr>
<td></td>
<td>1209</td>
<td>C-O-C stretching</td>
<td>[51,80–82]</td>
</tr>
<tr>
<td></td>
<td>1055</td>
<td>C-O stretching vibration</td>
<td>[51]</td>
</tr>
<tr>
<td>SPION/PVA/CS/GO</td>
<td>3420</td>
<td>O-H stretching</td>
<td>[71,72,75–77]</td>
</tr>
<tr>
<td></td>
<td>1128</td>
<td>Free amino group -NH(_2) at glucosamine C(_2) position or C-O-C stretching</td>
<td>[78,79]</td>
</tr>
<tr>
<td></td>
<td>1066</td>
<td>C-O stretching</td>
<td>[75–77,83]</td>
</tr>
<tr>
<td></td>
<td>577</td>
<td>Vibration Fe-O</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>446</td>
<td>Vibration Fe-O</td>
<td>[74]</td>
</tr>
</tbody>
</table>

The vibrational spectra of PVA showed the appearance of five peaks. First, O-H stretching is related to the 3416 cm\(^{-1}\) peak, while CH\(_2\) asymmetric and C=O stretching are expected to be at 2920 and 1738 cm\(^{-1}\), accordingly. C-H wagging at the peak of 1267 cm\(^{-1}\) and C-O stretching at 1097 cm\(^{-1}\) can be observed.

The band of absorption related to CS is given in Figure 4 and the vibrations at diverse wavelengths can be identified as follows: O-H stretching at 3437 cm\(^{-1}\), CO (amide) and NH primary amine bends at 1647 cm\(^{-1}\), C-O starch in the primary alcoholic group at 1379 cm\(^{-1}\), and, lastly, the free amino group -NH\(_2\) at the glucosamine C\(_2\) position at 1082 cm\(^{-1}\) can be observed.

The characteristic absorption of GO had been exhibited by the presence of peaks shown in Figure 4. To be more specific, the functional groups can be visually seen at specific wavelengths such as O-H stretching at 3409 cm\(^{-1}\), a carboxyl group stretching vibration at 1628 cm\(^{-1}\), and a C-O-C as well as C-O stretching band at 1209 and 1055 cm\(^{-1}\), correspondingly.

For the nanocomposites—SPION/PVA/CS/GO, the peaks shown in the spectrum are nearly equivalent to those of every single component’s spectrum with some slight shifts. Specifically, the peak at 3420 cm\(^{-1}\) can be denoted as O-H stretching of every component while the one at 1626 cm\(^{-1}\) can be related to the carbonyl stretching vibration of SPIONS and GO. Furthermore, the absorption band at 1128 cm\(^{-1}\) may correspond to the free amino group at the glucosamine C\(_2\) position of CS or C-O-C stretching of GO. The peak at 1066 cm\(^{-1}\) can be the C-O stretching of the PVA or GO component. Last but not least,
the vibration of Fe-O of SPIONs can also be observed in the spectrum of nanocomposites at 577 and 446 cm\(^{-1}\). Because of the surfactant on the particles’ surface, the peaks may have shifted a couple of cm\(^{-1}\) compared to compositional peaks in FTIR spectra of the others. As a result, this FTIR analysis confirmed that the IONPs were in fact SPIONs, and the compound was successfully combined.

3.5. VSM Analysis

As shown in Figure 5, the VSM curves showed that IONPs were once again proven to be superparamagnetic [84–89].

![Figure 5. VSM result of SPION and SPION/PVA/CS/GO.](image)

Similarly, after modifying the surface of SPIONs with PVA, CS, and GO, the superparamagnetism was still intact despite the huge decreases in magnetization due to the possibility of the polymer shell coatings.

When a sample vibrates perpendicular to a uniform magnetizing field, VSM is a versatile approach for determining the magnetic moment of the sample [90,91]. VSM was used to measure the magnetic characteristics of SPIONs and SPION/PVA/CS/GO at room temperature. All magnetization curves, as can be observed, have s-shaped shapes across the applied magnetic field and no remanence or coercivity, indicating that they all exhibit superparamagnetic activity [92]. The saturation magnetization (Ms) of SPIONs was 70.83, which is consistent with earlier studies [74,93,94]. When PVA/CS/GO were added, the Ms fell from 70.83 to 10.94. These findings indicate that polymer coatings could lower the Ms of nanoparticles. This may be because a thicker layer of polymer is produced on the surface of the magnetic nanoparticles [95]. Hence, the proposed structure of SPION/PVA/CS/GO was shown in Figure 6.

