Efficient Removal of Methylene Blue from Aqueous Solution by Adsorption on Cerium Vanadate Nanoparticles

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ABSTRACT: Cerium vanadate nanoparticles (CVNPs) were used as a solid phase adsorbent for removing methylene blue (MB) from aqueous media. The nanoparticles were obtained through a direct precipitation procedure in aqueous solutions, and were characterized by X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). The results proved the product to comprise 25-45 nm particles. Batch adsorption experiments to determine the optimal adsorption conditions and the different factors which influence the adsorption efficiency (i.e. pH, amount of CVNPs, contact time, and the concentration of MB) were also evaluated. The experimental data were analyzed using the Langmuir and freundlich adsorption models. The data were satisfactorily fitted to the Langmuir model and a maximum adsorption capacity of 181.8 mg/g was obtained at pH of 3.0. Further kinetics studies were performed on the parameters. The adsorption of the model dye (MB) was found to reach equilibrium after 10 min, following a pseudo-second-order kinetic model. Desorption of the dye and recycling potential of the adsorbent was also studied.

Keywords: Dye removal, Methylene Blue, Cerium vanadate nanoparticles, Adsorption kinetics

INTRODUCTION
Treating wastewater is a serious problem in different countries, and dyes are among the most important contaminants present in textile, paper, plastic, food and cosmetic industry waste waters (Rafatullah et al., 2010), which usually contain different synthetic dyes which might even be visible to human eye. Many of these compounds have toxic, carcinogenic, mutagenic and teratogenic effects of living organisms (Mekkawy et al., 1998; Oxspring et al., 1996) Removing dyes from waste waters, has recently received considerable attention and a range of methods like adsorption, flocculation, oxidation and electrolysis (Zhang et al., 2017; Wawrzkiewicz, 2012;
Crini, 2003). Among these approaches, adsorption techniques offer simple, yet effective and economical tools for treating wastewaters (Shuang et al., 2012) The unique physico-chemical qualities of nanomaterials including their considerable surface area and the large number of defective sites present in their structure are expected to have enhanced uptake and adsorption properties, in comparison to their micro-sized counterparts (Banerjee et al., 2014; Maddah et al., 2015; Naderi et al., 2016a; Naderi et al., 2016b; Rahimi-Nasrabadi et al., 2017a). MB (C₁₈H₁₈ClN₅S) is an important compound used for treating different conditions such as schizophrenia, methemoglobinemia, and herpes infections (Reza Abbasi et al., 2017; Floyd et al., 2004). Methylene blue (MB), a planar molecule, is a common cationic model dye used in adsorption evaluation experiments (Kaşgöz and Durmus, 2010). This is a highly soluble compound with adverse effect such as respiratory problems, eye burn, nausea, and confusion (Crini, 2006). Consequently treating these MB-containing waste waters is a critical objective (Métivier-Pignon et al., 2003). This is performed through procedures like coagulation, flocculation, oxidation, adsorption, membrane separation, as well as, biological and electrochemical techniques (Kaşgöz and Durmus, 2010; Panswad and Wongchaisuwan, 1986; Ciardelli et al., 2001; Beakou et al. 2017). Among these techniques, adsorption-based methods are among the successful methods (Batmaz et al., 2014; Dehghan Abkenar, et al., 2015) This mechanism involves the transfer of a dissolved dye molecule through the interface of two immiscible phases, and does not involve the formation of harmful by-products, due to the physical nature of the adsorption process.

In this light developing renewable, efficient and cheap synthetic and/or natural adsorbents in an ongoing process, which has attracted a great deal of interest (Ipek et al., 2017; Liu et al., 2018; Rahimi-Nasrabadi et al., 2017b; Hosseini et al., 2017) and hence the focus of the present study is preparing cerium vanadate nanoparticles (CVNPs) by direct precipitation of solutions of the ingredients (i.e. Ce (NO₃)₃.6H₂O and NH₄VO₃) as an easy, fast, regulated and cost-effective technique. The products were next characterized through conventional techniques and used as a novel adsorbent for removing methylene blue from aqueous media. The factors influencing the adsorption process (i.e. pH, amount of the CVNPs, MB concentration and contact time) were also optimized.

