Research Article

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Malachite green dye removal using ceramsite-supported nanoscale zero-valent iron in a fixed-bed reactor

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Abstract: In this study, we prepared and characterized ceramsite-supported nanoscale zero-valent iron (nZVI). Malachite green (MG) dye removal from aqueous solutions using a fixed-bed reactor packed with the above composite material was investigated. This research was carried out according to the prophase study of the preparation and characterization of ceramsite material for water treatment using sintering method from solid wastes. The results indicated that ceramsite could be loaded with nZVI, mainly because of its magnetic property. With the decrease in the initial concentration and influent flow rate or the increase in the reaction temperature, the breakthrough curve became less steep. Meanwhile, the breakthrough and saturation points gradually shifted rightward. When the initial concentration was 10 mg·L⁻¹, the reaction temperature was 25°C, and the influent flow rate was 5 mL·min⁻¹, the breakthrough curve presented an irregular “S” shape, the breakthrough and saturation times were 230 and 515 h, respectively. The characterization of MG dye-containing wastewater treatment using ceramsite-supported nZVI in a fixed-bed reactor by employing the Yoon-Nelson kinetic model was superior to those using the Thomas and Adams-Bohart kinetic models, with $R^2 > 0.96$.

Keywords: ceramsite-supported nZVI, fixed-bed reactor, dye wastewater, breakthrough behavior, kinetic analysis

1 Introduction

Zero-valent iron (ZVI) is a low-price and low-toxicity material that exhibits active chemical properties, strong reduction ability, and high electronegativity, and can be obtained from numerous sources [1,2]. Furthermore, ZVI possesses an electrode potential $E_0$ (Fe²⁺/Fe) of $–0.44$ V. Metal ion (such as Cu²⁺) reduction can be realized with standard electrode potential greater than $–0.44$ V in aqueous solutions through iron reduction, microelectrolysis, coagulation and adsorption, and breaking the chemical bonds of certain compounds (such as $–N≡N–$) to remove pollutants from aqueous solutions [3,4]. Compared with ZVI, nanoscale zero-valent iron (nZVI) has a unique “core–shell” structure (FeO core and Fe₃O₄ shell) and excellent activity, which results in effective adsorption, transformation, and mitigation of pollutants in aqueous solutions [5]. Moreover, nZVI is environment-friendly, cheap, and easy to synthesize [6].

In practice, however, nZVI is susceptible to Van der Waals forces because of its intrinsic electrostatic attraction and magnetism, which easily forms cluster-like chain structures and causes agglomeration of precipitation. So, oxidization and deactivation may occur [7,8]. Solving the problems mentioned above, graphite, bentonite, biochar, among others, have been used to support nZVI [9–11]. This method has the following advantages: (i) the distribution is even and the dispersity is improved, (ii) the electron transfer ability and processing ability are enhanced, and (iii) the original physical and chemical properties are maintained and the reaction activity is improved. Therefore, the development of novel supporting material is a critical topic of research in China and foreign countries.

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Ceramsite is a man-made light mesoporous material [12,13], with a particle diameter of 5–20 mm, and it comprised various raw materials by sintering or sintering-free method mixed with additives, such as bonding agent, expansion agent, or gas-generating agent. Ceramsite is mostly in the form of round or elliptical spheres, with a smooth and hard enamel layer on the surface and a honeycomb-like microporous internal structure. The solid-waste-based chemical components are similar to the chemical components of nonrenewable natural resources, such as shale and clay. Therefore, combining solid waste resources with ceramsite production is feasible [14,15]. In comparison to the conventional preparation method, this novel method can “turn waste into treasure and turn harmful things into profitable things” in accordance with the principles of sustainable development. In addition, in this method, the principle of “use waste to treat waste” for pollution control is propagated. Thus, this approach formed a recycling approach that facilitated environmental, economic, and social benefits. Owing to low density, high strength, large specific surface area, developed pore structure, stable chemical properties, and corrosion resistance, ceramsite is widely used in many fields, such as garden flowers, industrial buildings, sewage, and wastewater treatment [16–18].