![Figure 6. Proposed structure of SPION/PVA/CS/GO.](image)
3.6. BJH Analysis

According to Figure 7, the adsorption–desorption isotherm demonstrates that the volume of adsorbate uptake begins at 0.1 \( p/p_0 \) and increases at higher \( p/p_0 \).

![Graph showing BJH Analysis](image)

Figure 7. The BET result of relative pressure over volume of SPION/PVA/CS/GO.

The mesoporous structure associated with a small amount of micropores was indicated by a type IV isotherm in the adsorption/desorption isotherm of SPION/PVA/CS/GO [96]. It is distinctive, with pores that are between 2 and 50 nm in size [97]. The BJH average pore diameter of the synthesized SPION/PVA/CS/GO sample is summarized in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m(^2)/g)</td>
<td>5.8</td>
<td>7.5</td>
</tr>
<tr>
<td>Pore diameter (Angstrom)</td>
<td>10</td>
<td>126</td>
</tr>
<tr>
<td>Pore volume (cm(^3)/g)</td>
<td>0.017</td>
<td>0.017</td>
</tr>
</tbody>
</table>

As shown in Table 4, the result of BJH and BET indicates the surface area of the initial sample is 5.8 m\(^2\)/g. The adsorption–desorption isotherm shows that the adsorbate uptake starts at 0.1 \( p/p_0 \) and the volume adsorbed increased at higher \( p/p_0 \). Furthermore, total pore volume and the mean pore diameter of SPION/PVA/CS/GO sample were 0.017 cm\(^3\)/g, and 10 Å, respectively.

3.7. Adsorption

As shown in Table 5, the values of loading amount (\( Q_t \)), percent loading capacity (%LC), and entrapment efficiency (%EE) for the adsorption process were calculated throughout each hour’s interval based on the results from UV-Vis spectrometry at the wavelength of 664 nm of MB and using the preceding calculation formulas.
Table 4. BJH and BET analysis of SPION/PVA/CS/GO sample.

<table>
<thead>
<tr>
<th>Initial MB Concentration (mg/mL)</th>
<th>$Q_t$ (mg/g)</th>
<th>%LC (%)</th>
<th>%EE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>20.934 ± 0.268</td>
<td>2.093 ± 0.027</td>
<td>83.737 ± 1.072</td>
</tr>
<tr>
<td>0.02</td>
<td>28.768 ± 1.18</td>
<td>2.877 ± 0.118</td>
<td>86.304 ± 3.54</td>
</tr>
<tr>
<td>0.025</td>
<td>36.385 ± 0.095</td>
<td>3.638 ± 0.009</td>
<td>87.324 ± 0.227</td>
</tr>
</tbody>
</table>

As shown Figure 8, after 24 h at room temperature, in three different concentrations, only 24.432%, 47.066%, and 53.962% of MB were adsorbed according to the increase in concentrations of 0.015, 0.020, and 0.025 mg/mL, respectively.

Figure 8. (a) Adsorption amount over time. (b) Entrapment efficiency over time. (c) Loading capacity over time.

This shows that concentration has significant effects on the adsorption capacity. According to Dai and Huang and others, the greater MB concentration and an abundance of free adsorption sites accessible during the first adsorption phase caused the adsorption capacity to rise quickly initially before rising slower until equilibrium [98].

After 48 h at room temperature, the %EE increased by at least 3% per concentration. It can be shown through two time intervals that the difference in %EE between the two concentrations of 0.015 and 0.020 mg/mL is rather significant (22%); however, the difference between 0.020 and 0.025 mg/mL is roughly 6%.

