Research Article

Investigating Methylene Blue Removal from Aqueous Solution by Cysteine-Functionalized Mesoporous Silica

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In this study, mesoporous silica nanoparticles (MSNs) were synthesised using the Stober method and functionalised with cysteine (MSN-Cys) for removal of Methylene Blue (MB) from aqueous solution using the batch method. The adsorbent nanoparticles were characterised by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), FTIR, BET, and TGA. Several influential factors on the adsorption of MB onto the surface of MSN-Cys particles were investigated, including pH, initial concentration, and contact time. The adsorption capacity of MB from aqueous solution increased from circa 70 mg/g MSN-Cys in acidic media to circa 140 mg/g MSN-Cys in basic media. Adsorption isotherms and kinetic models of adsorption were used to clarify the adsorption process. The measured adsorption isotherm was fitted with a Freundlich model for all solutions, and the kinetic model was determined to be pseudo-second-order.

1. Introduction

Dyes are widely used in many industries, as food additives, colorings, printing, plastics, and leathers [1, 2]. Dyes are chemically stable and difficult to decompose biologically, especially when they are present in water [3–7]. A small amount of dye can change the colour of water and decrease sunlight penetration, which prevents the growth of water bacteria [3, 4]. Moreover, the aromatic rings of most dyes make them toxic and carcinogenic to humans [8, 9].

Various physical, biological, and chemical methods have been used to remediate organic dyes from wastewater, such as photodegradation, microwave catalysis, biodegradation [10], coagulation-flocculation [10], oxidation or ozonation [11, 12], membrane separation [13], and adsorption. Adsorption is based on the conversion of pollutants from a liquid to a solid phase. The adsorption process has recently received attention due to its simplicity, inexpensiveness, efficacy, high capacity, and ease of regeneration [14]. Adsorption has been widely applied to porous materials such as activated carbons [15, 16], metal-organic frameworks (MOF) [17, 18], and mesoporous silica [19, 20].

Mesoporous silica nanoparticles (MSNs) are a porous material that has unique properties, such as a large surface area and pore volume, uniform pore size, high rigidity, thermal stability, low cost, being environmentally friendly, and facile modification [21–26]. MSNs have been used in the water purification process to remove dyes [27–29]. The adsorption of dyes on mesoporous silica is achieved by chemical/physical bonding between the active groups on the surface of the MSNs and the dye molecules. Ramezani and Zare-Dorabei reported the incorporation of Zr into SBA-15 (Zr-SBA-15) to increase the number of active sites for the removal of Methylene Blue (MB) and Malachite green from water using the solid-phase extraction method [19]. Magnetic mesoporous silica was utilised for removal of MB from water under ultrasound irradiation to accelerate the chemical process [20]. This study found that ultrasound irradiation reduced adsorption time by enhancing the dispersion of nanoparticles in the aqueous solution.

The adsorption efficiency of MSNs could be further improved by functionalising active sites on their surface [21]. Among these functional moieties are amine [27, 30, 31] and carboxylic acid [32–34]. Chueachot et al. reported the removal of MB from an aqueous solution using amine-
functionalised mesoporous silica nanospheres via the batch method [27]. The maximum adsorption capacity of MSN-NH$_2$ was found to be 35 mg/g in basic media. Tsai et al. reported the functionalisation of mesoporous silica SBA-16 with carboxylic acid as an effective adsorbent for the removal of cationic dyes due to electrostatic interaction between dyes and the nanoparticle surface [34]. Ho et al. prepared MSNs functionalised with amino and carboxylic groups for the removal of acid blue 25 and MB from wastewater [35]. MSN-COOH was found to be a good adsorbent for MB, with excellent adsorption capacity and selectivity.

Amino acids consist of an amine and a carboxyl group attached to an alpha-carbon atom. There are a number of studies in which a silica surface has been modified with amino acids and used for medical applications [36, 37] or removal of heavy metals [38, 39]. Silica nanoparticles have been fabricated with the amino acid cysteine for removal of uranium (VI) from aqueous solution with high adsorption efficiency [38].

The aim of this study was to prepare nanostructured materials that have two functional groups (amine and carboxylic acid groups) as effective moieties to remove toxic ionic dyes. At pH values below the pKa of carboxylic acid functional groups, nanoparticles exhibited cationic character, which reduced the adsorption capacity of cationic dyes. At pH values above the pKa of amine groups, the nanomaterials showed anionic character, which increased the amount of dye adsorbed on the surface. To my knowledge, very few studies have reported the utilisation of amino acid-modified MSNs for dye removal. In the present work, cysteine-functionalised MSNs were successfully fabricated through a three-step modification process (Figure 1) and characterised by FTIR, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), BET, and TGA. These materials were then applied as absorbers for removal of MB, a cationic dye, from aqueous solution. The effects of pH, the initial concentration, and contact duration were studied on the adsorption of MB. Moreover, the adsorption process was modelled using adsorption isotherms and kinetic models.