Furthermore, to ameliorate the wastewater treatment performance of ceramsite material, supporting technology has attracted more attention [19,20]. In addition, with the rapid development of nanotechnology, several nanoscale metallic oxides, such as NiO nanoparticles [21] and ZnO nanoparticles [22], were used as a modifier during the modification process. Therefore, supporting technology has also been employed to prepare ceramsite composites, which exhibit excellent ceramsite properties and advantages in other metal oxides (sub-oxides) and compounds [23].

In this study, ceramsite-supported nZVI packing pack was prepared. A study was conducted to investigate the influences of the initial concentration, reaction temperature, and influent flow rate on the breakthrough behaviors of MG dye removal from aqueous solutions by ceramsite-supported nVZI in a fixed-bed reactor, and the corresponding kinetic analysis was performed.

2 Materials and methods

2.1 Reagents and equipment

MG dye of analytical grade (C23H25ClN2, CI = 42,000, λmax = 619 nm, and chemical structure displayed in Figure 1) and nZVI (particle size is 50 nm) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd and Shanghai Maogon Nano Technology Co., Ltd, respectively. The gauze pieces and nylon cable ties were supplied by Caoxian Hua Lu Hygiene Material Co., Ltd and Shandong Gunuo Plastic Co., Ltd, respectively. The BT101LY/YZ1515 flow-type peristaltic pump and V-type laboratory mixer were purchased from Baoding Rongbai Precision Pump Manufacturing Co., Ltd, and Lange (Guangzhou) Machinery Technology Co., Ltd, respectively. The fixed-bed reactor was assembled in the laboratory, where the reaction column and fixed-bed frame were made of commercially available organic glass and stainless steel, respectively. Distilled water was used as an aqueous solution in this experiment.

2.2 Experimental method

2.2.1 Draw standard curve

The MG dye was dried at 100°C for 120 min, subsequently, 1,000 g of the dried MG dye was accurately weighed and placed into 1,000 ml of distilled water to form MG dye stock solution with a concentration of 1,000 mg·L⁻¹. The targeted concentration of MG dye wastewater was obtained through serial dilution with distilled water. Next, 5, 10, 15, 20, 25, 30, 35, and 40 mg·L⁻¹ MG dye solutions were prepared, and the absorbance was tested at λ = 619 nm, whose results are displayed in Figure 1. The concentration was x-coordinate and absorbance was y-coordinate. Here, R² > 0.995, indicating that a linear correlation existed between the concentration and absorbance, rendering easy calculation of relevant concentrations. The concentration of MG dye in effluent-to-be-tested
was calculated as per the linear fitting equation presented in Figure 1.

### 2.2.2 Preparation

In this study, ceramsite with a particle size of approximately $10 \pm 0.2\, \text{mm}$ was prepared by processing dewatered sewage sludge, coal fly ash, and river sediment in steps such as screening, mixing, molding (granulation), drying, preheating, sintering, and cooling. The experimental process was detailed in our previous report [24]. Next, the ceramsites were broken and screened to obtain ceramsite supporters with particle sizes of approximately $1.0 \pm 0.2\, \text{mm}$, which were then pretreated. The experimental procedures were detailed in a previous study [25].

Ceramsite-supported nZVI was synthesized through ball milling in the following steps: first, ceramsite and marketed nZVI were placed in a V-type laboratory mixer with a 5:1 proportion by mass. Second, the mixer was rotated at 22 rpm for 30 min for mixing and collision to physically combine the constituents to form ceramsite-supported nZVI. Finally, 10.0 g ceramsite-supported nZVI was accurately weighed and placed on a double-layer gauze piece, and wrapped with a nylon cable tie to prepare a packing pack. Such a new-type packing pack can increase the effective area of MG dye molecular channel in the liquid phase and ensure excellent distribution. Besides, the pack can reduce the liquid-level gradient and pressure drop of the tray and improve the mass transfer effect.