However, there is a noticeable variation in the growth of %EE in three concentrations after 72 h. In contrast to the increase of 0.025 mg/mL, the %EE for 0.015 and 0.020 mg/mL grew by around 6% over the course of 24 h rather than 3% as before. Furthermore, it was discovered that the conversion of methylene blue to the MB⁺ cationic form causes the adsorption of methylene blue to slow down over time based on the values of adsorption amount and contact time [99]. However, the highest obtained capacity after 312 h was only 36.385 ± 0.095 mg/g when the initial concentration of MB was 0.025 mg/mL. This result can be quite lower than the values in Table 5, due to some differences in conditions, such as temperature, concentration, adsorption time, and optimal ratio of the substances.

According to Table 6, for the entrapment efficiency percent, the slope of 0.015 mg/mL is 0.2064, while the other two, 0.020 and 0.025 mg/mL, are 0.1387 and 0.1175, respectively. It seems to show that the lower the concentration is, the steeper the slope is. The higher the concentration is, the larger the y-intercept is, indicating that the initial entrapment efficiency was larger at a higher concentration. For the time being, MB samples with a
concentration of 0.020 mg/mL or higher are appropriate for circumstances requiring a high initial entrapment efficiency of 45%.

Table 6. Linear regression of $Q_t$, %EE, and LC%.

<table>
<thead>
<tr>
<th>Relationship</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>%LC 0.015 mg/mL MB = 0.0052(time) + 0.4721</td>
<td>0.9956</td>
</tr>
<tr>
<td>%LC 0.020 mg/mL MB = 0.0046(time) + 0.9893</td>
<td>0.9893</td>
</tr>
<tr>
<td>%LC 0.025 mg/mL MB = 0.00049(time) + 2.129</td>
<td>0.9959</td>
</tr>
<tr>
<td>$Q_t$ 0.015 mg/mL MB = 0.0049(time) + 21.29</td>
<td>0.9959</td>
</tr>
<tr>
<td>$Q_t$ 0.020 mg/mL MB = 0.0462(time) + 15.079</td>
<td>0.9893</td>
</tr>
<tr>
<td>$Q_t$ 0.025 mg/mL MB = 0.00516(time) + 4.7239</td>
<td>0.9959</td>
</tr>
<tr>
<td>%EE 0.015 mg/mL MB = 0.2064(time) + 18.896</td>
<td>0.9956</td>
</tr>
<tr>
<td>%EE 0.020 mg/mL MB = 0.1387(time) + 45.238</td>
<td>0.9893</td>
</tr>
<tr>
<td>%EE 0.025 mg/mL MB = 0.1175(time) + 51.097</td>
<td>0.9959</td>
</tr>
</tbody>
</table>

As shown in Table 7, using the pseudo-second order and simplified Elovich kinetic model at different initial methylene blue concentrations, the adsorption rate can be determined and the loading amount at equilibrium can be determined as well.

Table 7. Kinetic models of SPION/PVA/CS/GO (1:0.5:0.5:2 w/w/w) adsorbing methylene blue after 312 h.

<table>
<thead>
<tr>
<th>Initial MB Concentration (mg/mL)</th>
<th>0.015</th>
<th>0.020</th>
<th>0.025</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-first order nonlinear</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$ (mg MB (g particles)$^{-1}$</td>
<td>13.315</td>
<td>22.265</td>
<td>29.011</td>
</tr>
<tr>
<td>$k_1$ (g mg$^{-1}$ day$^{-1}$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$X^2$</td>
<td>15.755</td>
<td>8.924</td>
<td>6.349</td>
</tr>
<tr>
<td><strong>Pseudo-second order nonlinear</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$ (mg MB (g particles)$^{-1}$</td>
<td>13.321</td>
<td>22.265</td>
<td>29.011</td>
</tr>
<tr>
<td>$k_2$ (g mg$^{-1}$ day$^{-1}$)</td>
<td>171.82</td>
<td>56.22</td>
<td>915.92</td>
</tr>
<tr>
<td>$X^2$</td>
<td>15.756</td>
<td>8.924</td>
<td>6.349</td>
</tr>
<tr>
<td><strong>Pseudo-second order linear</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$</td>
<td>38.17</td>
<td>31.25</td>
<td>27.40</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.017</td>
<td>0.015</td>
<td>0.006</td>
</tr>
<tr>
<td>R²</td>
<td>0.980</td>
<td>0.976</td>
<td>0.864</td>
</tr>
<tr>
<td><strong>Simplified Elovich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (mg/(g day))</td>
<td>10.752</td>
<td>76.904</td>
<td>245.24</td>
</tr>
<tr>
<td>$\beta$ (mg/g)</td>
<td>0.182</td>
<td>0.196</td>
<td>0.190</td>
</tr>
<tr>
<td>R²</td>
<td>0.871</td>
<td>0.930</td>
<td>0.886</td>
</tr>
</tbody>
</table>

