Article

Quaternization of Poly(2-diethyl aminoethyl methacrylate) Brush-Grafted Magnetic Mesoporous Nanoparticles Using 2-Iodoethanol for Removing Anionic Dyes

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Abstract: Magnetic mesoporous silica nanoparticles (Fe₃O₄-MSNs) were successfully synthesized with a relatively high surface area of 568 m²g^{−1}. Fe₃O₄-MSNs were then modified with poly(2-diethyl aminoethyl methacrylate) (PDEAEMA) brushes using surface-initiated ARGET atom transfer radical polymerization (ATRP) (Fe₃O₄@MSN-PDMAEMA). Since the charge of PDEAEMA is externally regulated by solution pH, tertiary amines in the polymer chains were quaternized using 2-iodoethanol to obtain cationic polymer chains with a permanent positive charge (Fe₃O₄@MSN-QPDMAEMA). The intensity of the C—O peak in the C1s X-ray photoelectron spectrum increased after reaction with 2-iodoethanol, suggesting that the quaternization process was successful. The applicability of the synthesized materials on the removal of methyl orange (MO), and sunset yellow (E110) dyes from an aqueous solution was examined. The effects of pH, contact time, and initial dyes concentrations on the removal performance were investigated by batch experiments. The results showed that the Fe₃O₄@MSN-PDMAEMA sample exhibited a weak adsorption performance toward both MO and E110, compared with Fe₃O₄@MSN-QPDMAEMA at a pH level above 5. The maximum adsorption capacities of MO and E110 using Fe₃O₄@MSN-QPDMAEMA were 294 mg g^{−1} and 194.8 mg g^{−1}, respectively.

Keywords: magnetic mesoporous nanoparticles; polybase brushes; polymer quaternization; dyes removal; kinetics; isotherms

1. Introduction

According to recent United Nations projections, the world's population will increase by more than a third by 2050. Currently, many countries worldwide suffer from a shortage of water, and therefore, achieving sustainable water management is a major challenge for such countries. Sustainable water management contains industrial wastewater treatment [1,2]. In recent decades, industrial wastewater treatment has become increasingly complex. Increased population growth has led to an increase in industrialization and, consequently, an increase in the release of pollutants into wastewater, which threatens health and the environment [3–7].

Among these pollutants are dyes that are widely used in the most common industries, such as textiles, paper, and plastics [8–11]. Dyes are considered as one of the major pollutants because of their complex molecular structure, stability, and effect on plant

photosynthesis, as well as having low biodegradability, high toxicity, and cancerous properties [12–14]. Most dyes can be positively or/and negatively charged and could change regarding the pH. Moreover, they can also combine with metal ions in wastewater to form complex pollutants. Several methods are used to remove these complex structures such as precipitation [15], membrane filtration [16,17], photocatalytic reduction [18], electrocoagulation [19], biological treatment [20], electrochemical removal [21], and adsorption [22–28]. In the past few decades, great attention has been paid to the adsorption process due to its ease of application on a large scale and its efficiency [29–34].

Recently, several conventional adsorbents (e.g., activated carbons [35], ordered mesoporous carbons [36], metal–organic frameworks [37], carbon nanotubes [38], graphene-based nanocomposites [39], activated carbons [40] and natural clay [41]) have been used for the removal of dyes from contaminated water solutions. However, most of these solid adsorbents are not widely practiced due to poor selectivity, high cost, difficult disposal, and complex preparation processes. Therefore, it is of great importance to find an adsorbent that is highly efficient, economic, and selective toward organic dyes.

Mesoporous silica nanoparticles (MSNs) are one of the most widely used adsorbent materials in water purification due to their non-toxicity, high adsorption capacity, tunable pore structures, pore size, shorter equilibrium time, and abundant surface functional groups [42,43]. To increase the adsorption efficiency of the porous silica particles, their surfaces have been modified with different functional groups such as amine, carboxyl, thiol, and epoxy [44–46]. The contaminants are often removed through electrostatic interactions between the target analytes and the functional groups present on the surface of the nanoparticles.