### 2.2.3 Fixed-bed experiment

The fixed-bed reactor used in this study consisted of an influent tank, a flow-type peristaltic pump, reaction columns, packing pack layers, a fixed-bed frame, and an effluent tank, seen in Figure 2. The inner diameter, height, and effective volume of the reaction column were $14.0\, \text{cm}$, $100.0\, \text{cm}$, and $4.4 \times 10^3\, \text{cm}^3$, respectively. The top of the reaction column was an inlet/outlet, the bottom of the reaction column had a perforated partition and a water inlet, and the middle layer of the reaction column was filled with ceramsite-supported nZVI packing pack. Under normal pressure and driven by a peristaltic pump, the wastewater sample passed through the entire fixed-bed reactor from the bottom to the top. The MG dye content in the effluent was tested at $\lambda = 619\, \text{nm}$ under various initial concentrations (10, 20, and 30 mg.L$^{-1}$), reaction temperature (5, 25, and $45 \pm 2\, \text{°C}$), and influent flow rate (5, 15, and 25 mL.min$^{-1}$) conditions at regular intervals.

![Schematic of the fixed-bed reactor](figure2)

**Figure 2:** Schematic of the fixed-bed reactor; 1 – flow-type peristaltic pump, 2 – influent tank, 3 – reaction column, 4 – packing inlet/outlet, 5 – packing pack, 6 – effluent tank, 7 – fixed-bed frame.

### 2.3 Analysis

Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) (Quanta-250 type), X-ray diffraction (XRD) spectrometry (D8Bruker ADVANCE type), and vibrating sample magnetometry (VSM, Lake Shore 7404 type) were performed. The MG dye content in the effluent was measured through UV754N ultraviolet-visible spectrophotometry. The physical properties of samples included breaking and wear rate, silt carrying capacity, solubility in hydrochloric acid, void fraction, and BET-specific surface area were measured according to China’s Standard Methods of Artificial Ceramsite Filter Material for Water Treatment (CJ/T 299-2008), the details for this standard were provided in the previous study [26].

The breakthrough curve was plotted considering the operating time as $x$-coordinate and the MG dye concentration in the effluent as $y$-coordinate. When the MG dye concentration in the effluent reached the breakthrough point, the reaction column was considered broken through. The breakthrough time designed for this experiment was the time that the MG dye concentration in the effluent required to reach 5% of the MG dye concentration in the influent (i.e., $C_t = 5\% \, C_0$). When the MG dye concentration in the effluent reached the saturation point, the packing had lost its activity, known as exhausted packing. The saturation time designed for this experiment was the time that the MG dye concentration in the effluent required to reach 90% of the MG dye concentration in the influent (i.e., $C_t = 90\% \, C_0$). After that, Thomas, Yoon-Nelson (Y–N), and Adams-Bohart (A–B) fixed-bed reaction kinetic models
were employed to nonlinearly fit the test results of the breakthrough curve [27,28], and their expressions are shown in Eqs. 1–3:

\[
\frac{C_i}{C_0} = \exp \left[ \frac{K_{TH} \times Q \times m}{Q} - K_{TH} \times C_0 \times t \right]
\]

where \( C_0 \) is the initial MG dye concentration, mgL\(^{-1}\); \( C_i \) is the MG dye concentration in the effluent at time \( t \), mgL\(^{-1}\); \( t \) is the operating time of the fixed-bed reactor, min; \( K_{TH} \) is the Thomas rate constant, mL-\( (mg\cdot min) \); \( q_e \) is the equilibrium adsorption capacity, mg g\(^{-1}\); \( m \) is the mass of the packing, g; \( Q \) is the influent flow rate, mL\( (mg\cdot min) \); \( K_{YN} \) is the Y–N rate constant, min\(^{-1}\); \( r \) is the time required for 50% packing breakthrough, min; \( K_{AB} \) is the A–B rate constant, L-\( (mg\cdot min) \); \( N_0 \) is the saturation concentration, mgL\(^{-1}\); \( Z \) is the height of the reaction column, cm; \( U_0 \) is the ratio of the volumetric flow rate to the cross-section from the beginning to the end of breakthrough; \( R^2 \) is the correlation coefficient.

\[
\frac{C_i}{C_0} = \exp \left[ K_{YN} \times t - K_{YN} \times \tau \right]
\]

\[
\frac{C_i}{C_0} = \exp \left[ K_{AB} \times C_0 \times t - K_{AB} \times N_0 \times \frac{Z}{U_0} \right]
\]