From Table 7, the R² values of the linear plot at MB concentrations of 0.015, 0.020, and 0.025 mg/mL for the pseudo-second order were 0.980, 0.976, and 0.864, respectively. Compared to the pseudo-first order, nonlinear pseudo-second order, and the simplified Elovich model, the linear pseudo-second order can be a superior fit for SPION/PVA/CS/GO adsorbing methylene blue, as shown in Figure 9.
The intraparticle diffusion model of SPION/PVA/CS/GO adsorbing methylene blue. Figure 10.

As shown in Figure 10, the intraparticle diffusion can be used to fit the adsorption capacities of MB onto SPION/PVA/CS/GO. The values of $k_2$ and $I$ were calculated, as shown in Table 8.
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Table 8. The intraparticle diffusion model of SPION/PVA/CS/GO adsorbing methylene blue.

<table>
<thead>
<tr>
<th>Initial MB Concentration (mg/mL)</th>
<th>kI</th>
<th>I</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>5.629</td>
<td>-0.892</td>
<td>0.9614</td>
</tr>
<tr>
<td>0.020</td>
<td>5.132</td>
<td>9.836</td>
<td>0.9896</td>
</tr>
<tr>
<td>0.025</td>
<td>5.364</td>
<td>15.908</td>
<td>0.9701</td>
</tr>
</tbody>
</table>

However, the diffusion pattern in the particle demonstrated that I ≠ 0, as illustrated in Table 8. This indicated that this adsorption involves higher intraparticle diffusion. The only straightforward explanation for a negative intercept value was the result of the combined impacts of surface response control and film diffusion processes [102–105].

The methylene blue adsorption mechanism of SPION/PVA/CS/GO may also result from hydrogen bonding between negatively charged surfaces and positively charged methylene blue during electrostatic interaction, and the π−π* stacking with the aromatic ring of methylene blue [106,107]. These mechanisms are in addition to film diffusion, intraparticle diffusion, chemisorption, and physical adsorption. Additionally, boundary layer diffusion and external diffusion can regulate the adsorption mechanisms. Thus, in addition to the rate-controlling step, various kinetic models and intraparticle diffusion also played a role in the adsorption’s control [108,109].

3.8. Desorption

The release percentage fluctuates and is dependent on the initial loading circumstances, such as temperature and initial MB concentration, as shown in Table 9, even though MB is released at a constant temperature and pH of 3.8.

Table 9. The percentage of release average of MB from SPION/PVA/CS/GO after 30 days.

<table>
<thead>
<tr>
<th>Concentration MB mg/mL</th>
<th>Mass MB mg Initial Average</th>
<th>% Release Average</th>
<th>% Release Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>0.63</td>
<td>4.88</td>
<td>0.35</td>
</tr>
<tr>
<td>0.02</td>
<td>0.83</td>
<td>8.94</td>
<td>0.66</td>
</tr>
<tr>
<td>0.025</td>
<td>1.09</td>
<td>5.25</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The release percentage might rise when the initial loaded MB concentration does as well, although the highest release percentage was seen at 0.02 mg/mL of loaded MB. To examine the desorption mechanism, the desorption kinetics were analyzed, as shown in Figure 11.

Figure 11. The releasing kinetics after 30 days of MB on SPION/PVA/CS/GO.
As shown in Table 10, combining cumulative release percentage, desorption kinetics models, and the chi-square values, the best-fitted kinetic models were determined.

Table 10. The Korsmeyer–Peppas, 0th order, and Higuchi calculation for the desorption of SPION/PVA/CS/GO for MB.