To bind these functional groups on the surface of the silica, the self-assembly technique has been widely applied [47,48]. The density of these functional groups on the surface is the crucial factor to increase the efficiency of adsorption. Furthermore, in order to improve the active sites available on the surface of the nanoparticles, surface modification with polymer brushes has been proposed [49]. Polymer brushes (surface-confined macromolecular architectures) are being increasingly used for a variety of applications and consist of a linear backbone densely grafted with polymeric side chains [50]. The confined and compact structure of the polymer brushes can provide the nanoparticle surface with remarkable properties such as stimuli responsiveness, in which the polymer can change its conformation structure by changing the surrounding environment, such as pH and temperature [51–53]. A variety of polymer brushes were applied to the surface of silica nanoparticles such as poly(2-(tert-butylamino) ethyl methacrylate) and poly(2-diethyl aminoethyl methacrylate) to study their responsive behaviors [54,55]. The results show that in the acidic medium, the polymer chains expand, while in the basic medium, the polymer chain collapse.

The novelty of this work is to synthesize new materials using the quaternization process for potential applications. To the best of our knowledge, there is very little work in the literature on the use of pH-responsive polymer brushes in water remediation. In this paper, we developed effective materials based on silica nanoparticles and pH-sensitive poly(2-diethyl aminoethyl methacrylate) brush for removing dyes from water. The objectives are divided into two parts. First, mesoporous silica nanoparticles (MSNs) were prepared, then their surface was grafted with pH-sensitive poly(2-diethyl aminoethyl methacrylate) brush. Next, the tertiary amines were quaternized with 2-iodoethanol to eliminate the influence of pH on the adsorption performance of the material. The prepared materials were characterized by several techniques, including FTIR, XPS, SEM, and TEM. Finally, the performance of the prepared materials in removing methyl orange (MO) and sunset yellow (E110) dyes from an aqueous solution was investigated. A variety of sorption isotherms, including Langmuir and Freundlich models, as well as kinetic models, were applied to the experimental data to predict the adsorption capabilities of the synthesized adsorbents.

2. Materials and Methods

2.1. Materials

Ethanol (99.8%, HPLC grade), methanol (99.8%, HPLC grade), isopropanol (99.8%), dichloromethane (DCM, HPLC grade), pyridine (analytical grade), n-hexane (HPLC grade), toluene (HPLC grade), 2-iodoethanol (99%), dimethylformamide (DMF, 99.9%), ammonium hydroxide (28 wt %), tetraethylorthosilicate (TEOS, 98%), 3-aminopropyltriethoxysilane (APTES, >98%), 2-bromo-2-methylpropionyl bromide (BIBB, 98%), (2-(diethylamino) ethyl-methacrylate) (PDEAEMA, 99%), N-cetyltrimethylammonium bromide (CTAB, 98%), 2,2'-bipyridyl (bipy, 99%) ammonium nitrate (NH_4NO_3 , >99%), sunset yellow (E110, 90%), and methyl orange (MO, 85%) were bought from Sigma-Aldrich. Copper (II) bromide (CuBr_2 , 98%) was bought from BDH chemicals. Iron (II) chloride (99%) and iron (III) chloride (99%) were bought from Loba Chemie. Sodium chloride and hydrochloric acid were obtained Alfa Aesar. Deionized water (DI-water) was taken from Elga Pure Nanopore System (18 Ω).

2.2. Methods of Nanoparticles Preparation

2.2.1. Iron Oxide Nanoparticles (Fe_3O_4)

Iron (II) chloride (3.12 g) and iron (III) chloride (4.80 g) were dissolved in DI-water (30 mL) and stirred at 90 °C under N_2 gas. Then, ammonium hydroxide (20 mL) was added to the reaction mixture and kept under stirring for 150 min. Finally, the solid was separated and washed with water and ethanol.

2.2.2. Iron Oxide Covered with Mesoporous Silica (Fe_3O_4 @MSNs)

Iron oxide coated with mesoporous silica (Fe_3O_4 @MSNs) was synthesized according to previously reported studies by Beagan et al. [56]. To this end, 0.5 g of Fe_3O_4 was suspended in 150 mL of DI-water, followed by the addition of CTAB (1.0 g) at 38 °C. Then, ammonium hydroxide (7 mL) was added to the reaction mixture. A solution containing 5 mL of TEOS and 20 mL of n-hexane was slowly added to the reaction mixture with stirring. After 15 h, the solid was separated and washed with DI-water and ethanol.

2.2.3. Amino Functionalized Iron Oxide Coated with Mesoporous Silica (Fe_3O_4 @MSN- NH_2)

Fe_3O_4 @MSN- NH_2 nanoparticles were obtained by suspending 1.5 g Fe_3O_4 @MSN nanoparticles in a solution containing 0.5 mL APTES and 60 mL methanol. The mixture was refluxed for 15 h. The solid was separated and washed with DI-water and ethanol.