3 Results and discussion

3.1 Characterization

3.1.1 Physical property

As Table 1 shows that the breaking and wear rate, silt carrying capacity, solubility in hydrochloric acid, void fraction and BET-specific surface area of the lab-made ceramsite-supported nZVI were 3.77%, 0.48%, 1.55%, 50.39%, and 9.82 × 10\(^4\) cm\(^2\) g\(^{-1}\), respectively. These physical properties fully complied with China’s Industrial Standard (CJ/T 299-2008), suggesting that this composite may be an ideal available material for wastewater treatment. Besides, when compared with ceramsite, the ceramsite-supported nZVI has better physical properties, for example, its BET-specific surface area was increased by 10.43 times.

3.1.2 SEM-EDS analysis

Figure 3 displays the SEM images and EDS spectra of ceramsite and ceramsite-supported nZVI. Figure 3a reveals that the ceramsite surface is smooth, bright, and uneven, with a high degree of densification, and a porous structure with a pore size of approximately 10 µm can be observed on the surface. With such dense and developed microstructure, ceramsite is regarded as an ideal supporting material [29]. Figure 3b illustrates that on the ceramsite surface, almost no porous structure and obvious defects were detected, but even distribution of nZVI was also observed. Studies have shown that nZVI not only accumulates on the ceramsite surface but also deposits in the pores of ceramsite [30]. This deposition is the primary way of nZVI load on ceramsite.

The EDS analysis results showed that the ceramsite phase was mainly composed of C, O, Na, Mg, Al, Si, K, Ca, Fe, and Cu, as detailed in Figure 3a. By contrast, the composition of elements on ceramsite surface changed considerably after supporting treatment. The Fe element content increased sharply from 1.70% to 81.07%, yet some elements such as Na, Mg, Al, and S were not detected, as shown in Figure 3b. This phenomenon could be attributed to the nZVI deposition on the surface and pores of ceramsite, which eliminated the bonding points of these elements.

3.1.3 XRD analysis

XRD was performed to characterize the crystal structure of ceramsite and ceramsite-supported nZVI, and the results were illustrated in Figure 4. According to Figure 4(b), the

| Table 1: Physical properties of ceramsite and ceramsite-supported nZVI |
|---------------------------------------------------------------|
| **Parameters**       | **Ceramsite** | **Ceramsite-supported nZVI** | **Threshold** |
|----------------------|--------------|------------------------------|---------------|
| Breaking and wear rate (%) | 0.2          | 3.77                        | ≤6            |
| Silt carrying capacity (%) | 0.2          | 0.48                        | ≤1            |
| Solubility in hydrochloric acid (%) | 0.01         | 1.55                        | ≤2            |
| Void fraction (%) | 71.1         | 50.39                      | ≥40           |
| BET-specific surface area (×10\(^4\), cm\(^2\) g\(^{-1}\)) | 0.75         | 7.82                        | ≥0.5          |

Note: The threshold of CJ/T 299-2008, China.
The crystal phase of ceramsite was mainly composed of magnetite, quartz, albite, anorthite, chromium-vanadium oxides, and aluminosilicate. As shown in Figure 4(a), the characteristic peaks of 2θ at 35.54°, 44.56°, 57.08° and 62.84°, which were consistent with the characteristic peaks of the ZVI lattice planes {110}, {200}, and {211}, indicating that the nZVI was loaded on the ceramsite [31]. In addition, the characteristic peaks of 2θ at 30.14° and 53.6°, that probably corresponded to the characteristic peaks of the Fe₃O₄ and Fe₂O₃ lattice planes, respectively, which suggested that oxidization had taken place, and formed iron oxides.

### 3.1.4 VSM analysis

Figure 5 illustrates the VSM spectra of ceramsite blank material and ceramsite. Figure 5(a) indicates that the ceramsite blank material did not exhibit any magnetism. In contrast, the magnetic property of the ceramsite was considerably enhanced after sintering treatment, as shown in Figure 5(b). Some researchers also obtained similar conclusions [32,33]. The major reasons for this phenomenon could be attributed to a certain amount of Fe element in the raw material for ceramsite preparation [34,35], so the chemical reactions occurred in the sintering process to form magnetic oxides.