2. Materials and Methods

2.1. Materials. Deionized (DI) water was obtained from Elga Pure Nanopore system. N-Cetyltrimethylammonium bromide (CTAB, 98%, Germany), ammonium hydroxide (28 wt%, Germany), tetraethyl orthosilicate (TEOS, 98%, Germany), methanol (99.8% HPLC grade, UK), ethanol (99.8%, HPLC grade, UK), hexane (99.9%, Germany), and 3-glycidoxypropyltrimethoxysilane (GPTS, 97%, USA) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 36%, UK) and toluene (99.9%, Germany), tetraethyl orthosilicate (TEOS, 98%, Germany), and 3-glycidoxypropyltrimethoxysilane (GPTS, 97%, USA) were purchased from Fisher Scientific. Cysteine (98%, USA) was obtained from Acros. All chemicals were used as received.

2.2. Preparation of MSNs. CTAB (0.5 g) was dissolved in DI water (80 mL), and then 3.5 mL of ammonium hydroxide was added at 37°C under magnetic stirring. A mixture of TEOS (2.5 mL) and n-hexane (5 mL) was added to this solution over 30 min. MSNs were collected after 15 h by centrifugation, then washed with DI water and ethanol, and dried at 120°C for 1 h. MSNs (1.5 g) were dispersed in a solution of HCl (4.5 mL, 12M) in 80 mL methanol under reflux. The products were obtained after centrifugation and then washed with ethanol [40].

2.3. Synthesis of Epoxy-Functionalised MSNs (MSN-GPTS). MSNs (1.5 g) were dispersed in a solution of GPTS (0.4 mL) in toluene (60 mL) and heated under reflux for 15 h. The sample was collected by centrifugation and then washed with toluene and ethanol.

2.4. Synthesis of Cysteine-Functionalised MSNs (MSN-Cys). 1 g of MSN-GPTS was placed in a flask with 150 mL of alkaline aqueous solutions (pH 8.5), and then cysteine (1.5 g) was added to the suspension. The mixture was ultrasonicated for 15 min and then heated at 65°C in an oil bath equipped with a magnetic stirrer for 24 h [36].

2.5. Adsorption Studies. The adsorption behaviour of MB onto MSN-Cys was studied by varying contact time, pH, and initial concentrations. A series of concentrations of Methylene Blue in DI water were prepared (50, 80, 100, 120, and 150 mg/L). In each experiment, 10 mg of MSN-Cys was suspended in 10 mL of MB solution and stirred (150 rotations (r)/min) at room temperature. Nanomaterials were obtained by centrifugation. MB content was measured by UV-vis spectrophotometry at 663 nm. The adsorption capacity (q_e) was estimated by the following equation:

\[
q_e = \frac{(C_o - C_e)V}{m},
\]

where $C_o$ and $C_e$ represent the initial concentration (mg/L) and concentration at equilibrium (mg/L) for MB, respectively, $q_e$ represents the adsorption capacity at equilibrium in mg/g, and $m$ and $V$ represent the mass of MSN-Cys (g) and the volume of MB solution (L), respectively.

2.6. Adsorption Isotherms. Three different isotherm models were used to fit the adsorption of MB on MSN-Cys. A linear form of the Langmuir model isotherm is represented by the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m},
\]

where $C_e$ and $q_e$ represent the concentration of MB solution (mg/L) and the adsorption capacity (mg/g) at equilibrium, respectively, $q_m$ represents the maximum adsorption capacity (mg/g) of MB onto the adsorbent, and $K_L$ represents the Langmuir constant (L/mg) related to energy of adsorption [41]. A linear form of the Freundlich model isotherm is represented by the following equation:
\[ \log q_e = \frac{1}{n} \log C_e + \log K_F, \]

where \( K_F \) represents the Freundlich adsorption constant \((\text{mg/g})/(\text{mg/L})^{1/n}\) related to adsorption capacity and \(1/n\) represents the adsorption intensity and surface heterogeneity [42].

