Methylene Blue Removal of Fixed-Bed Column Reactor with Pumice and nZVI-Pumice: Experimental and Modeling Study

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Keywords
Fixed bed column, Methylene blue, nZVI, Pumice, Thomas model

Abstract: Nano zero-valent iron (nZVI) emerges as a low cost and eco-friendly adsorbent to treat textile wastewater, which is rich in dye content. However, nZVI particles can easily agglomerate in aqueous environment due to electrostatic interaction, decreasing their treatment efficiency. Therefore, pumice, a low-cost and naturally found porous material with lower specific surface area (2m²/g), can be used as support material to reduce agglomeration of nZVI. Treatment efficiencies of pumice/nZVI packing (10:0 and 9:1 (w/w)) in column reactor for specified initial methylene blue concentrations (25, 50, 75 and 100 mg/L) were investigated in this study. Adsorption capacities of the adsorbents were calculated as 2.8 and 4.2 mg/g-adsorbent, respectively at 100 mg/L initial methylene blue concentration. Mixed bed column performed significantly better than its pumice-only counterpart for low initial concentrations. Thomas adsorption model was applied to experimental results with a moderate to high predictive power.

Pomza ve nSDD-Pomza ile Sabit Yataklı Kolon Reaktörde Metilen Mavisi Giderimi: Deneysel ve Modelleme Çalışması

Anahtar Kelimeler
Sabit yataklı kolon, Metilen mavisi, nZVI, Pomza, Thomas modeli

Özet: Nano sıfır değerlikli demir (nSDD) yüksek renk konsantrasyonlarına sahip tekstil atıksularının artırılmasına ekonomik ve çevre dostu bir adsorban olarak ortaya çıkmaktadır. Ancak nSDD partikülleri sulu çözeltilerde elektrostatik etkileşimler sebebiyle kolutça topaklaşmakta ve bu da arıtma verimini düşmesine neden olmaktadır. Dolayısıyla düşük maliyetli, doğal poröz yapıda ve etkileşim sebebiyle kolayca topkalıktan ve arıtma ve deneyindeki toplam kapasiteleri sırasıyla 2.8 ve 4.2 mg/g-adsorban olarak bulunmuştur. Özellikle düşük konsantrasyonlarda, pomza-nSDD kararının arıtma performansını önemli ölçüde artırığı görülmüştür. Thomas modeli deneysel verilerle uyumlu olup ve modelin öngörü gücünün düşük konsantrasyonda yüksekken, yüksek konsantrasyonlarda ortalama olduğu kavşana varılmıştır.

1. Introduction

Textile industry is known as a sector of high water demand, which is estimated as 80 – 100 m³ per ton of finished textile, hence having the biggest impact on environment through primary water consumption and wastewater production. Therefore, environmentally sustainable development in textile industry is necessary for closing of water cycle [1]. However, synthetic organic dyes are extensively used in textile production process [2] and large volumes of wastewaters with high concentration of dyes are generated. Direct release of these colored wastewaters without meeting required discharge limits would have adverse effects on environment and human health [3].
Methylene blue (MB) is one of the most important organic pollutants used in textile, food, dyeing, printing, cosmetic, plastics, paper and manufacturing industries [4]. MB is non-degradable in nature and it is significantly toxic [5,6]. On account of these properties, MB adversely affects the environment and human beings [7]. It may cause irritation, gastritis, diarrhea, cyanosis, tissue necrosis, nausea, jaundice and vomiting in humans [8,9].

There are several conventional treatment methods for textile wastewater including oxidation [10], electrochemical techniques [11], coagulation [12], ultrafiltration [13], adsorption [14] and nanomaterials [15]. However, some of these methods have disadvantages such as high costs, non-applicability in large scale, complexity of operation and production of toxic sludge [3,16]. Among them, adsorption is the most often used one, providing relatively less waste production, regeneration of materials at the end of the process, high efficiency, ease of operation, nonproduction of toxic sludge, and economical feasibility associated with low adsorbent cost [17–20].