**MATERIALS AND METHODS**

Metrohm 713 pH-meter and a λ 25 Shimadzo double-beam spectrophotometer were used for monitoring pH and MB concentration. The morphology and dimensions of the product were evaluated through X-ray powder diffraction (XRD) and scanning electron micrographs (SEM), on a Rigaku D/max 2500 V X-ray diffractometer (with a graphite monochromator and a Cu target), and a Philips XL30 instrument respectively. The loading of the samples into the SEM system was performed after being coated with a gold film using a BAL-TEC SCD005 sputter coater. Reagent–grade compounds were procured from Fluka and Merck companies and double distilled water (DDW) was used in all steps of the study. The glassware used for trace analysis were maintained in diluted nitric acid for at least one day and then washed repeatedly washed with DDW, prior to application. The stock MB solution was obtained through dissolving the dye (Figure 1) powder in DDW. The rest of the solutions were obtained through diluting the stock solution to the desired concentrations.

![Fig. 1. Molecular structure of Methylene blue dye](image-url)
Cerium vanadate nanoparticles (CVNPs) were obtained through a precipitation reaction using aqueous solutions of cerium nitrate hexahydrate and ammonium vanadate. In more detail, typically 1 mmol of cerium nitrate hexahydrate and 3 mmol of ammonium vanadate were dissolved in a proper amount of DDW, and after complete dissolution the cation solution was directly added into that of the anion in a dropwise manner under sonication at room temperature. After the completion of the reaction the product was separated through centrifugation, and repeatedly washed with DDW, and absolute ethanol and eventually dried at 70 °C for 4 hours.

The CVNPs were used to adsorb methylene blue from water samples and all were repeated 3 times. Equilibrium experiments involved adding 0.010 g of CVNPs to 10 mL of a 50 mg/L of MB solution (pH=3.0). The mixtures were gently shaken for 5 min under ambient conditions, and next the supernatant was centrifuged at 3800 rpm for 3 minutes. The MB concentration before, during and after the adsorption experiments were determined through spectrophotometry at 665 nm. Given the data the the dye removal efficiency, was calculated using the following equations:

$$%R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$

in which $C_0$ and $C_t$ are the initial MB concentration and this value at the end of the experiment at time (t) (mg/L).

The experiments also involved evaluating the effects of pH, the amount of CVNPs, contact time, and initial MB concentration on the adsorption efficiency. Further the kinetics of the adsorption phenomenon was evaluated through monitoring the adsorption capacity at various intervals. To obtain the adsorption isotherms, a range of dye solutions within the range of 10-500 mg/L were used in adsorption experiments until equilibrium conditions.

The amounts of the adsorbed MB ($q_e$) of dye were calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V$$

where $C_0$ and $C_e$ represent the initial and equilibrium MB concentrations (mg/L), $m$ is the CVNPs (g), and $V$ is the solution volume (L).

**RESULTS AND DISCUSSION**

Direct precipitation is an easy for the preparing insoluble compounds. However gaining control over the dimensions and morphology of the product is a rather complex step which requires a comprehensive understanding of the interactions among the reagents and particle formation mechanism (Liu et al., 2018; Rahimi-Nasrabadi et al., 2017b; Hosseini et al., 2017). To assess the quality of the product FE-SEM and XRD analyses were used. The FE-SEM image of the sample is illustrated in Figure 2, indicating that the particles were 25-45 nm in diameter. Further the XRD patterns (Figure 3) contain diffraction peaks which fully agree with the orthorhombic CeVO$_3$ with a pbnm space group indexed in JCPDS file, No. 01-078-2306. This is proof of the good crystallinity and phase purity of the produced CVNPs.

Using Debye–Scherrer:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

($\lambda=0.154059$ nm, $\beta$: the corrected band broadening, and $\theta$: the Bragg angle) the average crystal size of the CVNPS (Rahimi-Nasrabadi et al., 2017c; Rahimi-Nasrabadi et al., 2017d; Rahimi-Nasrabadi et al., 2017e) were calculated and found to be about 10 nm.
The studies were performed in the pH range of 2.0 to 10.0 and the results are given in Figure 4 from pH 2.0 to 10.0. pH adjustments were induced using concentrated HCl and NaOH solutions and the measurements were performed using a digital pH meter. MB is known to exist in cationic form in aqueous media and is hence attracted to negatively charged surfaces. Figure 4 indicated that the adsorption of MB is possible in a rather wide pH range of 3 to 9. At pH values below 3, the H⁺ ions can compete with MB in adsorption onto CVNPs, which lowers the adsorption of MB at pH=2.0. In extremely alkaline conditions, the aqueous OH⁻ may simultaneously adsorbed by the MB cations and the CVNPs leading to an
increase in the electrostatic repulsion between the adsorbent and the dye species and hence considerably lowering the MB adsorption. The sorption of MB on CVNPs under optimal conditions can be due to the attraction of the cationic MB toward the negatively charged surface of the adsorbent.