The linearised Temkin model isotherm is represented by the following equation:

\[ q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln K_T, \]

where \( R \) is the gas constant \((8.314 \text{ J/mol-K})\), \( b_T \) represents a constant related to the heat of adsorption, \( K_T \) represents the Temkin isotherm constant \((1/\text{L.g})\), and \( T \) is the absolute temperature in Kelvin [43].

2.7. Adsorption Kinetics. The kinetics of MB adsorption onto fabricated material was analysed by pseudo-first-order and pseudo-second-order equations.

2.8. The Pseudo-First-Order Equation. The pseudo-first-order equation is

\[ \log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t, \]

where \( K_1 \) is the rate coefficient of pseudo-first-order adsorption in L/min and \( q_t \) is the adsorption capacity at time \( t \) in mg/g [44].

2.9. The Pseudo-Second-Order Equation. The pseudo-second-order equation is

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t, \]

where \( K_2 \) is the rate coefficient of pseudo-second-order adsorption in g/mg-min [45].

2.10. Measurement and Characterisation

2.10.1. SEM. A JEOL JSM-6380 LA was used to image the fabricated nanoparticles prior to treatment.

2.10.2. TEM. A JEOL JEM-1230 was used to image the sample prepared on a copper grid.

2.10.3. FTIR Spectroscopy. A Thermo Scientific Nicolet IS10 was used to obtain infrared spectra in KBr pellets in the region of 4000–400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

2.10.4. BET Surface Area. A Micromeritics Gemini 2375 volumetric analyser was used to measure the surface area of nanomaterials with nitrogen physisorption isotherms. Each sample was degassed at 120°C overnight prior to analysis. Brunauer–Emmett–Teller (BET) surface areas were identified using experimental points at a relative pressure \( (P/P_0) \) of 0.05–0.25. The total pore volume was calculated from nitrogen gas adsorbed at 0.99 \( P/P_0 \) for each sample. The average pore size distribution was discovered using the Barrett–Joyner–Halenda (BJH) model.

2.10.5. Thermogravimetric Analysis (TGA). A SII TGA 6300 instrument was used to carry out TGA with a 10°C/min heating rate under \( N_2 \).

2.10.6. UV-Vis Spectrophotometer. A Shimadzu (UV-2600) was used to obtain UV spectra of MB solutions.

3. Results and Discussion

MSNs were synthesised by addition of TEOS in an aqueous solution of CTAB in the presence of ammonium hydroxide, with n-hexane as a pore-expanding agent. The template was extracted by the ion exchange method using HCl in methanol to allow reaction within the pores. GPTS was conveniently bonded to the surface of MSNs. The thiol group in cysteine can react with an epoxy group on the surface of MSNs in basic medium, producing MSNs that contained amine and carboxyl groups attached to a single carbon atom (Figure 1).

SEM and TEM were utilised to characterise MSNs. SEM images revealed the size, shape, and distribution of MSNs (Figure 2(a)). MSNs were almost nanospherical particles, ranging in size between 200 and 350 nm. Figure 2(b) shows TEM images of MSNs between 200 and 350 nm, in agreement with the SEM images. Fabricated nanoparticles were mesoporous, with a pore size of approximately 6 nm.

\( N_2 \) adsorption-desorption isotherms were classified as Type IV (for the ordered mesoporous materials) for all samples (Figure 3). Compared with bare MSNs, the hysteresis loop for MSN-GPTS and MSN-Cys moved to a relatively lower pressure; simultaneously, the surface area, pore size, and pore volume all decreased, confirming the modification process (Table 1).

MSNs, MSN-GPTS, and MSN-Cys were characterised by FTIR to confirm modification (Figure 4). Si–O band stretching of the silica network produced a broad peak at
1250–1050 cm$^{-1}$ and 810 cm$^{-1}$ [46]. Peaks at ~2900 cm$^{-1}$ and ~1430 cm$^{-1}$ were assigned to C-H groups of GPTS attached to the MSN surface. After reaction of MSN-GPTS with cysteine, a peak at ~1750 cm$^{-1}$ was attributed to –C=O carbonyl stretching in cysteine [40]. Moreover, it was observed that there was an increase in the intensity of C-H peaks, indicating successful attachment of cysteine.

MSN-Cys contains a carboxylic acid and a primary amine attached to a single carbon atom. The surface of MSN-Cys possesses zwitterionic, cationic, or anionic character, depending on the pH of the solution. At intermediate pH, cysteine-modified MSNs display a zwitterionic character. At a pH below its pKa, all the amine groups remain protonated; while the carboxylic acid groups are no longer ionised; hence, the surface acquires a cationic character, which reduces the capacity of MB adsorption. In contrast, the carboxylic acid groups remain ionised at pH above their pKa, while the amine groups become deprotonated, giving the surface an anionic character, which can increase the amount of MB adsorbed on the surface (Figure 5).