Textile wastewater treatment costs were reported to be in the range of 1.37-2.01 $/m^3 by using four different combinations of nanofiltration, ultrafiltration and microfiltration membranes [21]. Operation cost of COD removal from textile wastewater using electrocoagulation was in the range of 0.1 - 0.3 $/m^3 [22], considering only COD and turbidity removal. Chemical costs for alum coagulation and Fenton oxidation were 1.30 and 2.50 $/m^3, whereas color removal efficiencies were 34% and 24%, respectively [23]. Chemical cost of GAC adsorption was determined as 1.50 $/m^3 with a color removal efficiency of 88%. Considering highly colored textile effluent volumes per unit production, development of a cheap and effective treatment system is essential.

Due to its superior properties such as technical feasibility, non-toxicity, low cost, high reactive surface area and subsequently shorter treatment times, nZVI can be considered as a promising alternative for adsorbent material in dye removal [24]. However, in fixed bed operations, limitations emerge as nZVI particles agglomerate. Subsequently, hydraulic conductivity and surface area of nZVI particles decrease, compromising treatment efficiency [24-27]. In order to overcome these limitations and increase stability, support materials such as anionic polymer, chitosan, activated carbon, and starches are recommended as support material [26,28-31]. Moreover, due to their porous structure, pumice, bentonite and kaolinite have been preferred as support material to improve dispersibility of nZVI particles [26,28]. Among these porous materials, pumice is a volcanic rock with high surface area. Also, it is used as an effective, low-cost adsorbent to remove dye and heavy metals from water sources [31-34]. In the current literature, only a few studies focused on removal of heavy metals from water sources using pumice as support material for nZVI. However, no studies have been found about pumice usage as support material for nZVI to remove dye from wastewater.

In this work, adsorption performances of only pumice and mixed-bed nZVI-pumice by chromatographic separation were investigated for dye removal from model dye solutions by changing initial concentration. Also, the mixed-bed column behavior was interpreted by applying a dynamic model - Thomas model [35] to validate experimental data with theoretical ones obtained from breakthrough curves.

2. Materials and Methods

2.1. Materials

Commercial air-stabilized nZVI samples (NANOFER STAR; %60-80 nZVI-%20-40 iron oxides) were supplied from NanolIRON, s.r.o., CZ. The pumice used in this study originated from Isparta province. Pumice samples were supplied from Pumice Research and Application Center in Süleyman Demirel University, Isparta. Pumice samples were grounded and separated into fractions below 63 microns after grinding. Also, pumice and nZVI particles were mixed with grinding. Methylene blue (C_{16}H_{18}N_{2}SCl) was purchased from Fluka AG, reagent grade. Model dye solutions were prepared using deionized water. MB stock solution was prepared (1000 ppm) and serial dilutions were made to obtain MB concentrations of 25, 50, 75, and 100 ppm. Concentrations of MB were measured at λ_{max} of 664 nm by UV-visible spectrophotometer (Shimadzu, UV-2600).

2.1. Adsorption tests and Thomas model

Adsorption studies were conducted in a glass column at continuous flow mode (Figure 1). Column was packed with different adsorbents (pumice and pumice-nZVI mixed bed). Methylene blue solutions were fed from the top of the column and samples were collected at 3 min intervals from the bottom. In all experiments, room temperature and pH of solutions (7.0) were kept constant. Adsorption capacity of selected adsorbent was determined by using equation (1):

\[ q_e = \frac{C_0 - C_f}{m} \times V \]  

(1)

where \( q_e \) is the adsorption capacity of the adsorbent (mg MB/g adsorbent), \( C_0 \) and \( C_f \) are initial MB concentration and effluent MB concentration (mg/L), respectively, \( V \) is the volume of solution (L), and \( m \) is the amount of adsorbent (g).
Results and Discussion

3.1. XRD analysis of adsorbents

XRD spectrums for pumice, nZVI and pumice/nZVI mix are shown in Figure 2. Silicon dioxide (quartz), sodium aluminium silicate (albite), potassium, calcium, and AlPO₄ (berlinite) were matched to XRD spectrum of pumice. Amorph quartz structure of pumice was determined in the range of 20°-30° as expected [37-39]. Amorph quartz structure (20°-30°) was more pronounced in the mixed sample, which might be due to analytical limitations. Diffraction peak of zerovalent iron was observed at 44.9° (2 Theta) [40]. Also ferrous oxide was determined at 66.3° due to partial oxidation of nZVI surface as determined by Zhang et al. [40]. There were no impurities in commercial nZVI samples according to the XRD analysis. Albite, quartz, berlinite, potassium and iron matched phases of mix materials. Amount of iron was determined as 8.4% of total peak area. The iron content (8.4%) obtained was similar to the amount added (10%).