2.2.4. ATRP Initiator Functionalized Iron Oxide Coated with Mesoporous Silica (Fe_3O_4 @MSN-Br)

Fe_3O_4 @MSN-Br nanoparticles were obtained by dispersing 1.0 g of Fe_3O_4 @MSN- NH_2 in a solution of 25 mL of DCM and 1.5 mL of triethylamine. To the mixture, 1.2 mL of 2-bromo-2-methylpropionyl bromide was slowly added and stirred for 48 h at room temperature. The solid was separated and washed with DCM and ethanol.

To extract CTAB, Fe_3O_4 @MSN-Br nanoparticles were dispersed in a solution of ammonium nitrate in ethanol (10 mg/mL) and refluxed overnight with stirring. The solid was separated and washed with ethanol.

2.2.5. Poly(2-dimethyl aminoethyl methacrylate) (PDMAEMA) Brushes Grafted on Iron Oxide Coated with Mesoporous Silica (Fe_3O_4 @MSN-PDMAEMA)

In a 25 mL round bottom flask, 0.4 g of Fe_3O_4 @MSN-Br was dispersed in a solution containing 4 mL of ethanol and 1 mL of DI-water and degassed for 15 min. A solution containing 2-dimethyl aminoethyl methacrylate (DMAEMA) (2 mL), 2,2 bipy (0.0067 g), CuBr_2 (0.0009 g), ethanol (8 mL), and water (2 mL) were transferred into the reaction mixture and degassed for 15 min. To the polymerization mixture, 0.0076 g of ascorbic acid was added and stirred for 5 h. The solid was separated and washed with 10 mM of HCl solution and ethanol.

2.2.6. Quaternization of PDMAEMA Grafted on Fe₃O₄@MSNs (Fe₃O₄@MSN-QPDMAEMA)

Fe₃O₄@MSN-PDMAEMA (0.5 g) was dispersed in 40 mL of DMF. Then, 0.5 g of 2-iodoethanol was added to the solution under stirring and heated at 120 °C overnight. The solid was separated and washed with DMF and ethanol.

2.3. Measurement and Characterization

Scanning Electron Microscopy (SEM) images were acquired using the JEOL instrument, model JSM-7610F at 15Kv. Transmission electron microscopy (TEM) images were acquired using the JEOL instrument, model JEM-1400 at 100 Kv. PerkinElmer Spectrum BX instrument was used to obtain infrared spectra in the region of 400–4400 cm^{−1} with a resolution of 4 cm^{−1}. X-ray photoelectron spectroscopy (XPS) spectra were obtained using the JEOL instrument, model JPS-9030. The UV spectrum was obtained using SpectraMax 384 Plus UV/Vis spectrophotometer with a microplate reader. The surface zeta potential of the polymer-modified MSNs was measured using Zetasizer Nano ZS, Malvern. The specific surface area, pore size distribution, and pore volume of the synthesized materials were characterized using Brunauer–Emmett–Teller (BET) (Gemini VII, 2390 Surface Area, and Porosity USA). Prior to analysis, samples were degassed at 150 °C under nitrogen flow for 2 h to remove moisture and gasses. The crystalline phase of the fabricated magnetite nanoparticles was determined using powder X-ray diffraction technique, with Mini Flex II X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 1.5405 \text{ \AA}$) at 5°/min.

2.4. Adsorption Experiments

The adsorption behavior of the anionic dyes (MO and FCF) on the surface of Fe₃O₄@MSN-PDMAEMA and Fe₃O₄@MSN-QPDMAEMA was explored as a function of changing the initial concentrations, exposure time, and the solution's pHs. Generally, 10 mg of the sorbent was suspended in 15 mL of a solution containing a specific amount of the selected dye at 25 °C and a shaking rate of 150 rpm. The sorbent material was separated by centrifuge at a specific time. The amount of the chosen dye adsorbed on the surface was estimated using UV/Vis spectrophotometer. The adsorption capacity (q_e) at equilibrium (mg·g^{−1}) was calculated using Equation (1).

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

where C_0 is the dyes' initial concentration (mg·L^{−1}), and C_e is the concentration of dyes at equilibrium (mg·L^{−1}). V and m are the volume (L) and the mass of adsorbents (g), respectively.