<table>
<thead>
<tr>
<th>Korsmeyer–Peppas (KP)</th>
<th>0th Order</th>
<th>Higuchi</th>
<th>Chi-Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>k</td>
<td>n</td>
<td>k</td>
<td>k</td>
</tr>
<tr>
<td>0.015</td>
<td>1</td>
<td>0.5</td>
<td>0.003</td>
</tr>
<tr>
<td>0.02</td>
<td>1</td>
<td>0.5</td>
<td>0.003</td>
</tr>
<tr>
<td>0.025</td>
<td>1</td>
<td>0.5</td>
<td>0.003</td>
</tr>
</tbody>
</table>

According to Table 10, the Korsmeyer–Peppas models produce release exponents with values of 0.5, indicating that anomalous diffusion or non-Fickian diffusion—a combination of diffusion and case-II relaxation—is the releasing mechanism. Additionally, the release kinetics are time-dependent with the values of $n_{KP}$.

However, Korsmeyer–Peppas and Higuchi had the largest $\chi^2$ values among the three models, all of which were more than 1, indicating that the two models did not accurately reflect the experimental results. The 0th order has the least value of $\chi^2$. Therefore, the best-fitted model for the desorption in this investigation was of the 0th order. According to the 0th order, the rate is unaffected by changes in the concentration of the reactants.

4. Conclusions

The material can be employed as methylene blue adsorbents by coating superparamagnetic iron oxide nanoparticles with polyvinyl alcohol–chitosan polymer and graphene. The synthesized SPION has a diameter range of 13.57 ± 1.93 nm. Depending on the initial concentrations of methylene blue, which were 0.015, 0.020, and 0.025 mg/mL, the entrapment efficiency after 13 days in % was 81.82 ± 0.70, 86.27 ± 4.02, and 87.00 ± 0.16; the loading capacity in % was 2.093 ± 0.027, 2.877 ± 0.118, and 3.638 ± 0.009; the loading amount at time in mg/g was 20.934 ± 0.268, 28.768 ± 1.18, and 36.385 ± 0.095, respectively. The linear pseudo-second order was the fitted kinetic model for the adsorption. The pseudo-second order kinetic model predicted that methylene blue would chemisorb to the surface of the particles through the transfer of electrons (valence forces) between SPION/PVA/CS/GO and methylene blue. Total pore volume and the mean pore diameter of SPION/PVA/CS/GO sample were 0.017 cm$^3$/g and 9.998 Å, respectively, with type IV of BET result indicating that the sample was mesoporous.

The cumulative release percentage ranged from 4.88 ± 0.35% to 8.94 ± 0.66% when MB was released at pH 3.8 after 30 days. A concentration of 0.02 mg/mL had the most release percentage among three concentrations tested in this study. The zeroth order model was the best-fitted model for desorption of MB on SPION/PVA/CS/GO, which defined that the rate is unaffected by changes in the concentration of the reactants.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

- $C_0$: initial concentration (mg/mL)
- $C_t$: concentration at time $t$ (mg/mL)
- $V$: sample volume (mL)
- $m$: mass of the nanoparticles (g)
- $Q_e$: amount of MB absorbed per unit mass of nanoparticle at the equilibrium (mg/g)
- $Q_t$: amount of MB absorbed per unit mass of nanoparticle at time $t$ (mg/g)
- $\alpha$: theoretical initial adsorption rate
- $\beta$: theoretical desorption rate
- $k_1$: pseudo-first order rate constant ($s^{-1}$)
- $k_2$: pseudo-second order rate constant ($s^{-1}$)
- $k_a$: respective rate constant for adsorption
- $k_d$: respective rate constant for desorption
- $K_L$: constant related to the free adsorption energy and the reciprocal of the concentration at which half saturation of the adsorbent is reached
- $Q^0$: theoretical adsorption capacity (mg/g)
- $k_0$: constant mass fraction at a time ($t$) release
- $M_t$: released mass fraction at a time ($t$)
- $k_{KP}$: Korsmeyer–Peppas release rate constant
- $k_H$: Higuchi release rate constant
- $n_{KP}$: Korsmeyer–Peppas release exponent factor
- $\chi^2$: chi-square value
- $C_e$: equilibrium aqueous-phase concentration adsorbate (mg/L)
- $\theta$: fractional surface coverage
- $Q_m$: quantity of adsorbate adsorbed in a single monolayer (mg/g)
- $M_\infty$: the amount of MB at equilibrium state

References