To determine the optimal amount of CVNPs required for reaching the optimal adsorption efficiency the amount of the sorbent was varied in the range of 0.002 to 0.015 g, in 10 mL samples of a 50 mg/L MB solution at room temperature and at pH=3.0 Based on the results (Figure 5) the removal efficiency increased upon increasing the amount of CVNPs, which corresponds to the availability of more adsorption sites. Yet using 0.010g and 0.15g of VCNP a removal efficiency of 95%, and a maximum efficiency of 98.5%, were observed.

Fig. 4. The effect of pH on the adsorption of MB on the cerium vanadate nanoparticles

Fig. 5. The effect of different amount of the cerium vanadate nanoparticles on the removal efficiency
The effect of contact time on the adsorption efficiency was studied at an initial MB concentration of 50 mg/L, pH=3.0 and ambient temperature, through determining the MB content of the samples after 3, 5, 10 and 15 minutes. The results (Figure 6) clearly indicate that the adsorption shows a rapid increase at first, and then continues to increase at relatively lower speed overtime, and after about 15 min, 96% of the total dye content of the sample was adsorbed. To determine the adsorption mechanism, a pseudo first-order and a pseudo-second-order kinetic model were used to fit the experimental data.

The pseudo-first-order is described by the Lagergren (1898):

\[
\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

in which \(k_1\), \(q_e\) and \(q_t\) are the pseudo-first-order rate constant (min\(^{-1}\)), the amount of absorbed MB (mg/g) at equilibrium, and at time \(t\) (min).

The pseudo-second-order model, on the other hand, is expressed as (Ho and McKay 1998) (Ho and McKay 1998)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

in which \(k_2\) (g/mg/min) is the rate constant of the pseudo-second-order adsorption, and \(q_e\) and \(q_t\) are as above.

The kinetic constants were obtained through the linear regression for the two models (Figure 7) and the results are presented in table 1. The correlation coefficient (R\(^2\)) of the pseudo-first-order kinetic model was rather low and the \(q_e\) values (\(q_{e,\text{cal}}\)) calculated from the this model did not show good agreement with the experimental data (\(q_{e,\text{exp}}\)), reflecting the fact that the model is not appropriate. In the case of the pseudo-second-order model, on the other hand, R\(^2\) was 0.9934 and the \(q_{e,\text{cal}}\) were in good agreement with the \(q_{e,\text{exp}}\) values, indicating the applicability of the kinetic model to the adsorption of MB onto CVNPs.

Table 1. Adsorption kinetic parameters of MB adsorption onto the cerium vanadate nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
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<tbody>
<tr>
<td></td>
<td>(K_1) (min)</td>
<td>(q_{e,\text{cal}}) (mg/mg)</td>
</tr>
<tr>
<td><strong>Experimental data</strong></td>
<td>0.107</td>
<td>47.73</td>
</tr>
</tbody>
</table>
Fig. 7. The pseudo-first-order kinetics (a) and the pseudo-second-order kinetics (b) of adsorption MB on the cerium vanadate nanoparticles.

Fig. 8. The effect of MB concentration on dye adsorption capacity of the cerium vanadate nanoparticles.
Figure 8 illustrates the plot of adsorption capacity versus MB concentration from 10 to 500 mg/L. Clearly the adsorption capacity is a function of the initial dye concentration, which can be attributed to the driving force created by the stronger concentration gradients created by increasing the concentration. Adsorption increases with increasing the MB concentration, while the surface of the adsorbent is not saturated. Naturally after all adsorption sites are occupied, further increasing in the MB concentration does not increase the adsorption efficiency.

The Langmuir and the Freundlich models were used to define the sorption properties of the nanoparticles. The former model is based on assuming that the homogeneous sites of the adsorbent are covered by a monolayer of the die molecule and also that no species can be adsorbed after saturation is reached. The Freundlich isotherm model, on the other hand, uses an empirical equation to describe heterogeneous systems (Freundlich, 1906). The linearized expression of the Langmuir model is shown as:

$$\frac{C_r}{q_e} = \frac{1}{b q_m} + \frac{C_r}{q_m}$$

in which $q_m$ is the highest adsorption capacity (reached when the monolayer completely covers the surface) and $b$ expresses the equilibrium constant (L/mg).