Experimental data were used to fit Thomas adsorption model for estimating the theoretical condition. Thomas adsorption model calculates the maximum amount of sorbed material and rate constant of the adsorption column. Thomas model assumes kinetics of adsorption-desorption of Langmuir without dispersion. However, the main restriction of Thomas model is that adsorption is controlled by mass transfer at the interface and not limited by chemical reaction [36]. Equation of Thomas model can be described as:

\[
\frac{C}{C_0} = \frac{1}{1 + \exp(K_T(q_o m - C_0 \theta)/Q)}
\]

(3)

where \(K_T\) is the constant (mL/(min mg)) and \(\theta\) is the solution volume percolated through column.

3.2. Removal of methylene blue

Treatment performances of bare pumice and mixed bed were evaluated using breakthrough curves of the effluent MB concentrations. The breakthrough curve of a specific adsorbate through a column in general depends on interparticle mass transfer, adsorption equilibrium and hydrodynamic conditions of the column. Therefore, operational parameters including flow rate (Q), initial MB concentration (C₀), bed height (H), and temperature (T) greatly affect breakthrough and dynamics of a column [24]. In this study, effects of initial MB concentration and adsorbent type on breakthrough time for methylene blue solution were investigated. Figure 3 shows the effect of initial MB concentrations in the range of 25 mg/L to 100 mg/L on breakthrough time for packed beds having bare pumice (a) and mixed pumice-nZVI (b).

At high initial concentrations for both adsorbent types, breakthrough was reached faster and slope of breakthrough curve was sharper. Effect of initial concentration on breakthrough point was observed when it decreased from 100 to 25 mg/L for each case. This might be related to sharper decrease in active sites of adsorbent at higher initial concentrations, which resulted in faster attainment of the breakthrough point [41]. As the \(C_0\) increased methylene blue sorption rate increased. Subsequently, transfer of mass decreased, which resulted in decreasing of the length of adsorption zone. The MB removal rate of bare pumice was determined to be over 99% until 39th, 27th, 18th and
15th minutes for 25, 50, 75 and 100 ppm initial MB concentrations, respectively. However, MB removal rate of raw pumice decreased drastically, especially for 100 ppm and 75 ppm concentrations, which practically followed an identical trend. The change observed for 25 ppm curve (Figure 2a) was less drastic, drop from 99% to 20% adsorption happened within 27 minutes.

Mixing nZVI with pumice had a pronounced effect on the breakthrough curves (Figure 2b), being observed as a rightward shift on time scale. Especially the curve for 25 ppm has shifted significantly, more than tripling the time for achieving a treatment efficiency of 99%. Removal rate of mixed bed column reactor was over 99% at 132\textsuperscript{rd}, 39\textsuperscript{th}, 30\textsuperscript{th} and 18\textsuperscript{th} minutes for 25, 50, 75 and 100 ppm initial MB concentrations, respectively. Moreover, drops in treatment efficiencies as observed in breakthrough curves were not as drastic as their counterparts in pumice-only experiments. Determined MB removal rates have shown that nZVI supplement into the column filler has improved efficiency for 25 ppm \( C_0 \) significantly. There were also improvements observed for 50 ppm and 75 ppm experiments. However, the used pumice:nZVI ratio was clearly not having a significant effect on removal of 100 ppm MB. Removal phenomena of column reactor was determined better at low initial MB concentrations. This was due to decreasing of available sorbent area with increasing initial MB concentration. As the amount of adsorbed MB increased, decreasing sorption areas caused a decrease in concentration gradient between adsorbent and liquid phase. Several studies have been conducted for MB removal using different adsorbents from solutions. For instance, removal of MB using nZVI particles from water and water-ethanol aqueous solution with batch experiments was investigated [41]. Adsorption capacities were calculated as 9.6 mg/g for water and 2.5 mg/g for water-ethanol mixture (50:50) at adsorbent dosage of 0.025 g nZVI and initial dye concentration of 10 mg/L.