MB removal from aqueous solution by MSN-Cys at room temperature was studied by varying the initial concentration of MB (50, 80, 100, 120, and 150 mg/L). When the concentration of MB was increased, the amount of adsorbed MB increased. As shown in Figure 6, the highest amount adsorbed was observed in basic media, due to the interaction between the ionised surface of MSNs-Cys and MB (a cationic dye), in agreement with Ho et al. [35]. In acidic media, the amount of MB absorbed was the lowest, due to the repulsive forces between the cationic character of the surface and MB [35, 47].
Successful MB adsorption on the surface of MSN-Cys (MB@MSN-Cys) was evaluated by thermogravimetric analysis (TGA) (Figure 7). When treated with cysteine-modified MSNs, about 19% of weight was lost. When MB was adsorbed on MSN-Cys (150 ppm) at pH 1.5 and 7, the weight loss increased to ca. 30%. These results showed that the amount of MB adsorbed on the surface was estimated to be 110 mg/g. The weight loss with MB@MSN-Cys at pH 8.5 was ca. 38%, equating 190 mg/g MB adsorbed. These results were consistent with UV-adsorption studies.

MB adsorption capacities using MSNs with different functional groups have been reported in the literature. Table 2 shows the performance of fabricated nanoparticles (MSN-Cys) compared to different adsorbents. It can be seen that MSN-Cys adsorption capacity is higher than many modifications in previous studies.

The effect of contact duration on the adsorption of MB was investigated (10, 20, 40, 60, 80, 100, 150, or 200 min). Figure 8 illustrates the amount of MB adsorbed by MSN-Cys over time. The initial rate of adsorption increased sharply.
during the first 80 min, which could be ascribed to the large amount of accessible adsorption sites. When contact time reached ca. 80 min, uptake reached maximum MB adsorption. The highest amount of MB adsorbed in basic media was ca. 140 mg/g, compared to 70 mg/g in acidic media due to the negative charge of the material surface.

Adsorption isotherms of MB onto MSN-Cys are plotted in Figure 9, and the relevant parameters are listed in Table 3. The adsorption equilibrium data can be presented by the Freundlich model in all solutions based on the linear regression coefficient ($R^2$), as opposed to the Langmuir or Temkin models. This adsorption behaviour suggests that MB adsorption occurs heterogeneously, and MSN-Cys preferentially occupies the stronger binding sites. The values of parameter $n$ in the Freundlich isotherm are higher than 1 for natural and basic media, which indicate favourable adsorption [53].

Two kinetic models could be used to explain the adsorption mechanism of MB onto the surface of MSN-Cys. The linear curves plotted based on pseudo-first-order and pseudo-second-order kinetic models are shown in Figure 10, and Table 4 summarises the values of $q_e$, $k_1$, $k_2$, and $R^2$. The calculated adsorption from the pseudo-second-order model is closer to the experimental data than that from the pseudo-first-order model in all solutions. Correlation coefficients ($R^2$) are closer to 1 when fitted with the pseudo-second-order model as well, compared to the pseudo-first-order model.

Regenerability of MB@MSN-Cys was also examined to evaluate the performance of the adsorbent. MB@MSN-Cys was washed several times with an aqueous solution (pH = 1.5) under ultrasonication and then centrifuged and

Table 2: Comparison of removal of MB by different functional groups on mesoporous silica surfaces.

| Functional group | $q_e$ (mg g$^{-1}$) | Ref. |
|------------------|---------------------|-----|
| —                | 140                 | [48]|
| —                | 172                 | [20]|
| Amine            | 13                  | [27]|
| Cyclodextrin     | 60                  | [49]|
| Carboxylic       | 470                 | [33]|
| Carboxylic       | 43                  | [50]|
| Chitosan         | 43                  | [51]|
| Sulfonate        | 208                 | [52]|
| Cysteine         | 140                 | This study |

Figure 6: Effect of initial MB concentration on MB removal via MSN-Cys at different pH values (25°C for 200 min, 150 rpm).

Figure 7: Thermogravimetric analysis (TGA) of (a) MSN-Cys, (b) MB@MSN-Cys at pH 1.5 and 150 ppm, (c) MB@MSN-Cys at pH 7 and 150 ppm, and (d) MB@MSN-Cys at pH 8.5 and 150 ppm.
Figure 8: Effect of contact time for MB removal by MSNs-Cys from aqueous solution at (a) pH 1.5, (b) pH 7, and (c) pH 8.5 (150 ppm, 25°C, and 150 rpm).