**Figure 3:** SEM-EDS results of (a) ceramsite, (b) ceramsite-supported nZVI, and (c) exhausted ceramsite-supported nZVI.
generate magnetic Fe$_3$O$_4$, as detailed in Eqs. 4–6. In turn, this magnetic property renders ceramsite to magnetically adsorbed nZVI. This mechanism is the basic principle in which ceramsite can support nZVI with high stability.

\[
\begin{align*}
\text{FeO} + \text{Fe}_2\text{O}_3 & \xrightarrow{\text{High-temperature}} \text{Fe}_3\text{O}_4 \\
3\text{Fe}_2\text{O}_3 + \text{CO} & \xrightarrow{\text{High-temperature}} 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \\
3\text{FeS} + 5\text{O}_2 & \xrightarrow{\text{High-temperature}} \text{Fe}_3\text{O}_4 + 3\text{SO}_2
\end{align*}
\]

(4) (5) (6)

3.2 Influence of initial concentration and kinetic analysis

The influence of the initial concentration on the breakthrough curve of the removal of MG dye from aqueous solutions by ceramsite-supported nZVI in a fixed-bed reactor was investigated at the reaction temperature of 25°C and the influent flow rate of 5 mL·min$^{-1}$, and the results are shown in Figure 6a. Subsequently, Thomas, Y–N, and A–B fixed-bed reaction kinetic models were applied to nonlinearily fit the test data listed in Figure 6a, and the fitting results were presented in Figure 6b–d.

As displayed in Figure 6a, with the increase in the initial concentration, the breakthrough curve became steep, and both the breakthrough time and saturation time decreased. When the initial concentration was increased from 10 to 30 mg·L$^{-1}$, the breakthrough time decreased by 63% from 230 to 85 h, and the saturation time decreased by 46.6% from 515 to 275 h. The MG dye removal from water using ceramsite-supported nZVI in a fixed-bed reactor passed three steps, as shown in Figure 7. In detail, in the first step, owing to ceramsite-supported nZVI having a large specific surface area, the MG dye can be quickly adsorbed to its surface by the interfacial energy and surface tension effects. This adsorption process is very critical, especially for dye removal from wastewater [36], meanwhile, desorption can also occur [37]. In the second step, nZVI is easy to undergo electrochemical reaction, particularly in the presence of hydrogen ion and dissolved oxygen (Eq. 7), while ZVI content decreased (see the EDS spectrum in Figure 3c), which resulted in a large amount of dissolving Fe$^{3+}$, simultaneously, H$_2$O$_2$ was released, forming a Fenton system [38,39], which can lead to MG dye oxidation into small molecular substances, as shown in Eqs. 7 and 8. In the final step, the reaction products of Eqs. 7 and 8, included Fe$^{2+}$ and Fe$^{3+}$, were further hydrolyzed to form iron hydroxide and amorphous iron oxide [40], which can react to complex adsorption and coprecipitation with MG dye in water, as detailed in Eqs. 9 and 10. In addition, due to the existing synergistic effect between ceramsite carrier and nZVI modifier, it can promote the electron transfer in the ceramsite-supported nZVI system [41], improving the reaction activity of nZVI.

\[
\begin{align*}
\text{FeO} + \text{O}_2 + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\text{Fe}^{2+} + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \\
\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{FeOOH} + 3\text{H}^+
\end{align*}
\]

(7) (8) (9) (10)

When the initial concentration was changed from 10 to 30 mg·L$^{-1}$, $K_{\text{th}}$ value decreased from 17.91 × 10$^{-3}$ to 4.4 × 10$^{-3}$ mL·(mg·min$^{-1}$)$^{-1}$, whereas the $q_e$ value increased from 0.749 to 3.117 mg·g$^{-1}$, as illustrated in Figure 6b. Figure 6c shows that the change of the initial concentration had no obvious influence on $K_{\text{MN}}$ value, but had a large effect on $r$ value, which decreased from 414.538 to 159.075 min. This result indicated that with the increase in the initial concentration, the breakthrough time was
reduced, and the packing was easily saturated [42]. As presented in Figure 6d, $K_{AB}$ value reduced from $7.78 \times 10^{-4}$ to $3.06 \times 10^{-4}$ L(mg-min)$^{-1}$, yet $N_0$ value increased from 259.716 to 411.227 mg·L$^{-1}$. Hence, the removal of MG dye from aqueous solutions by ceramsite-supported nZVI in a fixed-bed reactor considerably depended on the mass transfer process inside the packing pack.