2.4.1. Adsorption Isotherms

The adsorption data of the selected dyes on the sorbents were fitted using different isotherm models. Equation (2) presents a linear form of the Langmuir isotherm model.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{C_e}{q_m} \quad (2)$$

where q_m represents the maximum capacity (mg/g) of the anionic dyes adsorbed on the sorbents. k_l is the Langmuir constant (L·mg^{−1}).

Equation (3) presents a linear form of the Freundlich isotherm model.

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (3)$$

where $1/n$ is the measure of intensity, and K_F is the Freundlich constant ((mg/g)/(mg/L)^{1/n}).

2.4.2. Adsorption Kinetics

The adsorption data of the selected dyes on the sorbents were assessed using pseudo-first- and second-order equations. Equation (4) presents the pseudo-first-order equation.

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (4)$$

where q_t is the adsorption capacity at time t ($\text{mg} \cdot \text{g}^{-1}$), and K_1 is the rate coefficient of pseudo-first-order adsorption ($\text{L} \cdot \text{min}^{-1}$).

Equation (5) presents the pseudo-second-order equation.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where K_2 is the rate constant of adsorption in the pseudo-second-order model ($\text{g}/\text{mg} \cdot \text{min}$).

3. Results

3.1. Characterization

The co-precipitation protocol was used to synthesize iron oxide nanoparticles (Fe_3O_4) by mixing two types of iron salts. As shown in Figure 1A, Fe_3O_4 nanoparticles are nearly spherical with an average particle size of ca. 21 nm. However, Fe_3O_4 nanoparticles have shown agglomeration as a result of their paramagnetic property. After coating Fe_3O_4 nanoparticles with mesoporous silica shell using TEOS as silica source and CTAB as directing agent in a basic solution, there was an increase in the particle size from 21 nm to ca. 230 nm, with the shape of semi-sphere-like nanoparticle, as shown in Figure 1B. The presence of Fe_3O_4 nanoparticles in the core of mesoporous nanomaterials is clearly seen in the TEM image (Figure 1C), indicating successful coating. The average core size was estimated to be 19 nm, which is in agreement with the SEM image of Fe_3O_4 nanoparticles. Figure 1D,E show SEM and TEM images of magnetic mesoporous silica nanoparticles after polymerization. There is a noticeable increase in the average diameter of $\text{Fe}_3\text{O}_4@\text{MSN}$ -PDEAEMA, with ca. 20 nm, compared with none coated nanoparticles. The PDEAEMA brushes showed as a layer surrounding the modified $\text{Fe}_3\text{O}_4@\text{MSNs}$.

The XRD patterns of both magnetite nanoparticles (Fe_3O_4 -NPs) and magnetite-modified silica nanoparticles ($\text{Fe}_3\text{O}_4@\text{MSNs}$) are demonstrated in Figure 2. The characteristic peaks in the spectrum of Fe_3O_4 -NPs agreed well with the standard cubic phase of magnetite Fe_3O_4 . The observed peaks at 2θ values of 30.2° , 35.6° , 43.2° , 53.9° , 57.3° and 62.9° , assigned to the lattice planes (220), (311), (400), (422), (511), and (440) (JCPDS 88-0866), respectively. These peaks also appeared in the $\text{Fe}_3\text{O}_4@\text{MSNs}$ sample except the peaks at 2θ values of 30.2° and 53.9° , which might be attributed to the presence of an amorphous silica shell. The sharpness and the intensity of most Fe_3O_4 peaks indicate that the crystalline nature of Fe_3O_4 was not affected by a mesoporous silica shell.

The nitrogen adsorption–desorption isotherms of Fe_3O_4 -NPs and $\text{Fe}_3\text{O}_4@\text{MSNs}$ are shown in Figure 3, and the related parameter results are listed in Table 1. It was observed that Fe_3O_4 -NPs and $\text{Fe}_3\text{O}_4@\text{MSNs}$ exhibited type-IV isotherm, which reveals the material's mesoporous characteristics. However, a variation in the hysteresis Loops was observed for both materials, as $\text{Fe}_3\text{O}_4@\text{MSNs}$ showed a typical H1 hysteresis loop, indicating the presence of a narrow range of uniform mesopores where networking effects are minimal, whereas H3 hysteresis loop was obtained for Fe_3O_4 -NPs indicates the existence of complex pore structure and networking effects are significant. A specific surface area of $568.3 \text{ m}^2/\text{g}$ and $61.8 \text{ m}^2/\text{g}$ were obtained for $\text{Fe}_3\text{O}_4@\text{MSNs}$ and Fe_3O_4 -NPs, respectively. $\text{Fe}_3\text{O}_4@\text{MSNs}$ had well-defined narrow pores size ca. 5 nm, whereas Fe_3O_4 -NPs had a broader pore size distribution of ca 20–50 nm, which could be related to the agglomeration of the magnetite NPs.