### 3.3. Thomas model of MB removal kinetics

Breakthrough curve is theoretically determined by solving (often numerically) rigorous partial differential equations arising from the application of material balance and mass transfer equations for the bulk and adsorbed phases. However, several models are used extensively to simplify calculations. Thomas adsorption model [38] is one of the most widely applied models in column reactor performance studies. Table 1 compares the capacity and Thomas adsorption model parameter values obtained using both bare pumice and pumice-nZVI mixture at different initial concentrations.

### Table 1. Thomas adsorption model outputs and adsorption capacities for both pumice and pumice-nZVI mixed bed

| Adsorbent type | \( C_0 \) (mg/L) | \( K_T \) (ml/min mg\(^{-1}\)) | \( q_{\text{exp}} \) (mg/g) | \( q_{\text{theo}} \) (mg/g) | SSE |
|---------------|-----------------|-----------------|-----------------|-----------------|-----|
| Pumice        | 25              | 6.398           | 1.355           | 1.403           | 0.006 |
|               | 50              | 2.447           | 1.927           | 1.891           | 0.074 |
|               | 75              | 2.724           | 1.896           | 1.543           | 0.011 |
|               | 100             | 1.865           | 2.798           | 2.597           | 0.111 |
| Pumice-nZVI   | 25              | 6.287           | 1.706           | 1.638           | 0.022 |
|               | 50              | 1.981           | 2.447           | 2.179           | 0.015 |
|               | 75              | 2.468           | 2.349           | 2.019           | 0.01  |
|               | 100             | 1.102           | 4.272           | 3.481           | 0.090 |

In this study, the Thomas adsorption model was utilized between saturation and breakthrough points in the column test using both pumice and pumice-nZVI mixed bed. For both adsorbent types, Thomas rate constant, \( K_T \), tended to decrease and \( q_{\text{exp}} \) increased when the initial concentration increased. In addition, experimental results were reproduced with high SSE values in the range of 0.006 to 0.111 as tabulated in Table 1. Correlation between experimental versus theoretical MB removal rates of pumice and pumice-nZVI were shown in Figure 4 and 5, respectively. Moderate positive correlation between experimental and modeling results have shown the predictive power of the model used. Predictive power of Thomas model was the best for 25 ppm initial MB concentration. With the increasing concentration, data got more scattered (Figures 4 and 5). Maximum adsorption capacities determined from the Thomas adsorption model \( (q_{\text{theo}} \text{, mg/g}) \) were very close to experimental column capacities \( (q_{\text{exp}} \text{, mg/g}) \). According to results, adsorption capacities of the adsorbents were determined as 2.8 (pumice) and 4.2 mg/g-adsorbent (pumice-nZVI), for initial MB concentration of 100 mg/L. Based on these results, we concluded that Thomas model suitably described adsorption of methylene blue by pumice and pumice-nZVI mixture in fixed bed column. An evaluation of maximum adsorption capacities reported in literature revealed comparability of our results (Table 2).
Table 2. Comparison of adsorption capacities of various adsorbents for the removal of MB