Within the research scope of the initial concentration, the characterization of removal of MG dye from aqueous solution by ceramsite-supported nZVI in a fixed-bed reactor by using the Y–N kinetic model was superior to those applying the Thomas or A–B kinetic model, with $R^2 > 0.96$.

### 3.3 Influence of reaction temperature and kinetic analysis

The influence of the reaction temperature on the breakthrough curve of the removal of MG dye from aqueous solutions by ceramsite-supported nZVI in a fixed-bed reactor was studied.
analyzed at the initial concentration of 10 mg L\(^{-1}\) and influent flow rate of 5 mL min\(^{-1}\), and the results were presented in Figure 8a. Next, Thomas, Y–N, and A–B kinetic models were used to nonlinearly fit the test data are shown in Figure 8a, and the fitting results are summarized in Figure 8b–d.

Figure 8a reveals that the breakthrough curve became less steep, and the breakthrough and saturation points gradually leaned to the right as the reaction temperature increased. When the reaction temperature increased from 5°C to 45°C, the breakthrough time increased by 135 h at a rate of about 48%, whereas the saturation time increased by 95 h, at a rate of approximately 17%. The results suggested that increasing the reaction temperature was conducive to improving the breakthrough ability of the ceramsite-supported nZVI packing pack. High reaction temperature had a beneficial effect on the reactions of Eqs. 7 and 8, producing more hydroxyl radicals, which can promote the Fenton reaction efficiency \([43,44]\).

When the reaction temperature was 25°C, \(K_{\text{Th}}\) value reached the peak and \(q_e\) value was dropped at its minimum. These parameters were compared with those at reaction temperatures of 5°C and 45°C, as shown in Figure 8b. As indicated in Figure 8c, when the reaction temperature was increased from 5°C to 45°C, both \(K_{\text{Y-N}}\) value and \(\tau\) value exhibited an increasing trend, implying that increasing the reaction temperature was beneficial to extending the breakthrough time while mitigating the adsorption saturation of ceramsite-supported nZVI. These results are consistent with the previous research results \([45,46]\). As presented in Figure 8d, \(K_{\text{AB}}\) value increased from \(5.85 \times 10^{-4}\) to \(7.94 \times 10^{-4}\) L \(\cdot (\text{mg} \cdot \text{min})^{-1}\); however, \(N_0\) value had little changes. Typically, according to the value of \(R^2\), within the research scope of the reaction temperature, the Y–N kinetic model could better describe the removal of MG dye from aqueous solutions by the fixed-bed reactor packed with ceramsite-supported nZVI than those of the Thomas or A–B kinetic model, with \(R^2 > 0.96\).

### 3.4 Influence of influent flow rate and kinetic analysis

The influence of the influent flow rate on the breakthrough curve of the removal of MG dye from aqueous
solutions by ceramsite-supported nZVI in a fixed-bed reactor was investigated at the initial concentration of 10 mg·L⁻¹ and reaction temperature of 25°C, and the results are detailed in Figure 9a. The test data illustrated in Figure 9a were nonlinearly fitted using the Thomas, Y–N, and A–B fixed-bed reaction kinetic models, and the fitting results are shown in Figure 9b–d.

As observed in Figure 9a, with the increase in the influent flow rate, the leftward shifting of the breakthrough curve was accelerated and the curve became sharp, which was followed by a decrease in both breakthrough and saturation times. Elevation of the flow rate could not only decrease the productions of iron hydroxide and amorphous iron oxide but also inhibit the effect of coagulation and flocculation [47,48].