The linearized form of the Freundlich is expressed as below:

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e$$

($K_f$ and $1/n_f$ being a rough indicator of the adsorption capacity, and the adsorption intensity. The slope $1/n_f$ ranges between 0-1 and reflects the adsorption intensity or surface heterogeneity. Closer to zero $1/n_f$ values reflects higher heterogeneity of the surface) (Haghseresht and Lu, 1998). These constants, determined using linear regression analysis, are given in Table 2, illustrating the Langmuir isotherm as fitting since it exhibits a higher $R^2$ as opposed to the Freundlich model. The maximum adsorption capacity was found to be 181.8 mg/g.

The recyclability of a water purification adsorbent is of an important figure of merit. Consequently, the potential of regenerating the CVNPs was investigated through washing the adsorbed MB molecules from CVNPs using 10.0 mL of ethanol. After the recycling the adsorbent could be regenerated and used again. Desorption process was found to reach equilibrium within approximately 10 min, which was similar to the adsorption phenomenon. Once the elution was over the adsorbent was washed with DDW, dried at 50 °C under vacuum and used again. It was found that the regeneration was applicable for three runs without any loss in the capacity of the adsorbent.

The removal of MB by different adsorbents has been studied. Table 3 compares the adsorption capacity of the cerium vanadate nanoparticles with different adsorbents previously used for removal of MB dye. The results is shown that the adsorption capacity of the CVNPs for MB dye is higher than of the most of other previously reported adsorbents, indicating that this adsorbent has great potential application in dye removal from aqueous solution.

Table 2. Isotherm parameters for adsorption of MB on cerium vanadate nanoparticle

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tbody>
<tr>
<td></td>
<td>$q_m$(mg/g)</td>
<td>$b$(mg/L)</td>
</tr>
<tr>
<td>MB</td>
<td>181.8</td>
<td>0.0807</td>
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</tbody>
</table>
Table 3. Comparison of the maximum capacity factor of MB onto various adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Capacity Factor (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium vanadate nanoparticles</td>
<td>181.8</td>
<td>Proposed work</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂-CR</td>
<td>31.4</td>
<td>[Yimin, et al., 2018]</td>
</tr>
<tr>
<td>H₂SO₄ crosslinked magnetic chitosan</td>
<td>20.4</td>
<td>[Rahmi, et al., 2019]</td>
</tr>
<tr>
<td>Fe₃O₄-TAN</td>
<td>90.9</td>
<td>[Dehghan Abkenar, et al., 2015]</td>
</tr>
<tr>
<td>Silsesquioxane-based disulfide-linked polymer</td>
<td>12.9</td>
<td>[Liu, et al., 2019]</td>
</tr>
<tr>
<td>Magnetic Magnesium Silicate Hollow Nanotubes</td>
<td>175.1</td>
<td>[Yang, et al., 2017]</td>
</tr>
<tr>
<td>Mn@ CuS/ZnS-NC-AC</td>
<td>126.4</td>
<td>[Asfaram, et al., 2017]</td>
</tr>
<tr>
<td>nano-biosorbent based on modified dextrin</td>
<td>76.3</td>
<td>[Nazarzadeh Zare, et al., 2018]</td>
</tr>
<tr>
<td>tungsten trioxides (WO₃)</td>
<td>35.9</td>
<td>[Zhang et al., 2017]</td>
</tr>
</tbody>
</table>

CONCLUSIONS

An easy and efficient system was developed for removing MB from its aqueous solutions using cerium vanadate nanoparticles (CVNPs). The nanoparticles were directly precipitated using solutions of Ce(NO₃)₃.6H₂O and NH₄VO₃. Studies revealed the adsorption of MB on CVNPs to follow the Langmuir adsorption model, and a maximum adsorption capacity of 181.8 was reached. Adsorption kinetics of the process was also found to follow a pseudo-second-order kinetic model. The high speed of the adsorption process constitutes a further technical significance for the adsorbent. The method was hence concluded as a suitable means for the large scale elimination of MB and similar dyes from water.

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REFERENCES