Figure 1. Microscopic images of the synthesized nanoparticles: (a) SEM image of Fe_3O_4 nanoparticles; (b) SEM image of Fe_3O_4 @MSNs; (c) TEM images of Fe_3O_4 @MSNs; (d) SEM image of Fe_3O_4 @MSN-PDMAEMA; (e) TEM images of Fe_3O_4 @MSN-PDMAEMA.

Figure 2. XRD patterns of the magnetite Fe_3O_4 nanoparticles and Fe_3O_4 modified by silica shell.

Figure 3. N_2 adsorption–desorption BET isotherm for (a) Fe_3O_4 -NP and (b) Fe_3O_4 @MSNs. The insets show the BJH pore size distribution.

Table 1. Brunauer–Emmett–Teller surface analysis of Fe_3O_4 -NP and Fe_3O_4 -MSN.

Adsorbent	BET Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)
Fe_3O_4 -NP	61.75	0.30
Fe_3O_4 -MSNs	568.28	1.35

Figure 4 illustrates the FTIR spectra of as made Fe_3O_4 @MSNs, Fe_3O_4 @MSNs (without CTAB), Fe_3O_4 @MSN-Br, and Fe_3O_4 @MSN-PDEAEMA. The absorption peaks of Si–O–Si bonds were observed at ~ 1090 and ~ 1240 cm^{-1} for all samples. The stretching absorption vibration of Si–OH was allocated at ~ 3460 and ~ 970 cm^{-1} . The absorption peaks of C–H stretching bands were assigned at ~ 2940 cm^{-1} and ~ 2840 cm^{-1} for as made Fe_3O_4 @MSNs, where were disappeared after the CTAB extraction process. Compared with Fe_3O_4 @MSN-Br, a new peak was observed at ~ 1730 cm^{-1} after the polymerization process, referred to as C = O groups.

Figure 4. FT-IR spectra: (a) as-made $\text{Fe}_3\text{O}_4\text{@MSN}$; (b) $\text{Fe}_3\text{O}_4\text{@MSN-Br}$ (without CTAB); (c) $\text{Fe}_3\text{O}_4\text{@MSN-PDEAEMA}$.

The successful decoration of $\text{Fe}_3\text{O}_4\text{@MSNs}$ with polymer layers was evaluated by X-ray photoelectron spectroscopy (XPS), as shown in Figure 5. The C1s spectrum of non-modified PDEAEMA brush on the surface of $\text{Fe}_3\text{O}_4\text{@MSNs}$ was fitted with four peaks, at 285 eV, 285.9 eV, 286.8 eV, and 288.3 eV with peak-area ratios of 4.5:3.8:1:1, related to the C-H, C-N, C-O, and O = C-O, respectively. This is in good agreement with the theoretical value of 5:3:1:1 (Figure 5a). After quaternization, the tertiary amino groups in the polymer chains, the C1s spectrum was fitted with three peaks, at 285 eV, 286.3 eV, and 288.9 eV, related to the C-H, C-N/C-O, and O = C-O, respectively (Figure 5b). As expected, there was an increase in peak intensity ~286.3 eV, due to the increase in the amount of C-O bonds present in the organic layer. This observation confirmed the successful attachment of iodoethanol molecules.

Figure 5. C1s XPS spectra: (a) $\text{Fe}_3\text{O}_4\text{@MSN-PDEAEMA}$; (b) $\text{Fe}_3\text{O}_4\text{@MSN-QPDEAEMA}$.

The surface charges of $\text{Fe}_3\text{O}_4\text{@MSN-PDMAEMA}$ and $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ were also investigated using a zeta potential analyzer, and the results are shown in Figure 6. Both materials had similar zeta potential at pH below 7. However, above pH 7 the $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ potential remained almost constant, whereas a significant drop in the potential of $\text{Fe}_3\text{O}_4\text{@MSN-PDMAEMA}$ material was observed.