When the influent flow rate was increased from 5 to 25 mL·min⁻¹, the breakthrough time was reduced by 5.75 times from 230 to 40 h, whereas the saturation time decreased by nearly 3.22 times from 515 to 160 h. As shown in Figure 9b, the influent flow rate was inversely proportional to $K_{Th}$ value and directly proportional to $q_e$ value. As illustrated in Figure 9c, when the influent flow rate was increased from 5 to 25 mL·min⁻¹, $K_{YN}$ value increased by almost 3.92 times and $\tau$ value decreased by

**Figure 9:** Influence of the influent flow rate on the breakthrough curves of the treatment of MG dye from aqueous solutions using ceramsite-supported nZVI in a fixed-bed reactor (a), and the fitting results of Thomas (b), Y–N (c), and A–B (d) fixed-bed reaction kinetic models.

**Table 2:** A comparative study of the adsorption capacities ($q_e$) of MG dye on different adsorbent materials

| Adsorbent                              | Experimental     | $q_e$ (mg·g⁻¹) | References |
|----------------------------------------|------------------|---------------|------------|
| Tamarind fruit shell                   | Batch study      | 1.951         | [49]       |
| Novel nano zerovalent iron algal biocomposite | Column study | 0.560         | [50]       |
| Nano-iron oxide-loaded alginate microspheres | Batch study | 2.298         | [51]       |
| Raw rice husk                          | Column study     | 4.050         | [52]       |
| Physic seed hull                       | Batch study      | 1.938         | [53]       |
| Ceramsite-supported nZVI               | Column study     | 3.117         | This study |

MG dye removal using ceramsite composite
nearly 6.69 times. These results suggested that the service life of ceramsite-supported nZVI packing pack could be considerably shortened by increasing the influent flow rate. According to Figure 9d, with the increase in the influent flow rate, $K_{ab}$ value increased from $7.78 \times 10^{-4}$ to $27.55 \times 10^{-4}$ L·(mg·min)$^{-1}$, whereas no change was observed in $K_0$ value. Therefore, the influent flow rate did not considerably influence the mass transfer process of MG dye in aqueous solutions inside the fixed-bed reactor. For an efficient investigation, a comparative study on the adsorption capacities of MG dye on different adsorbent materials was summarized. As indicated in Table 2, the adsorption capacity of ceramsite-supported nZVI was generally better than the mentioned adsorbent materials, either as a batch study or column study, suggesting that the lab-made ceramsite-supported nZVI exhibited a promising efficiency to remove MG dye from water in a fixed-bed reactor. Thus, we concluded that the ceramsite-supported nZVI exhibited excellent hydraulic load adaptability, particularly in the fixed-bed reactor system. Based on the value of $R^2$, within the research scope of the influent flow rate, the Y–N kinetic model could accurately characterize the removal of MG dye from aqueous solutions by ceramsite-supported nZVI in a fixed-bed reactor ($R^2 > 0.98$), followed by the Thomas kinetic model, whereas the A–B kinetic model exhibited the worst performance in such characterization.

4 Conclusion

In summary, ceramsite-supported nZVI packing pack was successfully prepared using the ball milling method, mainly due to ceramsite-produced magnetism during the sintering preparation process. The packing packs were prepared based on ceramsite-supported nZVI, and applied to treat MG dyecontaining wastewater in a fixed-bed reactor, which can achieve an ideal treatment effect. Moreover, ceramsite-supported nZVI may remove MG dye from water by adsorption, redox, coagulation, and flocculation. The breakthrough behavior of MG dye removal from aqueous solutions using a fixed-bed reactor packed with ceramsite-supported nZVI, including the curve shape, breakthrough time, and saturation time, was significantly affected by the initial concentration, reaction temperature, and influent flow rate. In addition, compared with Thomas or A–B fixed-bed reaction kinetic models, the Y–N fixed-bed reaction kinetic model was superior to describe the removal performance of MG dye from aqueous solutions using ceramsite-supported nZVI in a fixed-bed reactor, with $R^2 > 0.96$, indicating that the rate of removing MG dye molecule from aqueous solutions was directly proportional to the probability in which the ceramsite-supported nZVI packing pack was broken through.

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