Figure 9: Continued.
**Figure 9:** Adsorption isotherms fitted to the adsorption equilibrium data: (a–c) the Langmuir model at pH 1.5, 7, and 8.5, respectively; (d–f) the Freundlich model at pH 1.5, 7, and 8.5, respectively; (g–i) the Temkin model at pH 1.5, 7, and 8.5, respectively (150 ppm, 25 °C, and 150 rpm).

**Table 3:** Linear isotherm parameters for MB removal by MSN-Cys at 150 ppm and 25 °C.

| Isotherms | Parameters | pH 1.5 | pH 7 | pH 8.5 |
|-----------|------------|--------|------|--------|
| Langmuir  | q_m (mg/g) | 61.35  | 250  | 384    |
|           | K_L (L/mg) | 0.03   | 0.01 | 0.05   |
|           | R^2        | 0.87   | 0.70 | 0.85   |
| Freundlich| K_F ((mg/g)/(mg/L)^1/n) | 0.05 | 2.10 | 3.90 |
|           | N          | 0.60   | 1.75 | 3.66   |
|           | R^2        | 0.98   | 0.97 | 0.98   |
| Temkin    | b_T        | 34.70  | 56.19| 37.69  |
|           | K_T (L/g)  | 0.04   | 0.15 | 0.99   |
|           | R^2        | 0.93   | 0.90 | 0.96   |
Figure 10: Kinetic models of MB removal by MSNs-Cys: (a–c) pseudo-first-order reactions at pH 1.5, 7, and 8.5, respectively; (d–f) pseudo-second-order reactions at pH 1.5, 7, and 8.5, respectively (150 ppm, 25°C, and 150 rpm).

Table 4: Coefficient of pseudo-first-order and pseudo-second-order reactions for MB removal by MSNs-Cys at 150 ppm and 25°C.

| Parameters               | 1.5  | 7    | 8.5  |
|--------------------------|------|------|------|
| **Pseudo-first-order**   |      |      |      |
| $q_e, \text{cal (mg/g)}$ | 6.59 | 6.27 | 2.78 |
| $k_1 (\text{min}^{-1})$  | 0.0003 | 0.0148 | 0.0002 |
| $R^2$                    | 0.94 | 0.83 | 0.75 |
| **Pseudo-second-order**  |      |      |      |
| $q_e, \text{cal (mg/g)}$ | 80.64 | 86.95 | 140.84 |
| $k_2 (\text{min}^{-1})$  | 0.0004 | 0.0004 | 0.17 |
| $R^2$                    | 1    | 0.93 | 0.99 |
dried at 100°C overnight. The adsorbent was reused for removal of MB (150 ppm) at different pH values. Figure 11 shows the performance of the adsorbent after this second removal cycle. The removal efficiency of MB reached 64%, 60%, and 83% at pH 1.5, 7, and 8.5, respectively.

4. Conclusions

In the present work, mesoporous silica functionalized with cysteine (MSN-Cys) was prepared in three steps. Epoxy-functionalized saline was anchored onto the surface of the MSN, followed by reaction with cysteine in basic media via an epoxy–thiol reaction. This nanomaterial exhibited cationic character below the pKa and anionic character above the pKa, with zwitterionic character at intermediate pH. The amount of adsorbed MB was found to be affected by the initial concentration of MB, contact duration, and pH of the solution. The amount of adsorbed MB increased when the concentration of MB increased, with the highest adsorption capacity at high pH with 140 mg of MB per gram of MSN-Cys due to the physical interaction between MB and the negative charge on the MSN surface. The adsorption isotherm was fitted with the Freundlich model for all solutions. The kinetics of MB adsorption on MSN-Cys was found to fit a pseudo-second-order kinetic model. The material was characterised using SEM, TEM, and FTIR.

Data Availability

SEM and TEM were used to support the findings that the prepared materials are mesoporous silica nanoparticles (MSNs). FT-IR spectra were used to support the findings that the functional groups are successfully attached onto the surface of the nanomaterials. The adsorptions of MB on MSNs at different pH were demonstrated to support the findings that MB is affected by different functional groups. The adsorption isotherm used to support the findings that all data are fitted with the Freundlich model was demonstrated. The kinetics of MB adsorption used to support the findings that all data are fitted with the pseudo-second-order kinetic model was demonstrated.

Conflicts of Interest

The author declares that there are no conflicts of interest.

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