| Adsorbent type                        | q_{max} (mg/g) | Operating conditions                                                                 | References |
|---------------------------------------|----------------|--------------------------------------------------------------------------------------|------------|
| Sand                                  | 0.07           | flow rate: 2 mL/min, bed depth: 15 cm, initial MB concentration: 100 mg/L, pH: 4.21, operating time for sand adsorbent: 270 min, operating time for graphite oxide-sand adsorbent: 680 min | [43]       |
| Graphite oxide-sand                   | 0.74           | flow rate: 2 mL/min, bed depth: 15 cm, initial MB concentration: 100 mg/L, pH: 4.21, operating time for graphite oxide-sand adsorbent: 680 min | [43]       |
| Cotton-alk                            | 0.024          | adsorbent dosage: 0.1 g, initial MB concentration: 250 mg/L, operating time: 10 min, stirring speed: 4000 rpm | [44]       |
| Silica microspheres decorated with polydopamine nano-particles | 14.68          | flow rate: 5 mL/min, bed depth: 0.3 cm, adsorbent dosage: 0.37 g, initial MB concentration: 100 mg/L, pH: 3.0, operating time: 20 min | [45]       |
| Biochar                               | 4.97           | flow rate: 1 L/h, bed depth: 0.32 m, adsorbent dosage: 400 g, initial MB concentration: 500 mg/L, pH: 7.0, temperature: 40 ºC | [46]       |
| Microcrystalline Cellulose            | 1.44           | adsorbent dosage: 5 g, initial MB concentration: 8 mg/L, pH: 6, temperature: 25 ºC, operating time: 3 min, stirring speed: 6000 rpm | [47]       |
| Clay                                  | 6.3            | adsorbent dosage: 0.1 g, initial MB concentration: 100 mg/L, temperature: 20 ºC, operating time: 1 h, stirring speed: 90 rpm | [48]       |
| Pyrolyzed petrified sediment          | 2.39           | adsorbent dosage: 0.5 g, initial MB concentration: 1x10^-2 g/L, pH: 7, temperature: 30 ºC, operating time: 1 h, stirring speed: 90 rpm | [49]       |
| Polyani-line nanotubes base/silica    | 10.3           | adsorbent dosage: 0.05 g, initial MB concentration: 3.1 mg/L, temperature: 25 ºC, operating time: 60 min, stirring speed: 700 rpm | [50]       |
| Mesoporous silica                     | 5.58           | flow rate: 2.68 mL/min, bed depth: 30 cm, adsorbent dosage: 0.1 g, initial MB concentration: 50 mg/L, pH: 2.0 | [51]       |
| Maize silk powder                     | 7.8            | adsorbent dosage: 80 mg, initial MB concentration: 20 mg/L                           | [52]       |
| nZVI-bamboo                           | 322.6          | adsorbent dosage: 0.02 g, initial MB concentration: 140 mg/L, temperature: 25 ºC, operating time: 120 min, stirring speed: 165 rpm | [53]       |
| iron-based nanoparticles              | 28.74          | adsorbent dosage: 0.03 g, initial MB concentration: 140 mg/L | [54]       |
| Zeolite                               | 3.79           | flow rate: 8.2 mL/min, bed depth: 30 cm, adsorbent dosage: 10 g, initial MB concentration: 50 mg/L, pH: 7.5, temperature: 25 ºC | [55]       |
| Graphene oxide Titanate nanotube      | 21.7           | adsorbent dosage: 0.1 g, pH: 6.8, operating time: 40 min, initial MB concentration: 10-60 mg/L, temperature: 25 ºC | [56]       |
| Iron nanoparticles                    | 16.1           | adsorbent dosage: 0.025 g, initial MB concentration: 10mg/L, temperature: 25 ºC, water-ethanol mixture: 50-50 | [57]       |
| nanoscale zero-valent iron/ Zeolite Socony Mobil-5 | 3.76           | adsorbent dosage: 0.5 g, pH: 2, stirring speed: 150 rpm, initial MB concentration: 20 mg/L, operating time: 90 min | [58]       |
| Pumice                                | 2.80           | flow rate: 2 mL/min, bed depth: 0.3 cm, adsorbent dosage: 0.08 g, initial MB concentration: 100 mg/L, temperature: 25 ºC | This study |
| Pumice-nZVI                           | 4.27           | flow rate: 2 mL/min, bed depth: 0.3 cm, adsorbent dosage: 0.08 g, initial MB concentration: 100 mg/L, temperature: 25 ºC | This study |

4. Conclusion

Continuous mixed-bed column studies were performed to elucidate performances of selected adsorbents on removal of MB. nZVI is a high-on-demand adsorbent for its large specific surface area (~30-55 m²/g) and oxidation capacities for treatment of various pollutants. However, agglomeration and subsequent decrease of specific surface area are the issues in handling nZVI particles. Pumice, which is also used as an adsorbent, is a naturally found porous material with a low specific surface area (~2 m²/g). In order to produce an adsorbent medium that is cost-effective and resistant to agglomeration, we supplemented pumice with nZVI particles. Experiments were conducted for pumice only and pumice-nZVI mix adsorbents. Laboratory-scale column studies demonstrated that MB removal efficiencies increased with increasing of binding sites of column bed. However; removal performance was greatly influenced by the initial dye concentration for bare pumice and nZVI-pumice fixed bed columns. Also, adsorption capacity of adsorbents increased with increasing initial MB concentrations whereas, breakthrough time decreased on increasing concentrations. Application of Thomas adsorption model demonstrated that it was successful in...
capturing the experimental removal efficiencies in fixed column beds.

**Figure 4.** Distribution of experimental and theoretical MB removal of pumice

**Figure 5.** Distribution of experimental and theoretical MB removal of pumice-nZVI

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