Figure 6. Zeta potential values for Fe₃O₄@MSN-PDMAEMA and Fe₃O₄@MSN-QPDMAEMA at different pH levels.

3.2. Adsorption Studies

3.2.1. Effect of pH on Adsorption

The influence of pH on the removal of two sulfonic acid-based dyes, MO and E110 by Fe₃O₄@MSN-PDMAEMA and Fe₃O₄@MSN-QPDMAEMA were examined, (Figure 7). Each sample (10 mg) was mixed with 200 mg/cm^{−3} of the targeted analytes at pH ranging from 4 to 9. Fe₃O₄@MSN-PDMAEMA sample exhibited a weak adsorption performance toward MO with 40% extraction efficiency at pH < 6, whereas 100% extraction efficiency was achieved using Fe₃O₄@MSN-QPDMAEMA. The observed behavior can be explained by knowing the actual pKa value of PDMAEMA (pKa = 6.8). As the pH increased above pKa, the polymer brush became deprotonated and collapsed. When the pH was below the pKa, the polymer was positively charged and swollen due to the protonation of the tertiary amine groups. However, previous investigations confirmed that the pKa value of PDMAEMA can be shifted to below 5 depending upon the polymer's grafting density and thickness [57–59]. Therefore, it is possible that the grafting density of the sample was high, causing a significant pKa shift, especially when silane as initiator was used. Hence, it should not be surprising that Fe₃O₄@MSN-PDMAEMA was less efficient in removing the negatively charged dyes, due to the deprotonation of polymer chains. E110 dye exhibited a better adsorption performance which might be attributed to the presence of two sulfonic acid moieties compared with the one in MO.

3.2.2. Equilibrium Isotherms

Detailed knowledge of the equilibrium adsorption isotherm is essential in examining the interactive behavior between the adsorbent and the adsorbate in any adsorption system. Langmuir and Freundlich isotherm models were employed, as shown in Figure 8. In order to study the isotherms, the concentration of the analytes was adjusted in the range of 50–250 mgL^{−1} and 300–1000 mgL^{−1} for MO and E110, respectively. The experimental parameters were performed using the optimum conditions. Langmuir isotherm assumes that a homogeneous interaction between the adsorbent and the adsorbate at the material's adsorption sites with the formation of a monolayer of the adsorbate on the material's surface [60]. In contrast, the Freundlich isotherm model assumes the possibility of the existence of the multilayer sorption mechanism at the surface of adsorbents with a heterogeneous energy distribution of active sites. The correlation coefficient (R^2) is the criterion

used to assess how well the data are fit with each model. The model with a higher R^2 value will be utilized to describe the adsorption mechanism. The equilibrium data of the adsorption of MO (Figure 8b) fitted well with the Langmuir model with R^2 of more than 0.99, indicating the formation of a monolayer of MO molecules on the surface of the adsorbent (homogeneous interaction) with a maximum adsorption capacity of 294 mg g^{-1} . On the other hand, the equilibrium data of the E110 adsorption fitted well with the Freundlich isotherm model, indicating the formation of multilayers of E110 molecules on the surface of the adsorbent (heterogeneous interaction) with a maximum adsorption capacity of 194.8 mg g^{-1} . The difference between the two dyes in terms of the interaction can be attributed to the presence of two sulfonic moieties in both sides of E110 molecules, making them more electronegative compared with MO molecules, and consequently, more attraction with the positively charged adsorbent surface.

Figure 7. Effect of pH on the adsorption of methyl orange and sunset dye by $\text{Fe}_3\text{O}_4\text{@MSN-PDPAEMA}$ and $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ at equilibrium.

The extraction of methyl orange and sunset yellow dyes using a variety of adsorbents has been extensively studied. Table 2 demonstrates a comparative study of the maximum adsorption capacities of some adsorbents for MO and E110 along with the current work. It is obvious that the adsorption capacities of our novel material are higher than other competitive adsorbents, indicating that $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ can be considered a promising adsorbent for the removal of both dyes from aqueous solutions.

Table 2. A list of maximum adsorption capacities for different types of adsorbents.

Sorbent	Capacity (mg/g)	Target Analyte	Ref.
Chitosan-coated sodium zeolites	287	MO	[61]
CDs/ZFO	181.2	MO	[62]
$\text{Fe}_3\text{O}_4\text{/PS/US}$	67.56	E110	[63]
$\text{Fe}_3\text{O}_4\text{@SiO}_2\text{@Kit-6/NH}_2$	8.41	E110	[64]
$\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$	294	MO	This Work
$\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$	194.8	E110	This Work

Figure 8. Dyes adsorption at 25 °C by the synthesized $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ at equilibrium with different initial analytes concentrations: (a,b) Freundlich and Langmuir isotherms of MO uptake, respectively; (c,d) Freundlich and Langmuir isotherms of E110 uptake, respectively.

3.2.3. Effect of Adsorption Time and Adsorption Kinetics

A kinetic study of the removal of studied analytes is crucial to understand and describe the kinetic mechanism of $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$. Each dye (14 mL) was placed in a 15 mL centrifuge tube of fixed initial concentrations, followed by the addition of 10 mg of $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$, and the mixture was shaken at 25 °C for different time intervals. The data were then fitted with pseudo-first-order [65–67] and pseudo-second-order kinetic models [68] (Figure 9a–d). Along with these two models, the intraparticle diffusion model was also studied to investigate the process of the sequestration of analytes from aqueous solution onto SNPs, (Figure 9e,f). It can be shown that the uptake data of both dyes by the adsorbent fitted well with the pseudo-second-order model, indicating an inclination toward chemisorption. This implies that the rate of the analyte's uptake depends upon the adsorption capacity and not the concentration of adsorbate [69].

The results obtained by the intraparticle diffusion model showed that rapid removal of the MO dye at the initial stage was caused by the presence of a considerable number of free active sites on the surface of $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ that analyte molecules could bind to (boundary layer diffusion effects). A reduction in the removal rate at the second stage was observed due to a significant drop in the number of the available active sites on the sorbent's surface. This resulted in the diffusion of the MO molecule through the pores (pore diffusion). In the case of E110 dye, a different behavior was observed, as the dye was adsorbed by the sorbent in one kinetic stage, which could be attributed to the multilayer adsorption of E110 dye on the adsorbent surface. The values of the intraparticle diffusion rate constants K_{id} of both dyes are summarized in Table 3. Higher K_{id} value indicates higher intraparticle mass transfer, which means that the kinetics of E110 uptake

by $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$ may be controlled by film diffusion mechanism, whereas pore diffusion was more active in the adsorption of MO.

Figure 9. (a,b) Pseudo-first-order and pseudo-second-order models of MO uptake by $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$, respectively; (c,d) pseudo-first-order and pseudo-second-order of E110 uptake by $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$, respectively; (e,f) intraparticle diffusion model of MO and E110 dyes uptake by $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$, respectively.

Table 3. Intraparticle diffusion model parameters for the removal of MO and E110 from aqueous solution by $\text{Fe}_3\text{O}_4\text{@MSN-QPDMAEMA}$.

Dye	Intraparticle Diffusion Model	
	K_{id} ($\text{mg g}^{-1} \text{h}^{-0.5}$)	R^2
MO	3.4	0.60
E110	1.02	0.71

4. Conclusions

In summary, we reported the synthesis of magnetic mesoporous silica nanoparticles, followed by the modification with 2-diethyl aminoethyl methacrylate (DEAEMA) using surface-initiated ARGET atom transfer radical polymerization (ATRP). Furthermore, the polymer chains were quaternized using 2-iodoethanol to obtain a cationic polymer that would not be affected by the solution's pH. The synthesized materials were characterized using a variety of advanced techniques. The characterization results showed that Fe₃O₄ nanoparticles were spherical in shape with particles sized ca. 29 nm. When the Fe₃O₄ were coated with a mesoporous silica shell, the particle size was increased to 230 nm, confirming the successful loading of the silica shell. Finally, the materials were evaluated for the removal of methyl orange (MO) and sunset yellow (E110) dyes from an aqueous solution. The results showed that the Fe₃O₄@MSN-PDMAEMA sample exhibited a weak adsorption performance toward both MO and E110, compared with Fe₃O₄@MSN-QPDMAEMA. The maximum adsorption capacities of MO and E110 using Fe₃O₄@MSN-QPDMAEMA were 294 mg g^{−1} and 194.8 mg g^{−1}, respectively. Thus, the high sorption ability, ease of applicability, abundance of the raw materials, and low price make Fe₃O₄@MSN-QPDMAEMA a promising adsorbent for the removal of both dyes from aqueous solutions.

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